Solution Behavior of Modified Polyethylenimine [PEI] Polymers by Light Scattering Investigations

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ABSTRACT

The eight average molecular weights, as well as other characteristics such as the second virial coefficients and root-mean-square (RMS) radii of gyration of poly [ethylene imine] (PEI) and various derivatives, have been determined in solution light scattering studies. The solution dynamics of PEI and carboxylated and phosphorylated derivatives were studied a pH of 3.3, 7.0 and 10.0. Measurements were made in freshly distilled and de-ionized water as well as in 0.1 M, 1 M and 5-M solutions of sodium chloride in water. Molecular weights were calculated from Berry plots. The purified polymer, PEI-1, gave a molecular weight of 39,600 g/mol., while the same polymer, which was not purified, PEI-2, has MW of 43,100 g/mol.

Increasing the concentration of sodium chloride leads to an increase in the root mean square radius of gyration, as the polymer chains become more extended and relaxed in a more concentrated salt medium. The apparent molecular weights are observed to decrease in proceeding from acidic to alkaline medium, especially with the phosphorylated polymer. However, the RMS radius of gyration of the carboxyl modified polymer was high at both ends of the pH scale, i.e., the polymer chains were extended at both the acidic and alkaline pH ends. The increase in RMS radius of gyration is indicative of increasing solvent-polymer interaction.

1. INTRODUCTION

Despite extensive studies in the last two decades, the dynamic light scattering behavior of flexible or branched polyelectrolytes in aqueous solutions is not yet fully understood[1]. Most of the studies that have been carried out in the past couple of decades have been done on model polymers such as polystyrene[2-4], polyethylene[5-9], polyvinylacetate [10-12] and polyisoprene[13]. Not much information had been available in the literature about the dilute solution properties of poly(ethylene imines) (PEI), branched or linear [14,15], compared to the industrial polymers named above. Part of the reason for the lack of studies on PEI, has been due to its weak polyelectrolyte character [16]. Modified polyethylenmines are especially becoming popular with the hope that modifications will enhance the solution behavior of the polymers.

The selective removal and/or recovery of harzadous and valuable metal ions and radionuclides from various dilute aqueous streams are major concerns to the United States Government and environmentalists. Heavy metal contamination of the environment is caused by the wide usage of heavy metals in industries to meet the demand of modern society. However, polyethylenimine (PEI) a water-soluble polymer, has been found to have a great affinity to binding with metals, principally due to its polyelectrolyte character as well as their large macromolecular sizes which make them very useful in sequestering metal ions from dilute solutions. A recent paper by Park and Choi[17], characterizes the solution properties of branched poly (ethylenimine).

Since its early development by Einstein [18], Raman [19], Debye [20], Zimm [21], [22] and others [23, 24], the theory of light scattering from macromolecular solutions and suspensions has represented one of the major successes of chemical physics. Light scattering, indeed, is one of the few absolute methods available for the determination of molecular mass and structure, and certainly is applicable over the broadest range of molecular weights of any method. Until samples were able to be separated by high performance size exclusion chromatography (HPSEC), or gel permeation chromatography[25], however, these measurements produced only weight average molecular weights, Mw, and the corresponding z-average square radii (r_g^2) z together with the second virial coefficient, A_2. The use of HPSEC has resulted in the ability to analyze the distribution of broadly

disperse samples as well as to obtain details of branching and molecular conformations. Thus, weight, number, and z-average values for both mass and size may be obtained for most samples by combining light scattering and HPSEC.

In this work, we present results of a study of the solution behavior of modified and PEI polymers in aqueous salt solutions. Light scattering measurements in solution of varying ionic strengths, pH, electrolyte concentrations have been made to attempt to determine how the polymers exist in solution and the effects of added electrolyte.

Basic Principles of Light Scattering

1) The amount of light scattered is directly proportional to the product of molecular weight and solute concentration.[26, 27]

2) The angular variation of scattered light is directly related to the size of the molecule[28].

Basic Theory and light scattering equations

$$K^*C/R(\theta) = 1/M\ P(\theta) + 2A_2C \qquad \text{eq. 1}$$

Where

K* $= 4\pi^2(dn./dc)2n2/(N_A\lambda^4)$, and n is the refractive index of the solvent.

C is the concentration of the solute molecules (g/ml).

R (θ) is the fraction of light scattered relative to the incident beam.

$\mathbf{N_A}$ is Avogadro's number.

λ is the wavelength of light.

Dn./dc is the refractive index increment, which tells how much the refractive index of the solution varies with solute concentration.

M is the weight-average molecular weight of the solute.

A is the second virial coefficient (a measure of solvent-solute interaction).

P (θ) is the "scattering function" which tells how the scattered light varies with angle. This variation is determined by $< r^2 >$, the mean square radius (also known as radius of gyration). The bigger the radius of gyration the bigger the angular variation.

$< r^2 >$ is the mean square radius, describing the distribution of mass within the molecule, and it is given by the equation:[29]

$$< r^2 > = \Sigma\, r_i^2 m_i / M \qquad \text{eq 2}$$

The symbol R (θ), the Rayleigh ratio describes the angle-dependent light scattering, and it is described as

$$R(\theta) = I_\theta r^2 / (I_0 V) \qquad \text{eq 3}$$

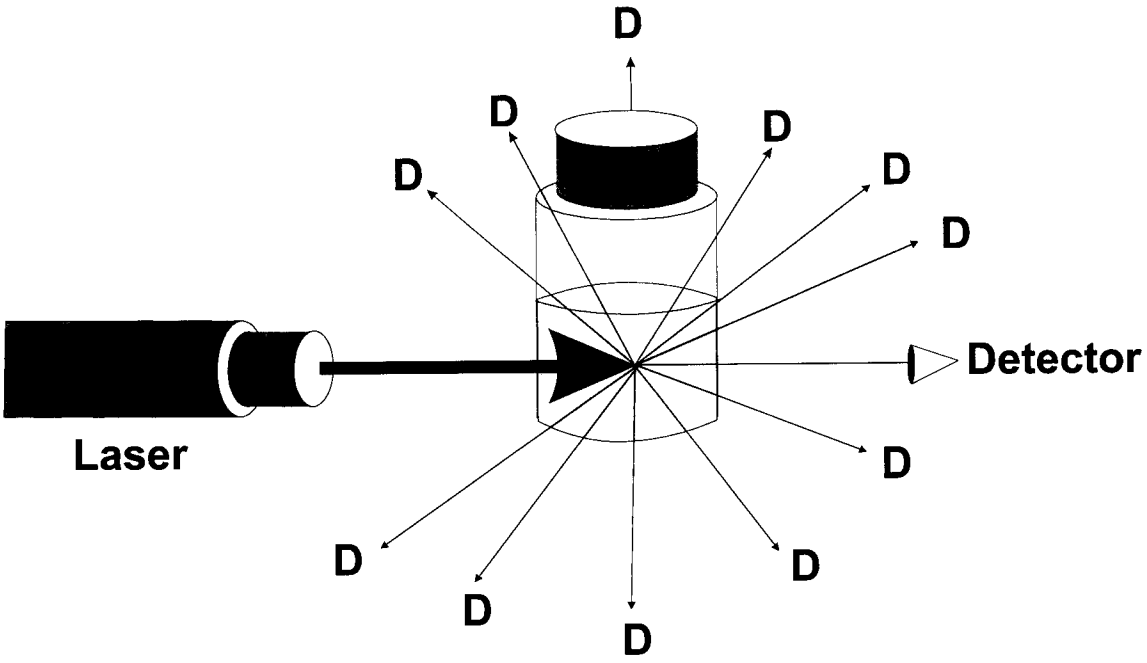


Figure 1. The light scattering pattern of particles in a solvent

I_θ is the scattered intensity, I_0 is the intensity of the incident beam, V is the volume of the scattered medium, and r is the distance between the scattering volume and the detector. Equation 3 implies that the dimensions of R (θ) are length^{-1}, and the DAWN instruments are provided with vertically polarized light sources. When studying a solution of solvent plus solute, it is convenient to use R (θ) to represent the *excess* scattering of the solution compared to that of solvent alone as:

$$R(\theta) = (I_\theta - I_{0,solvent})\, r^2 / (I_0 V) \qquad \text{eq. 4}$$

where $I_{0,solvent}$ is the scattered intensity of the solvent. Equation 3 is used for pure solvent and equation 4 is used for a solution. That means that we are merely describing the scattering after subtracting the "baseline" of pure solvent. In this case, R (θ) is often called the excess Rayleigh ratio of the solute. The knowledge of Rayleigh ratio at a number of different angles leads directly to the weight-average molecular weight and mean square size of the solute molecules, making R (θ) the most important measured quantity in light scattering experiments.

The determination of molecular parameters of solute particles in solution is carried out by using the equation derived by Zimm,[21] in which equation 1 is replaced by equation 5.

$$R(\theta)/K^*C = Mw\ P(\theta) - 2A_2CM_w^2P^2(\theta) \qquad \text{eq 5}$$

Where Mw is the weight-average molecular weight, and other parameters defined previously. P (θ) is related to $< r^2 >$ by the following equation:

$$P(\theta) = 1 - 2\mu^2 < r^2 > /3 + \ldots \qquad \text{eq 6}$$

where $\mu = (4\pi/\lambda) \sin(\theta/2)$, and gives us the relation between P (θ) and mean square radius for any molecules regardless of molecular conformation in the limit of $\mu^2 < r^2 > << 1$. For a polydisperse sample, the mean square radius obtained is z-average, usually written <r2>z.

The determination of molecular weights and mean square radii are through the use of Zimm, Debye or Berry plot[30]. The Zimm and Debye plots are similar. To construct a Debbie plot, Y axis-= R (θ)/K*C and X-axis = $Sin^2(\theta/2)$ + KC where K is a "stretch factor" which scales the contributions from c to be roughly equal to the contributions from $sin^2(\theta/2)$. It is chosen to be the reciprocal of the maximum concentration. In the case of the Zimm plot, we plot Y = K*C/R (θ) and X-axis = $Sin^2(\theta/2)$ + KC. The y-axis is the reciprocal of that used for Debye plot.

2. EXPRIMENTAL

Freshly made distilled and de-ionized water was used in this investigation. The pH values of the water were taken immediately and after 3 days, with Orion Research pH

meter. The Ph values of 3 different concentrations of Nalco solutions as buffer systems were also measured. These were 0.1 M Nalco, 1 M NaCl, and 5 M NaCl solutions respectively. The molecular weights (MW) of PEI were determined in water as well as 3 NaCl solutions. The distilled and deionized water was initially filtered with 2-μm membrane filters, to make the NaCl solutions. Then the p H Values of the solutions were measured

2.1 Molecular weight measurement by light scattering method

2.1.1 Measurement of dn./dc: This was done with Wyatt Technology Optilab Differential refractometer 903 using a series of solutions of the polymer with different concentrations. This is a measurement of differential refractive index changes with concentrations.

2.1.2 The light scattering measurements: were done on DAWN F Laser photometer (Wyatt Technology, Inc., CA), using a series of concentrations of the polymer solution. The final polymer solutions were filtered again with 0.2-μm membrane filters to avoid light scattering from extraneous dust and other particles. The MW was calculated from Berry plots.

2.1.3 Polyethylenimine was obtained from BASF. The polymers consisted of purified PEI, unpurified PEI, with about 50% water, some functionalized PEI, e g., carboxylated and phosphorylated polyethylenimines.

3. RESULTS AND DISCUSSION

3.1 Native, unfunctionalized polyethylenimine (PEI).

The effect of pH on polyelectrolytes in aqueous solutions is extremely important in the determination of their molecular dimensions. In this report, the pH of all the solutions including distilled water and the aqueous solutions were strictly controlled. The standard pH values of the starting solutions are shown in Table 1. The Molecular Weight characteristics for two batches of samples are provided in Tables 2 and 3. Tables 2 and 3 contain measured quantities such as RMS radius of gyration, $\langle r^2 \rangle$, second virial coefficient, A_2, and weight-average molecular weight, M_w. The RMS radius of gyration

describes the distribution of mass within the molecule. This defines the radius of the volume within which a single polymer molecule gyrates[32]. The Second virial coefficient derives from osmotic pressure. The free energy of mixing of a polymer solution with normal heat of mixing is given as:

$$< G = KT\,[N_1 \ln V_1 + N_2 \ln V_2 + \chi_1 N_1 V_2] \qquad \text{eq } 7.$$

The partial molar free energy of mixing is given as:

$$< G_1 = KT\,[\ln (1-V_2) + (1-1/X)\, V_2 + \chi_1 V_2^2] \qquad \text{eq } 8.$$

from which osmotic pressure, π is derived as:

$$\pi = KT/V_1\,[\ln (1-V_2) + (1-1/X)\, V_2 + \chi_1 V_2^2] \qquad \text{eq } 9$$

and finally gives rise to osmotic pressure as:

$$\pi = KT/V_1\,[V_2/X + (1/2 - \chi_1)\, V_2^2 + \ldots\ldots] \qquad \text{eq } 10$$

where V_1 = the molecular volume of the solvent and the coefficient of V_2^2 is known as the second virial coefficient, A_2, which is given as:

$$A_2 = V_2^2/N_O V_1\,(1/2 - \chi_1) \qquad \text{eq } 11$$

where V_2 is the specific volume of the polymer and A_2 is directly proportional toV_2^2. MW is molecular weight and M_w is the weight-average molecular of the polymers.

These materials were dissolved in 1 M NaCl solution, and adjusted to pH 7.0. PEI-1 has a weight-average molecular weight of 39,600 g/mol while PEI-2 has a weight-average molecular weight of 43,100 g/mol. This should be expected, because a purified

material (almost always slightly fractionated) has a higher molecular weight than the unpurified one. PEI-1 was received, as a purified polymer while PEI-2 was unpurified, as received from BASF. The process of purification, as in fractional precipitation, separates the useful high molecular weight fractions from the low molecular weight fractions, which are usually washed out[31]. This explains the sharp difference in the molecular weights of PEI-1 and PEI-2.

3.2 Functionalized PEI

Table 2 also shows the molecular weight values for the other materials, including those that were functionalized. PEI-6, PEI-8 and PEI-11 show high molecular weights. This might be due to the functionalization and eventual purification of the materials. Some of them have very large crystal sizes, e.g. PEI-8. The large molecular dimensions measured for some of the functionalized polymers could be due to the increased polyelectrolyte character due to derivatization and the increased tendency of larger macromolecular aggregations resulting from polar (ionic) attractions.

3.3 Effects of Salt Concentration, pH and Polymer concentration on the molecular weight of Phosphorylated PEI (PEIP)

Figure 3 summarizes the effects of % functionalization on the MW weight and second virial coefficient of PEIP. As the % functionalization increases from 25% to 100%, the molecular weight decreases, as polar and ionic interactions become stronger. At the same time, the second virial coefficient increases as the solvent (1 M NaCl solution) become a better solvent.

Figures 4 and 5 show the effects of pH on the polymer molecular dimensions. The molecular size at the pH examined; 2.5, 3.3, 7.15 and 10.12, shows that the molecular weight is the highest at the neutral pH range of about 7.15. At both ends of the pH scale, the molecular weights are much smaller. The acid and alkaline ranges exhibit strong polar and ionic interactions that effectively coil the polymer molecules. This trend is also true for the second virial coefficients and the root mean squared radius of gyration.

To effectively determine the dimensions of polymer chains, it is very important that no aggregations are formed in solution. To this end, a small quantity of NaCl dissolved in distilled and deionized water to prevent polymer aggregations. The salt concentrations used were 0.1 M, 1 M, 3 M and 5 M NaCl solutions, with the pH adjusted to 7.0. The effects of salt concentrations are shown in Figures 6 and 7. At low salt (0.1 M) NaCl concentration, both molecular weight and root mean radius of gyration were found to be very high, as the low salt concentration was not sufficient in buffering the polymer molecules. Increasing the salt concentration to 1 M leads to drastic reduction of both RMS radius and MW, and increasing the Salt concentration further stabilizes both of these values as shown in Figure 6. Figure 7 specifically describes the effect of salt concentration on the second virial coefficient, A_2, which decreases as ionic concentration increases to I M , but increases and stabilizes as the ionic concentration increases. Higher salt concentration makes a better solvent.

The effects of polymer concentration on MW of PEIP0.5 are shown in Table 8 & 9 and in Figure 8 & 9. At low polymer concentration, the molecular chains are more relaxed and stretched out, leading to a rather high RMS radius of gyration. As the polymer concentration increases the RMS radius of gyration decreases and eventually reaches equilibrium, as the polymer chains have no more space to extend.

3.3 Effects of salt concentration, pH and polymer concentration, on the molecular weight characteristics of PEIC, Carboxyl modified PEI.

The effect of pH on the carboxyl modified PEI, seems to be dependent on whether medium is acid or alkaline. Both molecular weight and the root mean square radius of gyration are relaxed at the acid pH region as seen in Figure 10 and Figure 11. PEI is more or neutral to acid or base, but when functionalized by carboxylation, the polymer chains become more acidic than basic. As the pH of the medium progressively becomes alkaline, both the molecular weight and root mean square radius of gyration decrease because the strong acid environment is progressively neutralized. It seems that the controlling factor here is the imbalance of ionic forces at both ends of the pH scale that

leads to repulsion and extension of the molecules or vice versa. The behavior of the second virial coefficient is similar to those of MW and A_2.

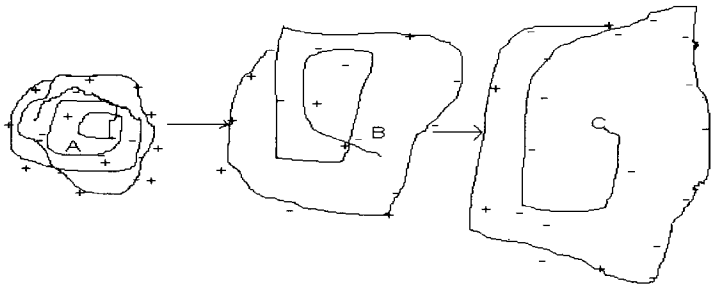
The effects of salt concentration on PEIC can be seen in Figures 12 and 13. At low ionic concentration, e.g., 0.1 M NaCl, both molecular weight and root mean square radius of gyration have small values. But at 1 M salt concentration, MW and RMS have their highest values. At both acid and alkaline regions, polar and ionic interactions are strongest. This leads to smaller molecular dimensions at these regions.

Polymer concentration has significant effect on the molecular weight of PEIC AS shown in Figures 14 and 15. At low polymer concentrations, the molecular weight and root mean radius of gyration, have low values. As the concentration increases, MW and RMS increase. At a polymer concentration of 4.00×10^{-3} g/ml, MW and RMS increase rapidly. These rapid increases in these molecular dimensions are due to aggregations of polymer chains, above the critical concentration of 4.00 x 10-3 g/ml. (Molecular Diagram 1). It is however better to run the experiments at lower polymer concentrations for very high molecular weight polymers, to avoid saturation of the detectors, due to excessive scattering of light rays from large particles, which eventually leads to faulty results.

There are some limitation to the tandem technique of light scattering and HPSEC. Theoretically, light scattering measurements may resolve size down to about a twentieth of the incident wavelength. For a given concentration c (g/ml), the scattered light signal is proportional to cMw. Thus, for molecular weights below a few thousand, relatively high concentrations may be required so that the molecules can produce a detectable LS signal. Furthermore, the technique requires a parallel or serial determination of mass concentration for each eluting fraction. At high molecular weights and very low concentration, conventional mass concentration detectors (based on measurement of refractive index change) have difficulty determining concentration values accurately. Finally, an accurate determination of the refractive index increment with molecular concentration, $dn./dc$ is required. For heterogeneous copolymers, $dn./dc$ must be measured at each elution, since it may be a function of molecular size. In our systems, we considered the polymers as predominantly homogeneous, and therefore a single value for

dn./dc was used. For polyelectrolytes, a more tedious dialysis step is rigorously required. This was overlooked in our procedure.

Nevertheless, even with these problems, light scattering certainly represents the most accurate and powerful molecular weight measurement and detection technique. Light scattering is absolute and does not require calibration of the columns.



Molecular Diagram 1

3.4 Critical Micelle Concentrations [CMC], and aggregations.

Some polymers form different agglomerations or aggregations in solution due to polar or ionic interactions or hydrogen bond formations. In either case it is extremely difficult to determine the exact molecular weights of the individual molecules. The critical micelle concentration (CMC) is the concentration above which polymer molecules aggregate together due to polar or other interactions. Due to the large molecular weight values measured for some of the polymers, we thought it extremely important to ascertain if the polymer molecules aggregated at certain concentrations for PEIC 0.5 and PEIP 0.5. We therefore measured the molecular weights for industrial use concentration (0.416 to 0.020 Wt %) and at low concentration (0.0106 to 0.000707 Wt %). For both polymers there seems to be no significant differences between the molecular weights calculated from low concentrations and those calculated from industrially used concentrations.

4. CONCLUSIONS

The absolute molecular weights (MW) of purified and unpurified polyethylenimines PEI as well as carboxylated and phosphorus modified version have been determined by light scattering method. Generally, it was observed that the MW of the phosphorus modified PEI, as well as the second virial coefficient and root mean square radius of gyration decrease as a function of increasing polymer concentration initially, then stabilize above a concentration of 4.00×10^{-3} g/ml. For PEIP polymer, the polymer concentration range should be between 4.00×10^{-3} to 1.00×10^{-2} g/ml. For PEIP polymers, there are strong ionic and polar interaction at both ends of the pH scale, whereas for PEIC, opposite charges attract more strongly as pH increases into the alkaline range leading to the decrease in MW, RMS radius of gyration and second virial coefficient.

Light scattering has been confirmed as the method of choice for mass and size characterization by virtue of new instrumentation and new techniques. On one hand, light scattering photometers have now been developed that can measure the angular variation of the scattered light intensity at 15 to 18 distinct scattering angles simultaneously and repeatedly. For smaller molecules, a 3-detector system will suffice. This has ensured a high degree of precision in the deduction of key molecular parameters from the measured scattered light intensities. New and improved electronics have increased sensitivity significantly while decreasing detector drift and other temperature dependent effects.

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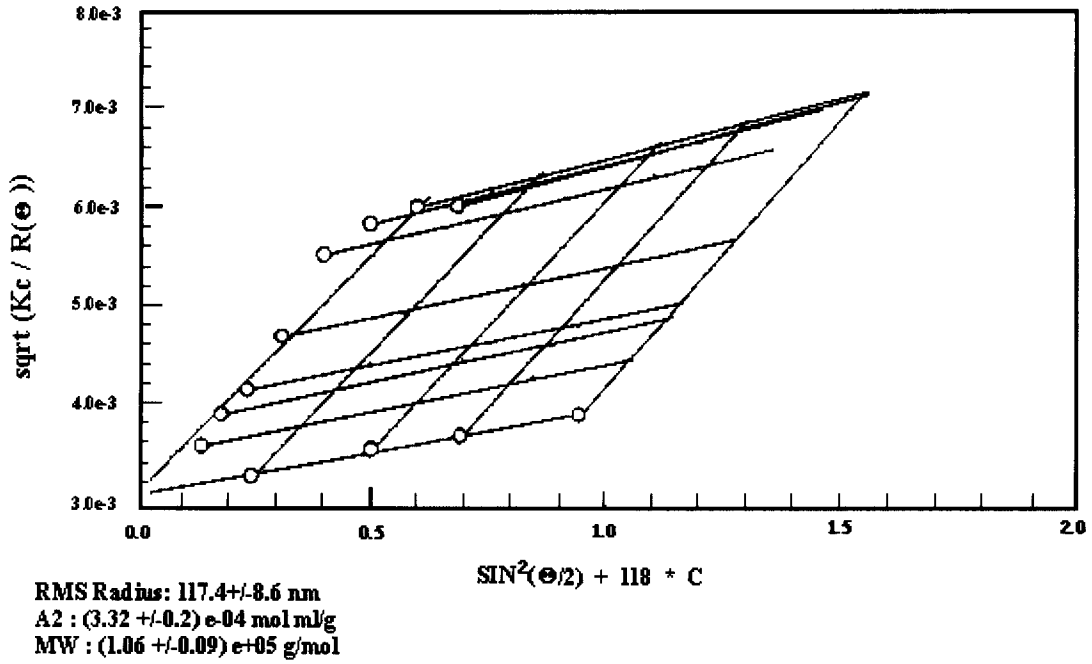
Table 1

Serial #	Solution	pH at 23 °C
1	Fresh distilled water	7.79
2	Distilled water after 3 days	7.78
3	0.1 M NaCl	6.82
4	1 M NaCl	6.17
5	5 M NaCl	5.61



DN/DC = 0.174, for Polyethylene imine (PEI).

Figure 2. A representative Berry plot used to calculate the molecular weight, second virial coefficient and the root mean square radius of gyration of PEI

Table 2

ID #	Remark	RMS (nm)	A2 (mol ml/g)	MW(g/mol)
PEI-1	PEI Purified	39.8+/-6.7	1.30+/-1.0e-04	3.96+/-0.1e+04
PEI-2	PEI Unpurified	38.8+/-6.9	5.71+/-2.0e-05	4.31+/-0.2e+04
PEI-3	Unpurified (Polymin P)	42.3+/-6.0	5.09+/-0.4e-04	5.19+/-0.2e+04
PEI-4	PEIP 0.5	39.3+/-4.3	4.96+/-0.7e-04	3.16+/-0.1e+04

PEI-5	PEIC 0.5	47.1+/-7.0	7.49+/-3.0e-04	1.60+/-0.07e+04
PEI-6	PEIP	45.6+/-5.6	3.88+/-0.2e-04	4.12+/-0.4e+05
PEI-7	PEIP	40.2+/-5.3	6.77+/-0.5e-03	5.97+/-0.3e+03
PEI-8	PEIC 0.5	49.6+/-6.5	5.40+/-0.7e-04	5.69+/-0.3e+04
PEI-9	PEIP	46.1+/-5.6	6.61+/-7.0e-04	9.61+/-0.7e+03
PEI-10	PEIP	44.5+/-6.9	1.89+/-0.4e-03	1.89+/-0.1e+04
PEI-11	PEIP 0.5	39.8+/-5.7	1.41+/-0.2e-04	1.12+/-0.04e+05
PEI-12	PEIP 0.5	38.1+/-4.9	1.09+/-0.4e-03	1.29+/-0.06e+04

Table 3

SERIAL #	RMS (nm)	A2 (mol ml/g)	MW (g/mol)
PEIC0.25 (1)	38.4+/-5.4	6.18+/-2.0e-05	5.86+/-0.3e+04
PEIC0.5(2)	37.6+/-6.6	3.40+/-1.0e-04	1.11+/-0.05e+04
PEIC0.5(3)	40.5+/-6.7	7.68+/-0.5e-05	1.18+/-0.05e+05
PEIC0.5(4)	36.6+/-4.9	4.22+/-0.8e-04	7.26+/-0.3e+04
PEIC0.5(5)	36.4+/-7.0	2.87+/-0.6e-05	3.43+/-0.2e+04
PEIC0.75(6)	37.8+/-5.6	6.52+/-0.9e-05	6.14+/-0.4e+04
PEIC1.0(7)	34.5+/-6.0	3.43+/-0.4e-04	4.76+/-0.3e+04
PEIC1.0(8)	36.8+/-5.0	2.64+/-0.05e-04	3.62+/-0.1e+04

Effects of % Functionalization on MW and A_2 OF PEIP

(pH 7.0/salt conc. I M NaCl/polymer stock conc. 4.83e-3,. at 25°C)

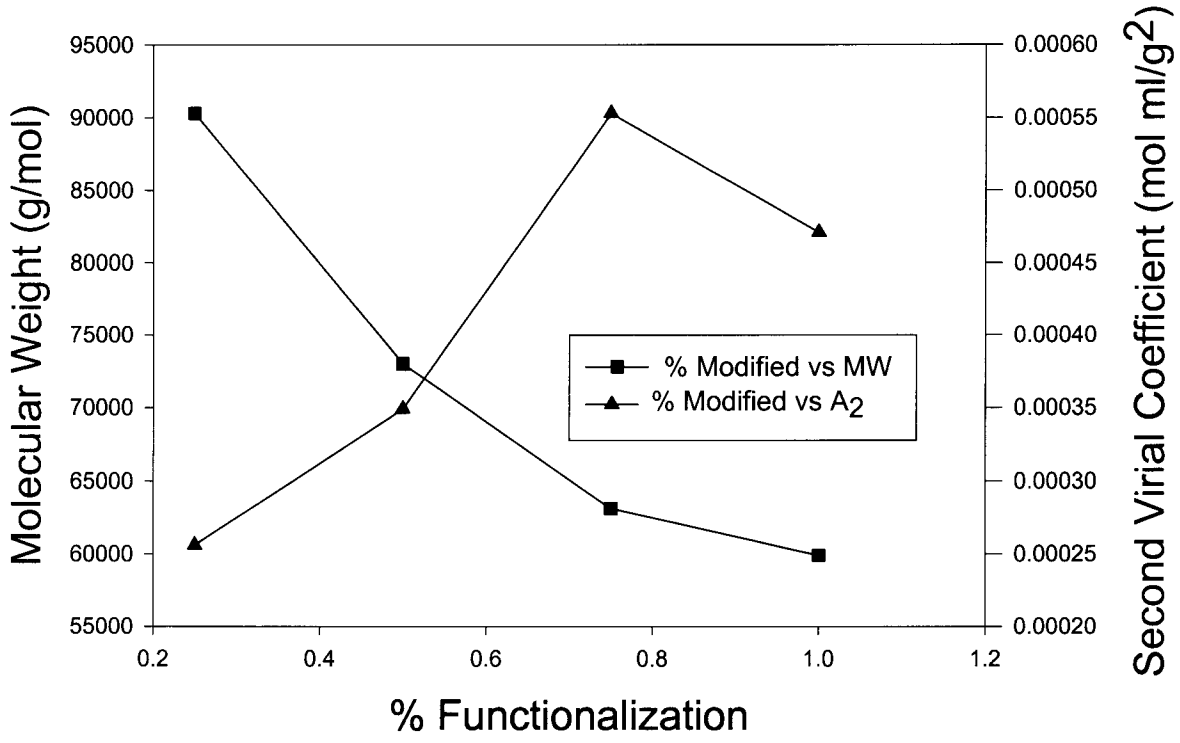


Figure 3

Effects of pH on MW and Second Virial Coeff. of PEIP1.0

(Salt conc.,1 M Nacl/distilled/deionized H_2O/polymer conc. 3.91e-3, T= 25 °C)

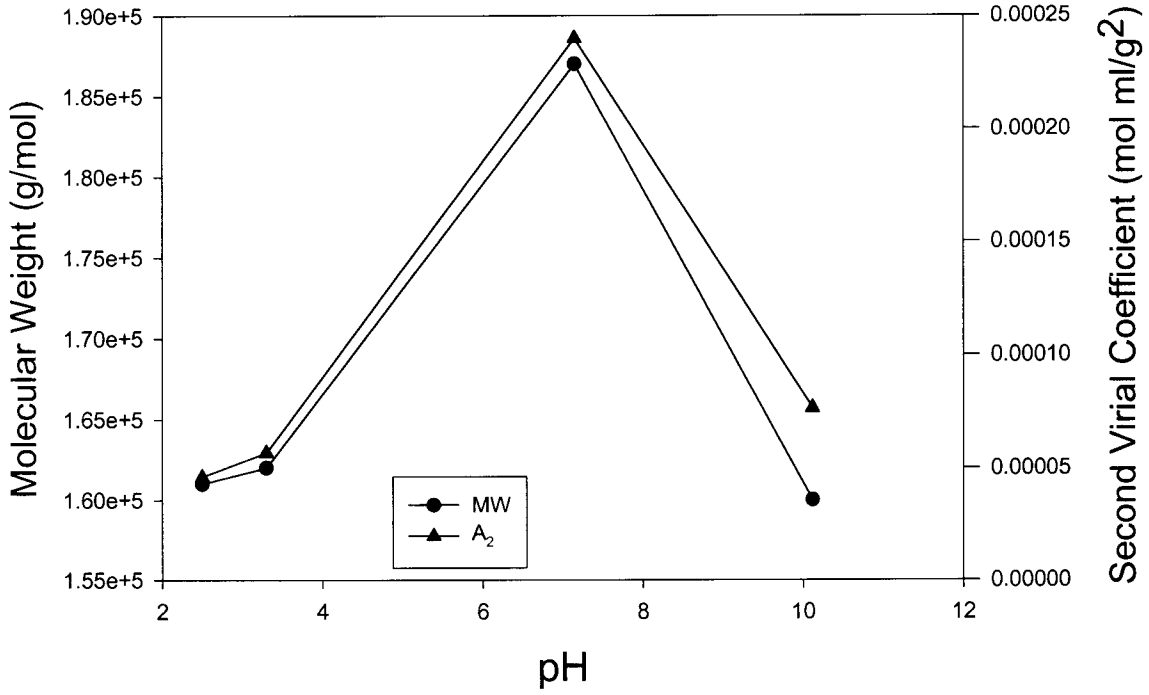


Figure 4

Table 4

pH	MW (g/mol)	A_2 (mol ml/g^2)
2.5	1.61e+05	4.60e-05
3.3	1.62e+05	5.67e-05
7.15	1.87e+05	2.40e-04
10.12	1.60e+05	7.65e-05

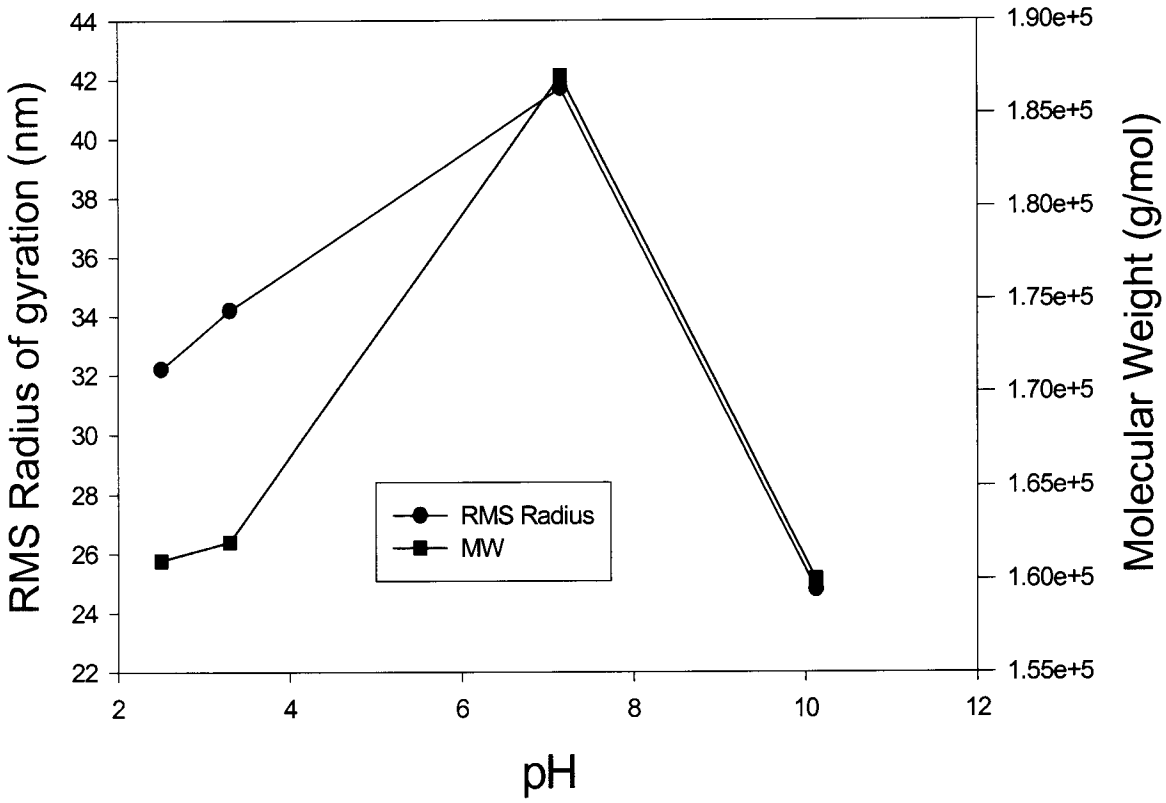


Figure 5

Table 5

pH	RMS Radius (nm)	MW (g/mol)
2.5	32.2	1.61e+05
3.3	34.2	1.62e+05
7.15	41.7	1.87e+05
10.12	24.8	1.60e+05

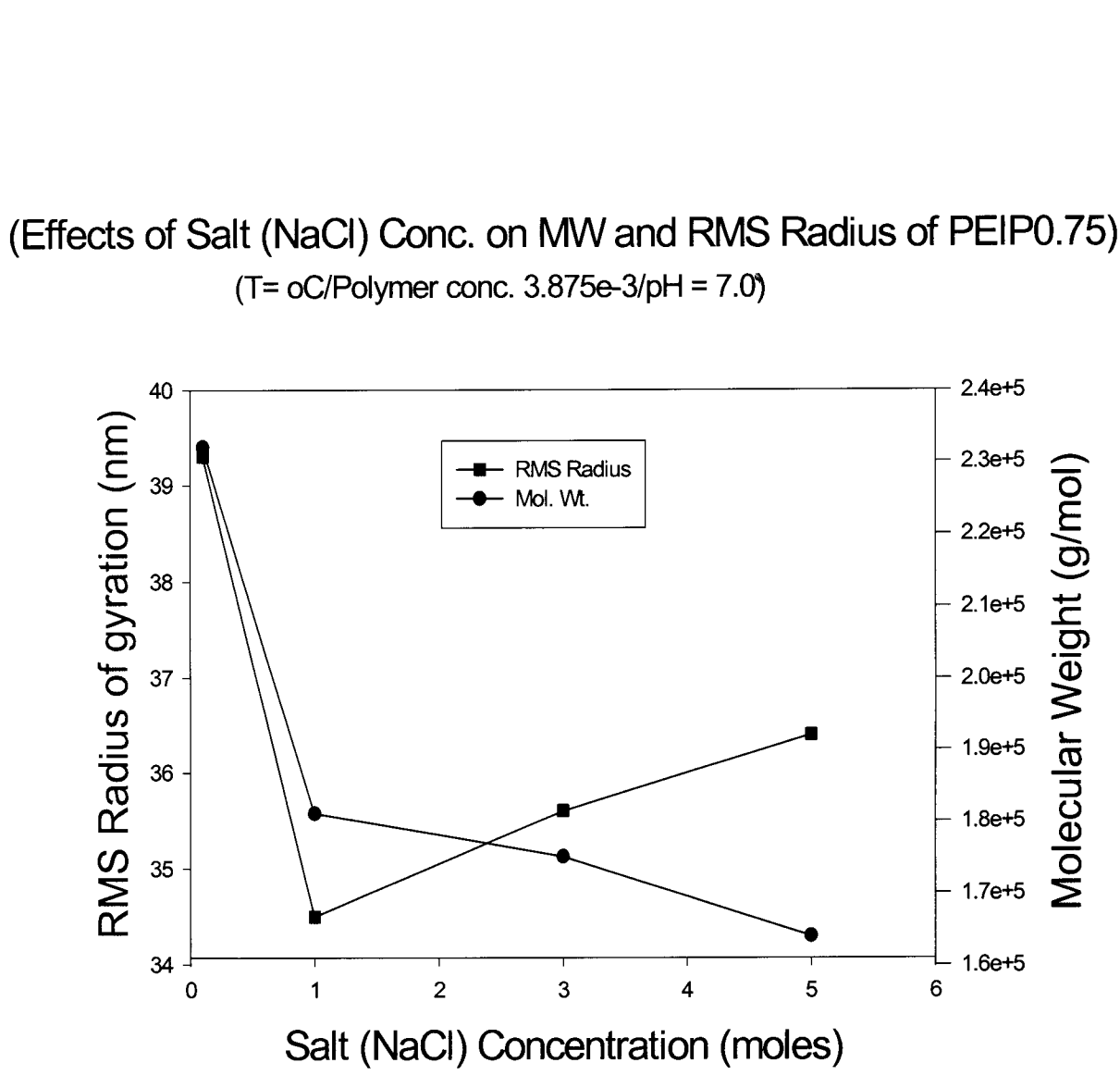


Figure 6

Table 6

Salt Conc. (moles)	RMS Radius (nm)	MW (g/mol)
0.1	39.3	2.32e+05
1	34.5	1.81e+05
3	35.6	1.75e+05
5	36.4	1.64e+05

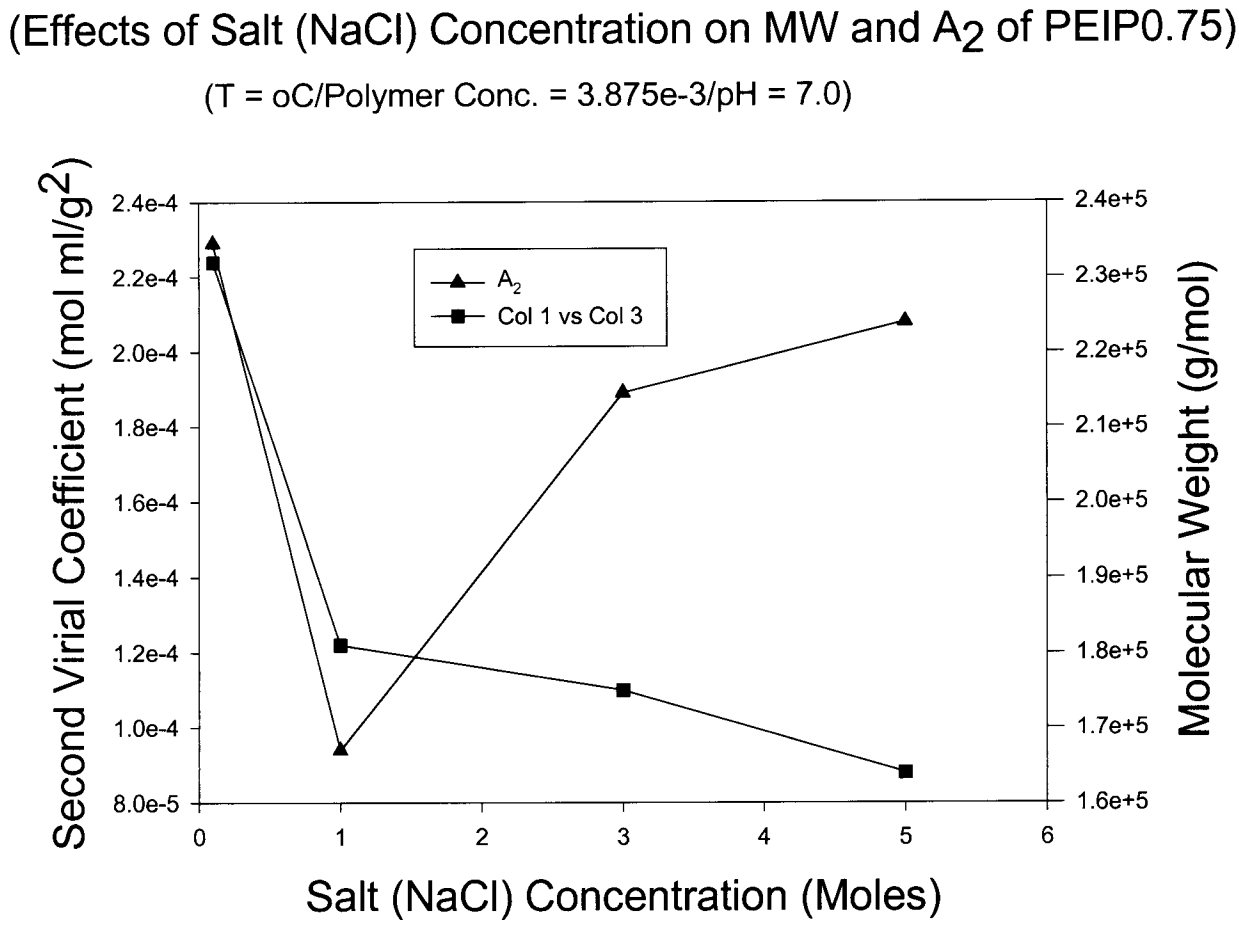


Figure 7

Table 7

Salt Conc. (moles)	Second Virial Coeff.(A_2)	MW (g/mol.)
0.1	2.29e-04	2.32e+05
1	9.40e-05	1.81e+05
3	1.89e-04	1.75e+05
5	2.08e-04	1.64e+05

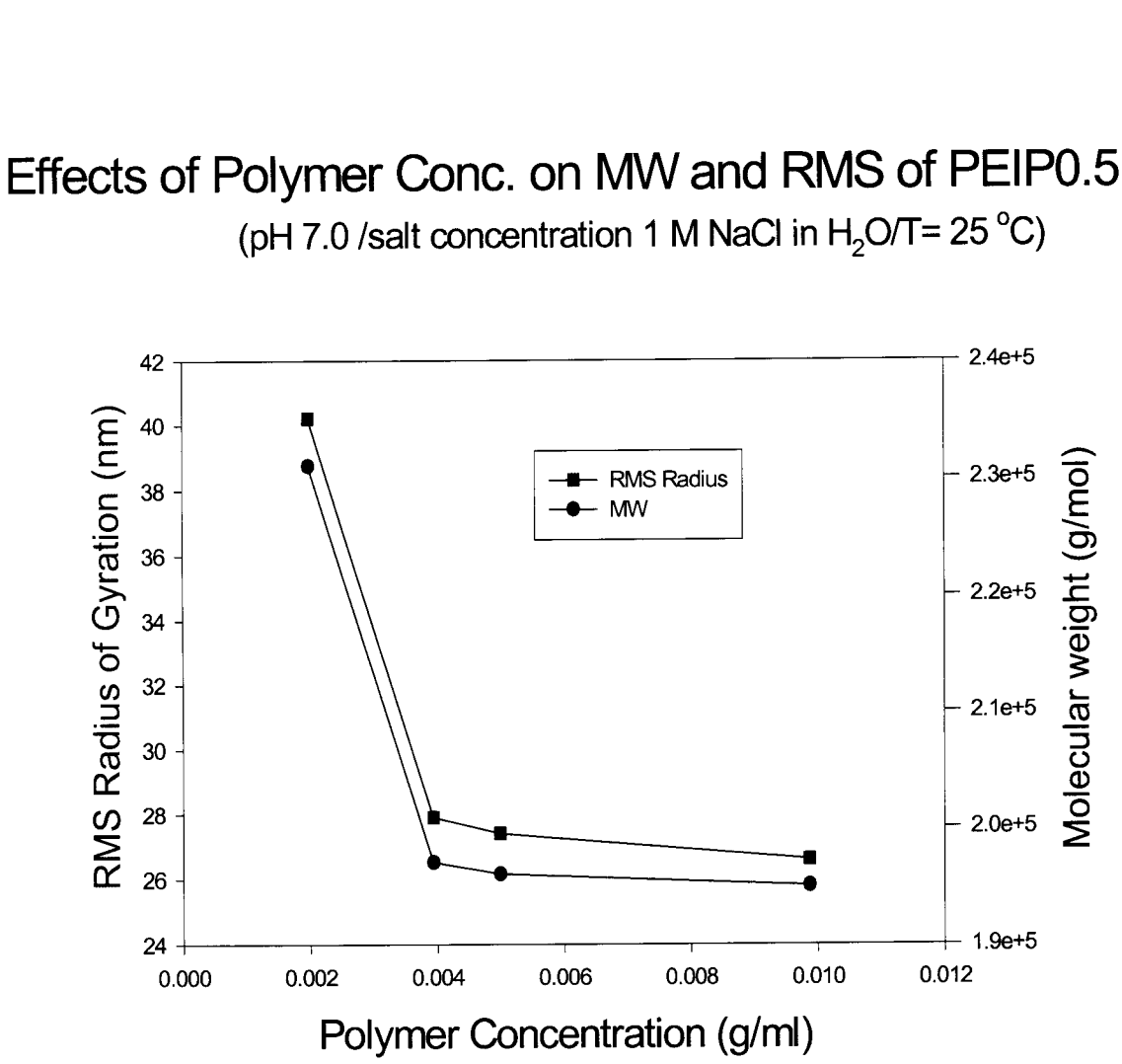


Figure 8

Table 8

Polymer Conc. (g/ml)	RMS Radius (nm)	MW (g/mol)
1.98e-03		
3.94e-03		
5.00e-03		
1.00e-02		

(Effects of Polymer Concentration on A_2 and MW of PEIP0.5)

(pH = 7.0/salt conc.= 1 M NaCl/T = 25 °C)

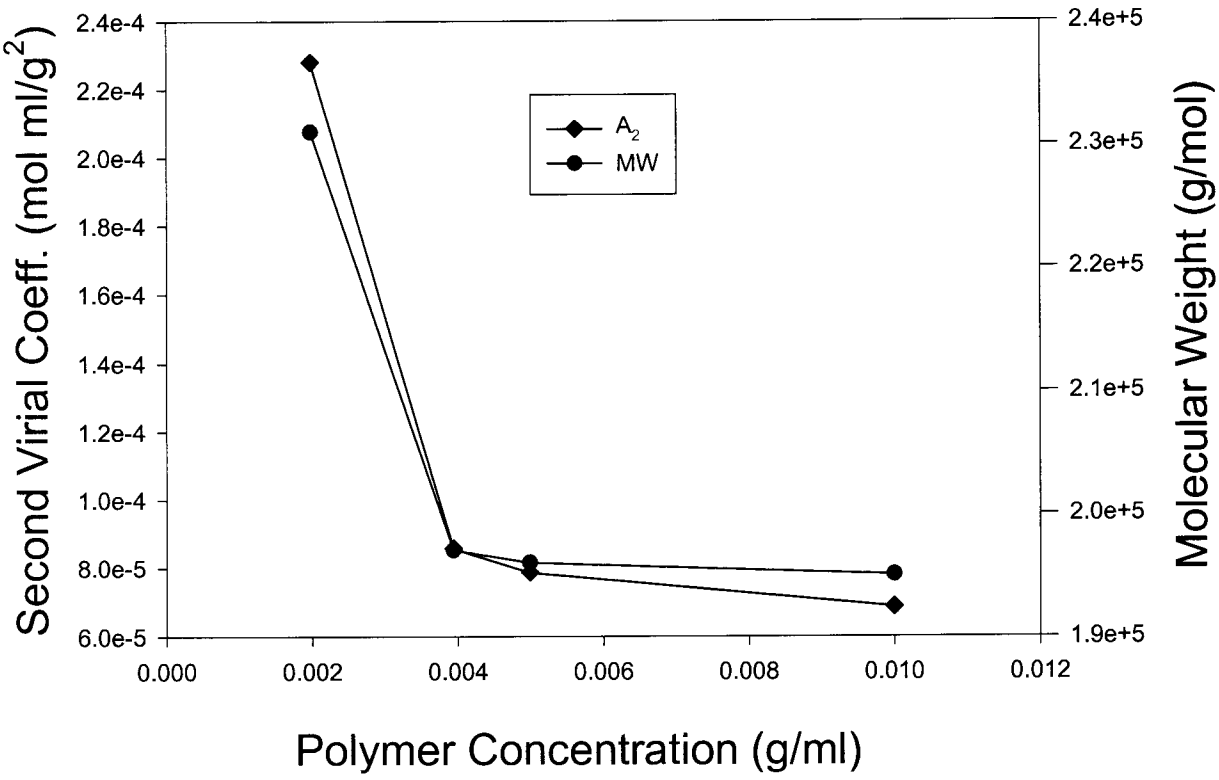


Figure 9

Table 9

Polymer conc. (g/ml)	A_2 (mol ml/g^2)	MW (g/mol)
1.98e-03	2.28e-04	2.31e+05
3.94e-03	8.57e-05	1.97e+05
4.99e-03	7.86e-05	1.96e+05
1.00e-02	6.86e-05	1.95e+05

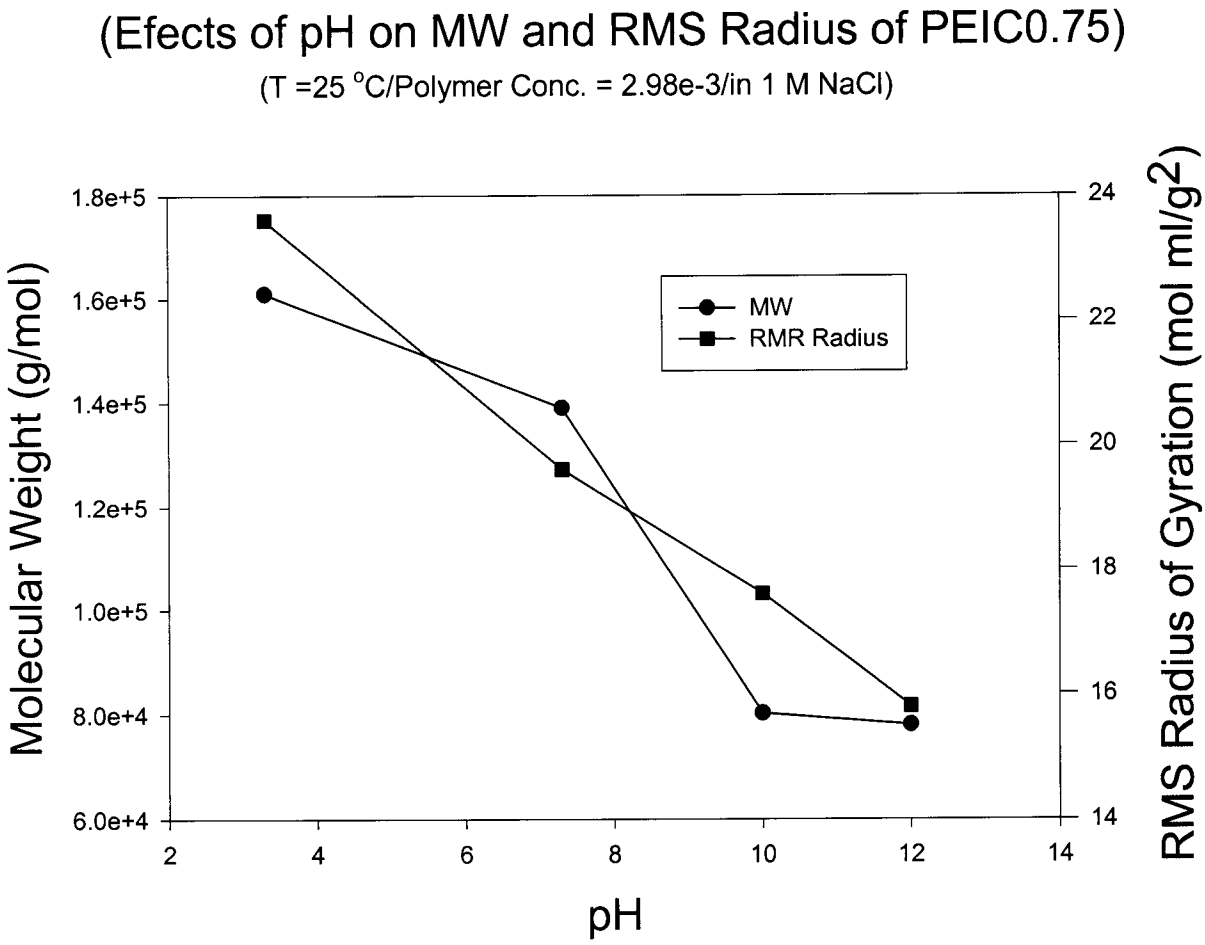


Figure 10

Table 10

pH	MW (g/mole)	A2 (mol ml/g^2)
3.30	1.61e+05	4.84e-04
7.30	1.39e+05	2.43e-04
10.00	8.02e+04	2.27e-04
12.00	7.80e+04	1.95e-04

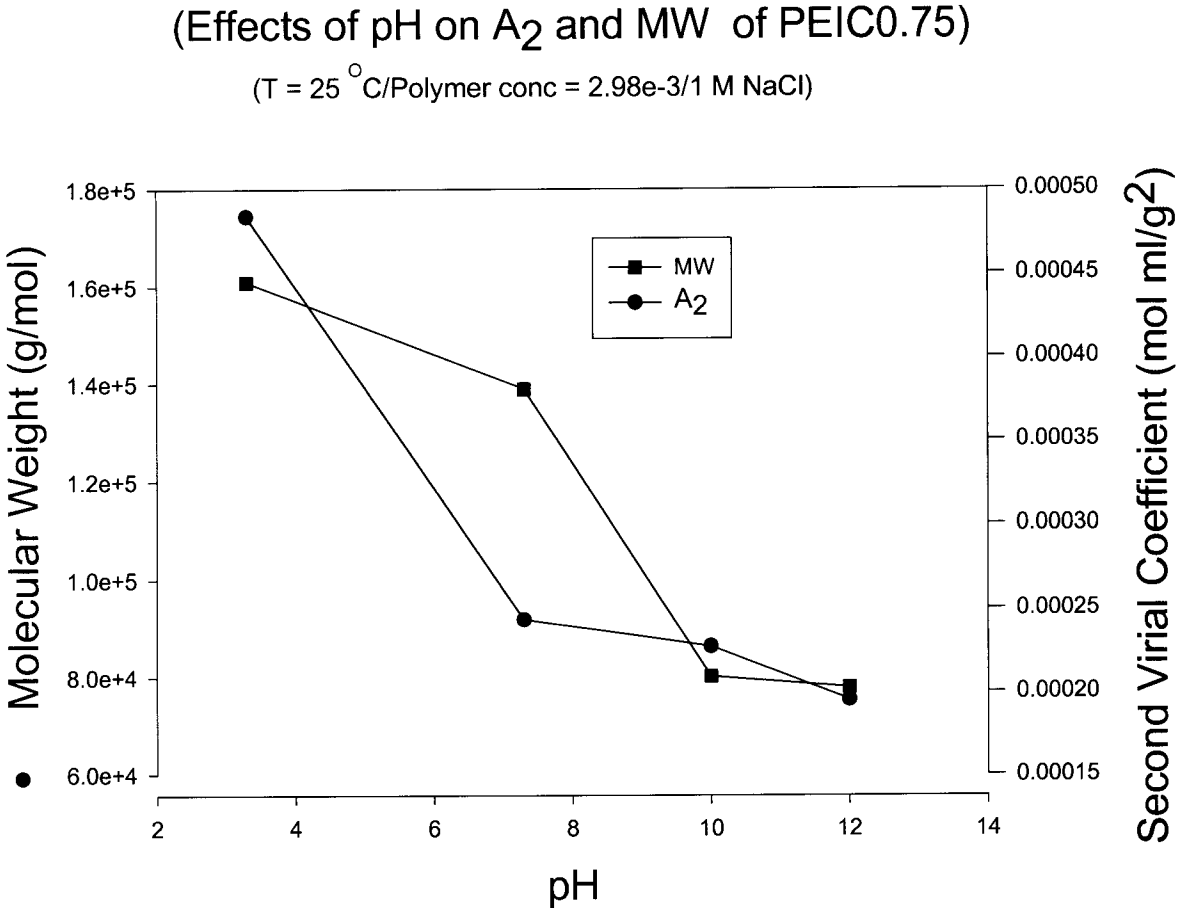


Figure 11

Table 11

pH	MW (g/mol)	A2 (mol ml/g2)
3.30	1.61e+05	4.84e-04
7.30	1.39e+05	2.43e-04
10.00	8.02e+04	2.27e-04
12.00	7.80e+04	1.95e-04

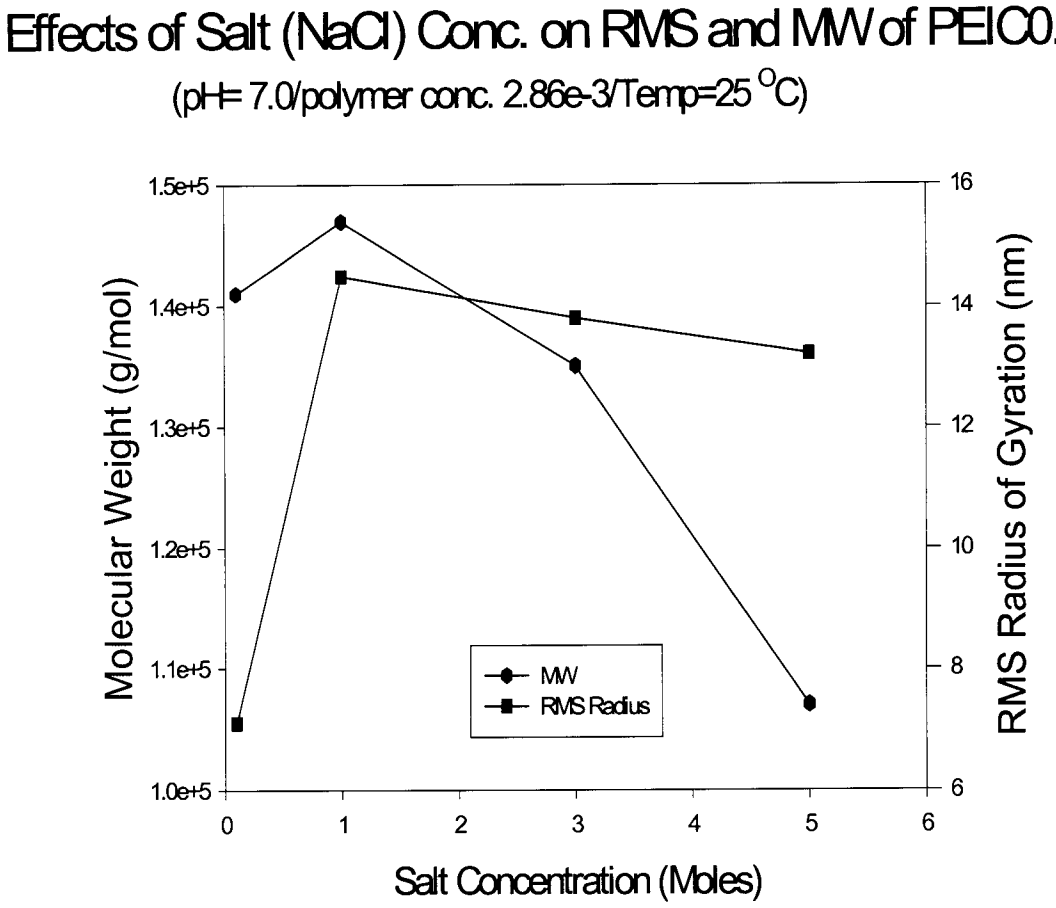


Figure 12

Table 12

Salt Conc. (Moles)	MW (g/mol)	RMS Radius (nm)
0.1	1.41e+05	7.1
1.0	1.47e+05	14.5
3.0	1.35e+05	13.8
5.0	1.07e+05	13.2

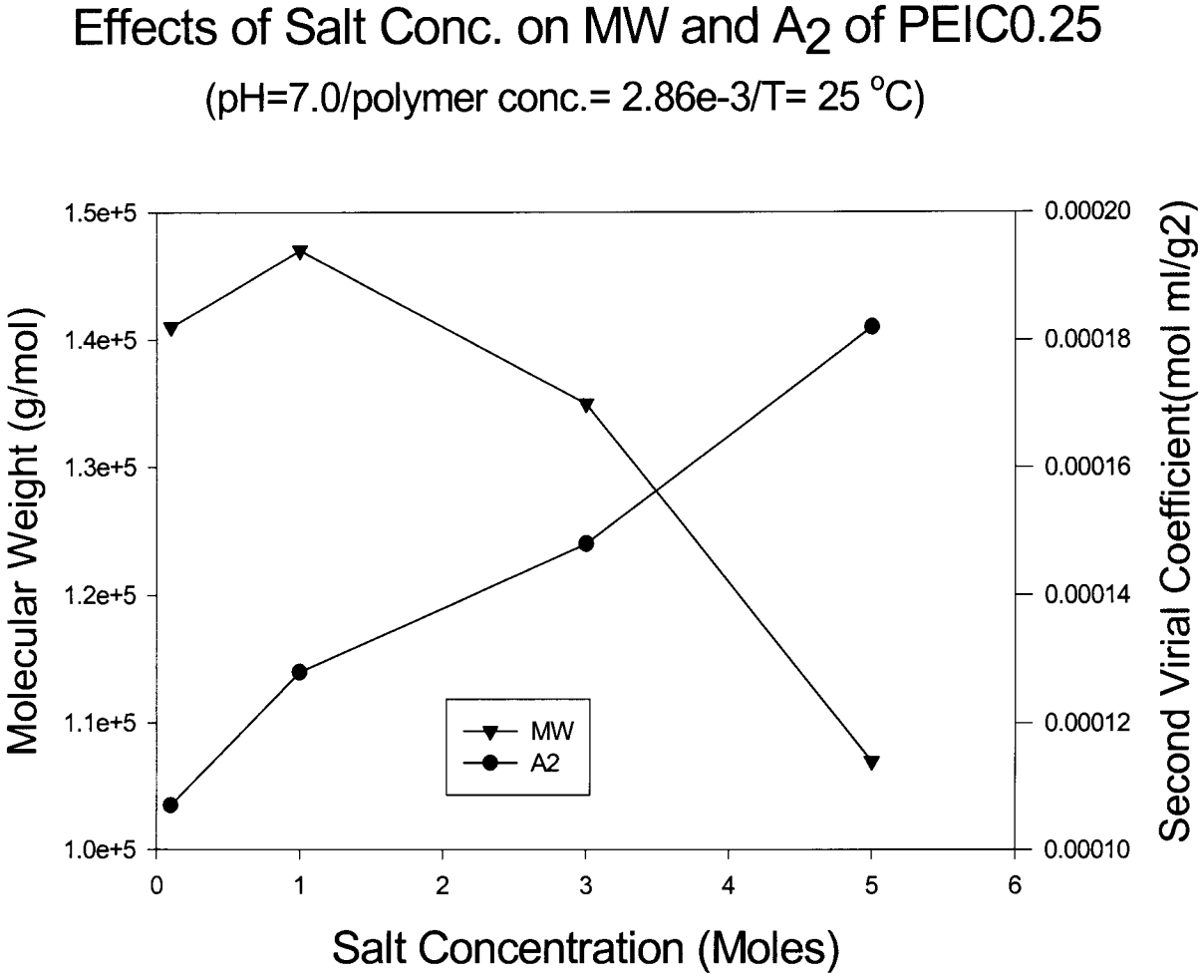


Figure 13

Table 13

Salt Conc. (moles)	MW (g/mol)	A2 (mol ml/g2)
0.1	1.41e+05	1.07e-04
1.0	1.47e+05	1.28e-04
3.0	1.35e+05	1.48e-04
5.0	1.07e+05	1.82e-04

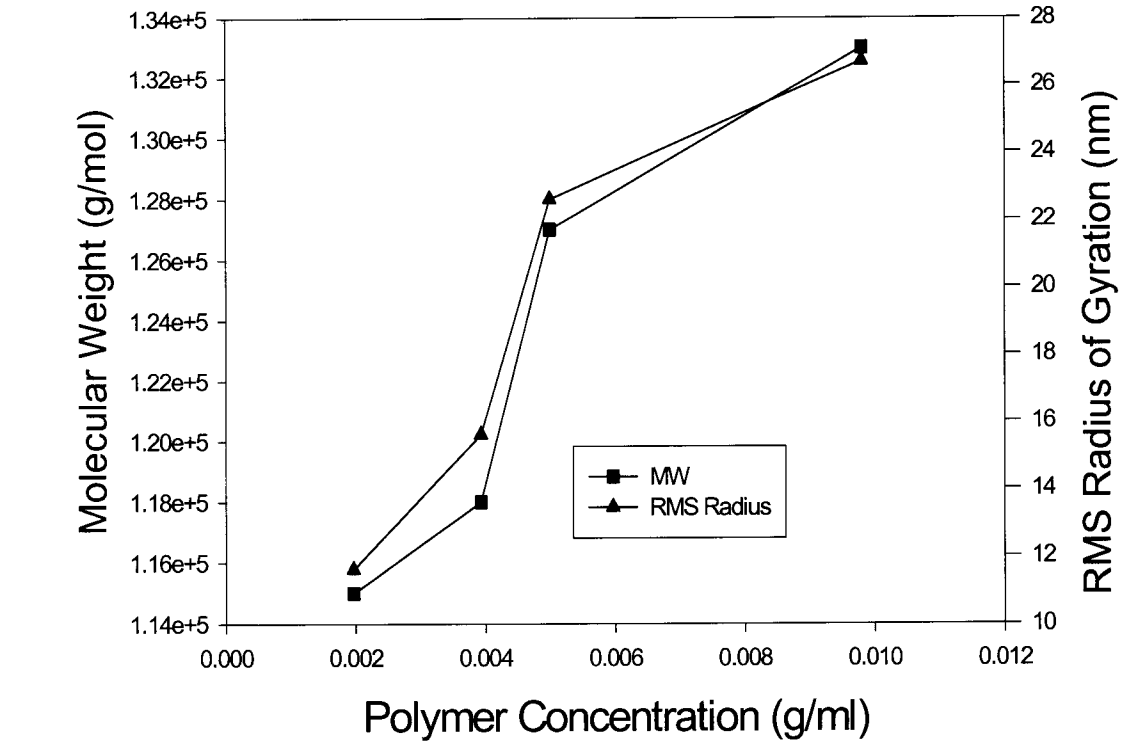


Figure 14

Table 14

Polymer Conc.(g/ml)	MW (g/mol)	RMS Radius (nm)
1.97e-03	1.15e+05	11.6
3.93e-03	1.18e+05	15.6
4.99e-03	1.27e+05	22.6
9.80e-03	1.33e+05	26.7

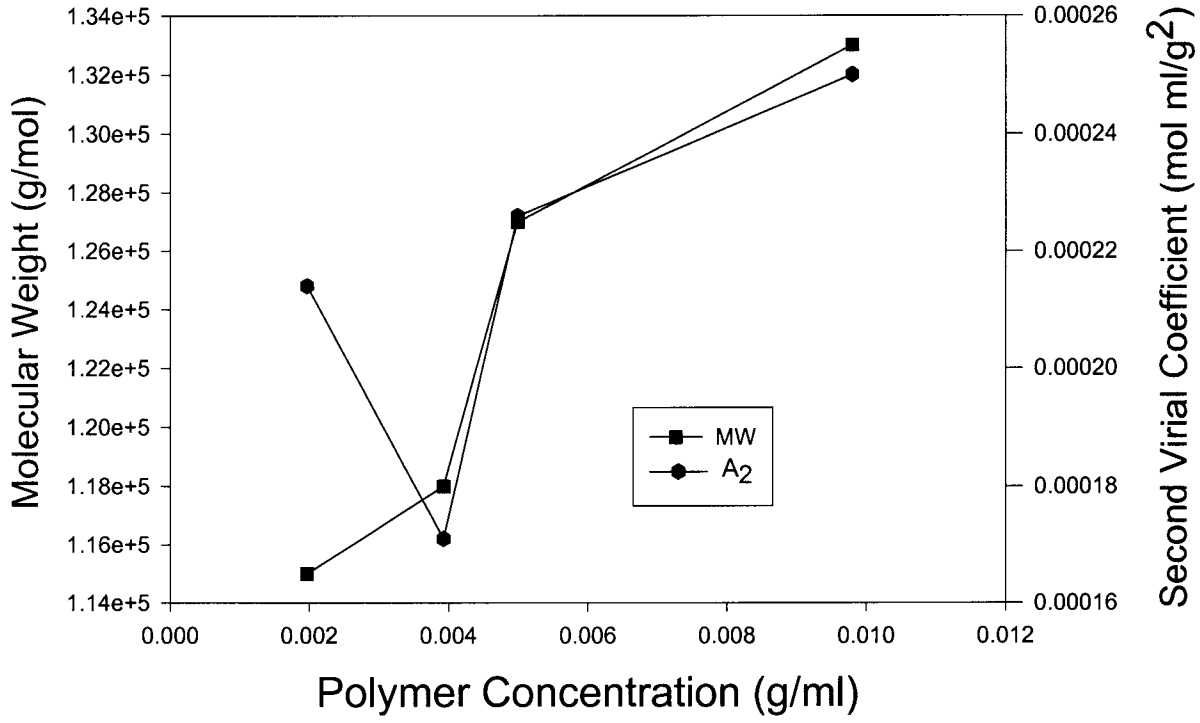


Figure15

Table 15

Polymer Conc. (g/ml)	MW (g/mol)	A2 (mol ml/g2)
1.97e-03	1.15e+05	2.14e-04
3.93e-03	1.18e+05	1.71e-04
4.99e-03	1.27e+05	2.26e-04
9.80e-03	1.33e+05	2.50e-04

Report on ^{113}Cd NMR studies of the Metal-binding characteristics of Polyethylenimine (PEI)

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1. INTRODUCTION

The selective removal and/or recovery of hazardous and valuable metal ions and radionuclides from various dilute aqueous streams are major concerns to the United States Government and environmentalists. Heavy metal contamination of the environment is caused by the wide usage of heavy metals in industries to meet the demand of modern society. However, polyethylenimine (PEI) a water-soluble polymer, has been found to have a great affinity to binding with metals, principally due to its polyelectrolyte character as well as their large macromolecular sizes which make them very useful in sequestering metal ions from dilute solutions. Metal-ion NMR is a useful tool in probing specific metal binding sites of macromolecules such as metalloproteins due to the sensitivity of these nuclei to their coordination environments. ^{113}Cd NMR spectroscopy has been used in studies of the structure and dynamics of inorganic and bio-inorganic molecules[1-4]. The utility of ^{113}Cd NMR as a metallobioprobe is due to the ability of the Cadmium (II) ion to form complexes over a range of conformation and ligand numbers. ^{113}Cd atom has a spin of ½ with no quadrupolar contribution to cause NMR relaxation, which broadens the NMR signals. A chemical shift range of over 900 ppm has been observed for ^{113}Cd, depending on the nature, number and geometric arrangement of the coordinated ligands [5-10]. Freeland et al.[11], have also demonstrated the high affinity of polyethylenimine for mercury. Also there have been several reports of the ability of protein fibers to absorb mercury from aqueous solution [12-14], and the possibility of using them in effluent purification processes or for clinical purposes[15]. Likewise, amine-modified cotton could adsorb mercury (Hg^{2+}) from solutions [16,17]. Hg^{2+} and Cd^{2+} ions have strong affinity for various chemical functional groups such as

carboxylate groups, amines, phenolic –OH groups, etc. Therefore, the use of cadmium and mercury NMR is very important in the study of the binding characteristics of PEI to metals.

2. EXPERIMENTAL

2.1 Materials:

Cadmium perchlorate EDTA, Cadmium oxide, Cadmium sulfate anhydrous and Cadmium chloride were purchased from Alfa Aesar, Deuterium oxide (D_20, 99.9%) deuterium chloride (DCl, 99.5%), Sodium deuteroxide (NaOD, 99.5%) were bought from Cambrigde Isotopes, Andover, Massachusetts. Poly(acrylic acid) (PAA, MW = 450.000), Polyethylenimine (PEI, MW = 10,000), Poly(methyacrylic acid, PMAA), Poly(methyacrylamide) PMA, water-soluble, hydrophilic, were purchased from Polysciences, Inc. Mercury (II) nitrate monohydrate, 15.5 N perchloric acid, potassium hydrogen phthalate, picolinic acid, 0.987 N NaOH, 0.953 N HCl, NaOH pellets, 2-propanol, Ethylenediamine, glycine and succinic acid were purchased from Aldrich Chemical Company.

2.2 Sample Preparation:

2.2.1 Preparation of 0.3 M $Cd(ClO_4)_2$ solution:

This was done by dissolving 1.251g of $Cd(ClO_4)_2.6H_2O$ in 10 ml of 0.1 M perchloric acid, to give 0.3 M $Cd(ClO_4)_2$ in 0.1 M perchloric acid.

2.2.2 Preparation of $CdCl_2$ solution:

This was done by dissolving 65 mg of CdO (12.86% natural abundance) in 2 ml of hot concentrated HCl acid. The aliquot was evaporated on a hot plate until it was dried out and the sediment turned to white powder. The sediment was then dissolved in 3.5 ml of D_2O.

mg of polyethylene (PEIC or PEIP) was dissolved in 1 ml of the $CdCl_2$ solution, for the NMR measurements.

3. RESULTS AND DISCUSSION

Results presented here collectively add up to a summary of the work done on the binding characteristics of PEI, PEIC and PEIP with ^{113}Cadmium.

3.1 Model Compound Studies

This work was a two-phase project. The first was to measure the chemical shifts of Cd-Polymers (PEIC and PEIP). The second phase was measuring the chemical shifts of well-defined molecular analogs of expected binding sites (model compounds/structures). Understanding the chemical shift anisotropy of Cadmium was necessary to understanding the chemical environments of the metal. This is specifically important in chelating environments where the nature of the ligands can change depending on a lot of factors. Some model compounds were studied in relation to their binding with cadmium. These are:

1. Ethylenediamine (2 amines)
2. Glycine, aminocarboxylate
3. Succinic acid
4. Polyacrylamide
5. Leucinamid hydrochloride
6. Butylamine (1 amine)
7. 3-Diamino-2-hydroxypropane

The chemical shift values of the Cadmium-PEI complex are shown in Figure 1 below. Two resonance values are shown at 305 ppm and 320 ppm. PEI is a purified polyethylenimine with only amine groups and no carboxylate groups. The chemical shift values move downfield with only amine groups present. As the polymer becomes functionalized, e. g. with addition of carboxylate groups, the resonances shift upfield. Figures 2 and 3 show the chemical shift values for the functionalized polymers coordinated to ^{113}Cadmium. As the percentage modification increases from 0% to 100% as the case may, the chemical shifts move upfield. $^{113}Cd^{2+}$ ion is an excellent metal ion probe due to its ability to form complexes with many different conformations and ligand

numbers[18]. Furthermore, the $^{113}Cd^{2+}$ chemical shift covers a wide range from about 800 to –200 ppm, and the nature of the coordinating ligands and their coordination numbers are strongly reflected in the chemical shift[19-21]. ^{113}Cd chemical shift in solutions of cadmium-containing coordination compounds is reflective of the directly bonded heteroatom of the ligand. In particular, ligands that bind through oxygen cause increased shielding of the Cd nucleus, while ligands that bind through nitrogen produce deshielding of the Cd nucleus. Ligands that bind via sulfur produce very large deshielding (downfield chemical shifts). This might partially explain the chemical shifts of the different levels of functionalization. Since the binding sites of Cadmium to PEIC are through oxygen in the carboxyl moieties, explains while the 75% and 100% modified PEIC are upfield to the 25% and 50% PEIC.

The use of Model compounds to investigate metal-binding characteristics of polymers is a standard procedure in NMR spectroscopy. Recently, an investigation of Cd (II)-carboxylate systems (mono- and di-carboxylic acids) in aqueous solution was carried out by Chung and Moon[22], using ^{113}Cd NMR spectroscopy. In this study, they found out that, in Cd(II)-carboxylate systems, an increase in the carboxylate-to-Cadmium ratio caused the chemical shift to move towards an upfield region: the cadmium ion becomes more shielded when coordinated water molecules are displaced by carboxylates. Figures 4 to 10 show the chemical shift values for Cd-Model compound complexes. Since PEI is basically an amine polymer, the critical requirement for a model compound was that it should have an amine group in most cases. Functionalization introduces carboxylate groups and it was important therefore to also use model compounds with this group. The chemical shift position is reflective of the number of amine or carboxylate groups present. Butylamine (with one amine) has shift value at 267 ppm (Fig. 5). Ethylenediamine with two amine groups has chemical shift at 351 ppm (Fig. 10). But introduction of carboxylate groups moves the chemical shift upfield, for example, glycine has one amine and a carboxylate group and has its chemical shift at 43.17 ppm. The chemical shifts for the model compounds are given in Table 3.

CONCLUSIONS

Polyethylenimine (PEI), a water-soluble polymer has been found to have great affinity to binding with metals, due to its polyelectrolyte character and large macromolecular size. PEI binds readily with Cd (II), Hg (II), etc., and therefore very useful for sequestering metal ions from aqueous streams. . ^{113}Cd chemical shift in solutions of cadmium-containing coordination compounds is reflective of the directly bonded heteroatom of the ligand. In particular, ligands that bind through oxygen cause increased shielding of the Cd nucleus, while ligands that bind through nitrogen produce deshielding of the Cd nucleus. Ligands that bind via sulfur produce very large deshielding (downfield chemical shifts).

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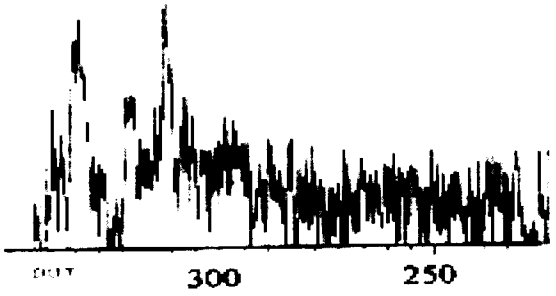


Figure 1. Shows the chemical shifts of the Cadmium-PEI complex. The purified PEI has two chemical shift values at 305 and 320 ppm.

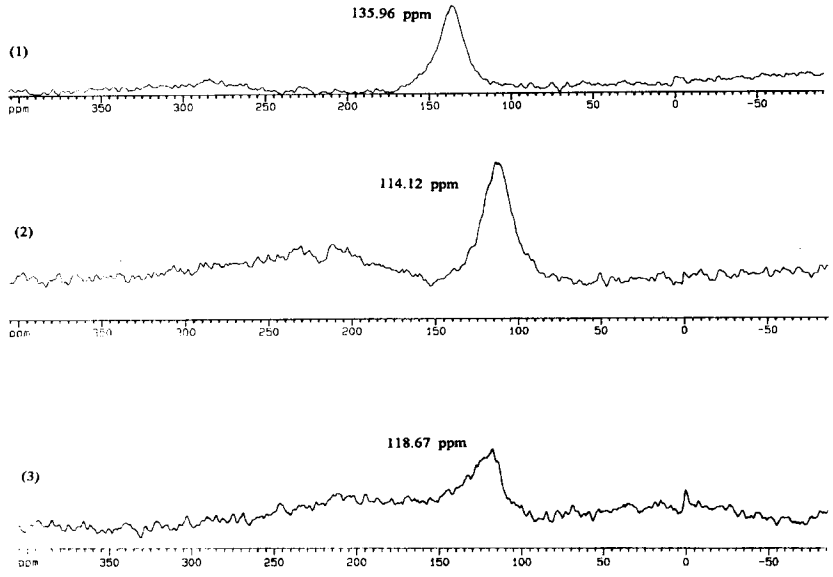


Figure 2. ^{113} Cd NMR spectrum of ^{113}Cd-PEIP complexes. Cd-PEIP complexes have chemical shifts at (1) 135.96 ppm for Cd-PEIP 0.25 complex, (2) 114.12 ppm for Cd-PEIP0.50 complex and (3) 118.67 for Cd-PEIP 0.75 complex.

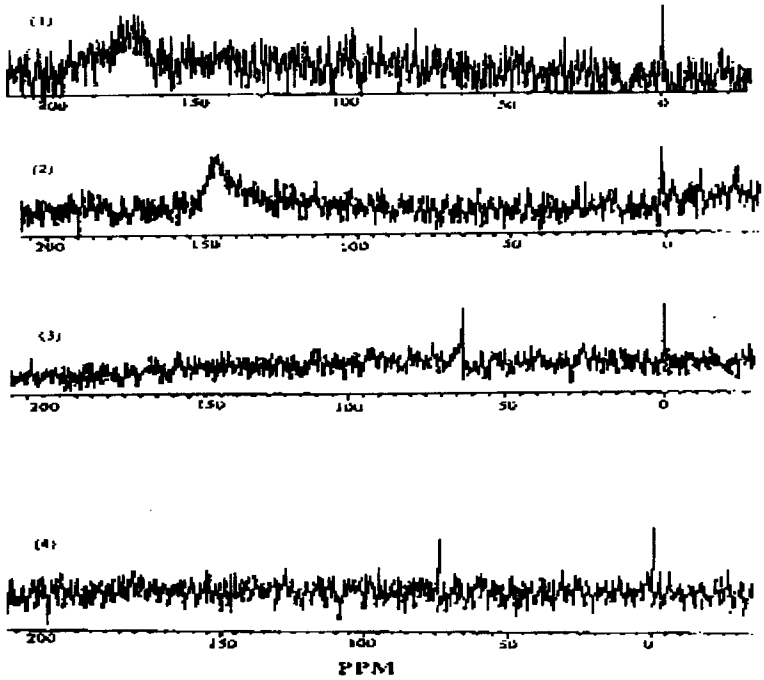


Figure 3. The ^{113}Cd-PEIC complex NMR spectra of different levels of functionalization of PEIC (Carboxyl-modified PEI), where (1) 25%, (2) 50%, (3) 75 % and (4) 100% modified.

MODEL COMPOUNDS

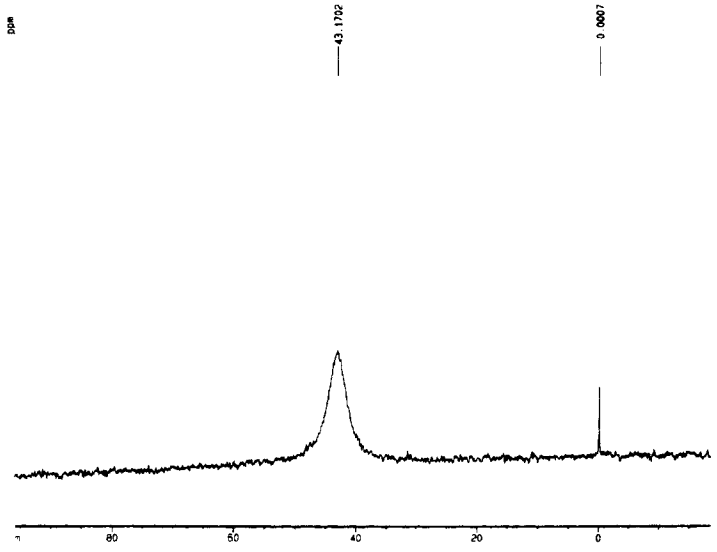
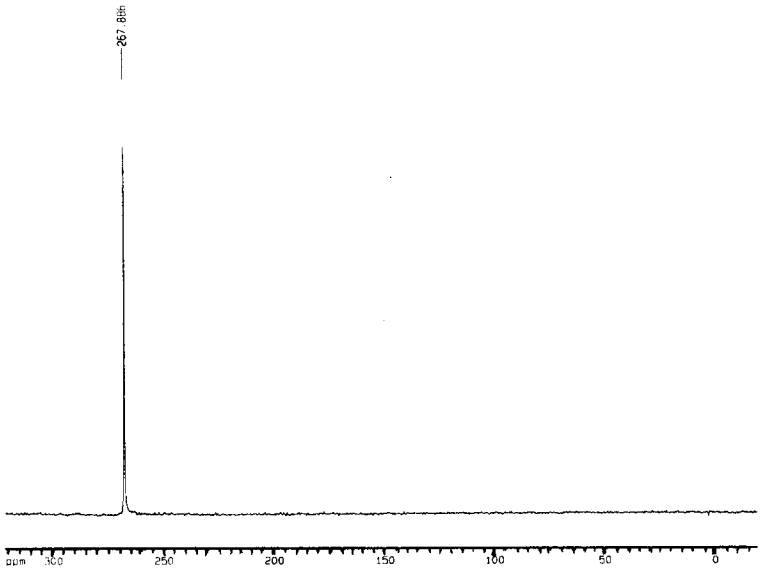
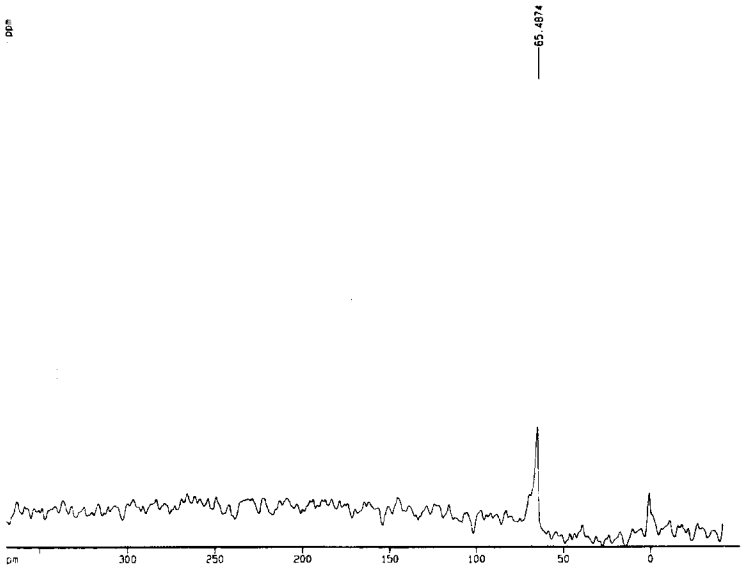


Figure 4. The ^{113}Cd-Glycine (^{113}Cd-Gly) spectrum. The chemical shift for Gly is 43.17 ppm.



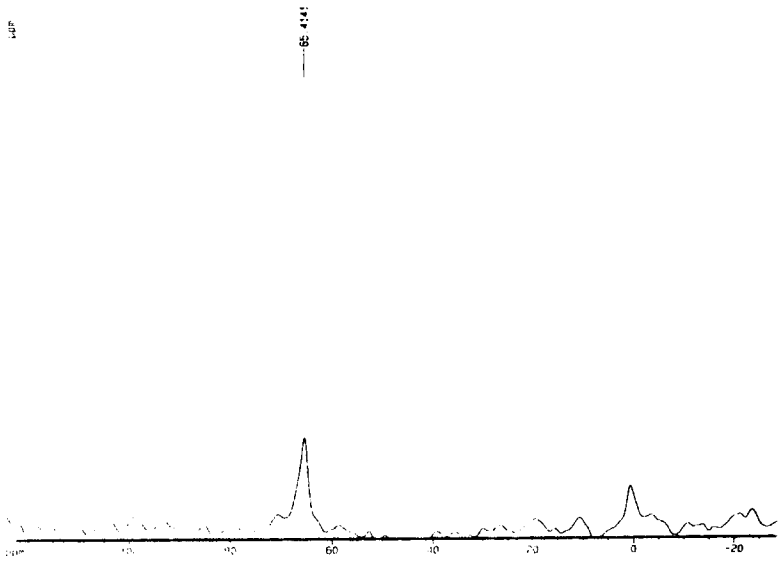
PPM

Figure 5. Shows the chemical shift of ^{113}Cd-Butylamine complex with δ= 267.87 ppm.



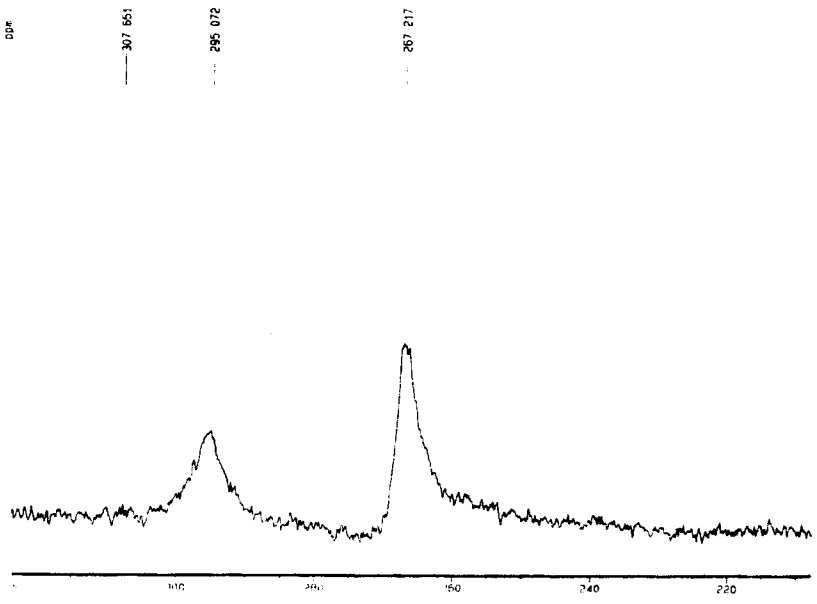
PPM

Figure 6. ^{113}Cd NMR chemical shift of ^{113}Cd-Polymethyacrylamide (PMA) at 65.48 ppm



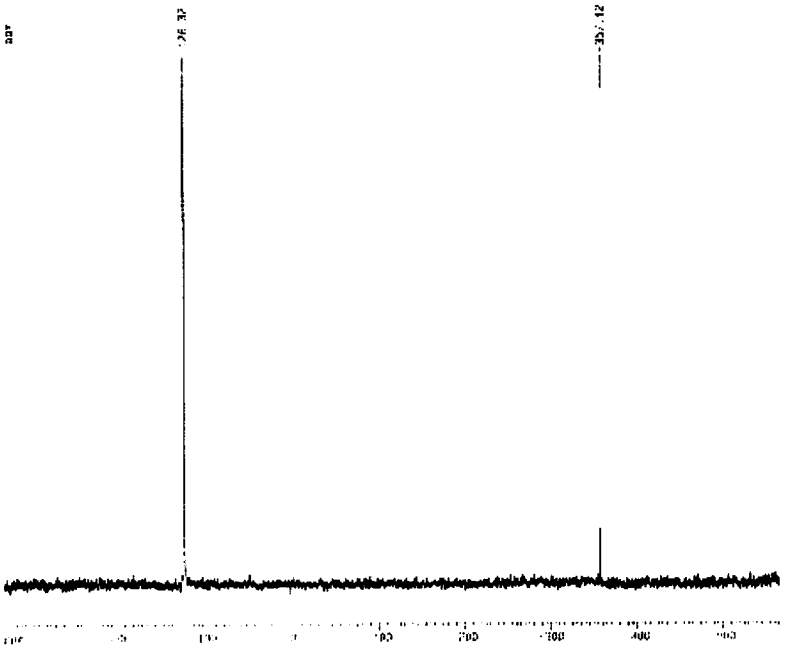
PMM

Figure 7. The chemical shift of ^{113}Cd-SUC (Cd-Succinic acid) at 45.41 ppm.



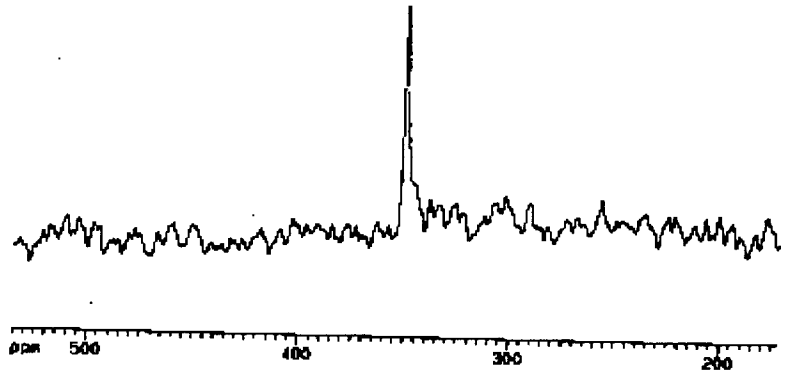
PPM.

Figure 8. Shows the chemical shift values of ^{113}Cd-I, 3-diamino 2-hydroxypropane (DHP), at 260 ppm and 290 ppm.



PPM

Figure 9. Chemical shifts of ^{113}Cd-Leucinamide(HCl) at 126.3 and -357.1 ppm



PPM

Figure 10. 113 Cd binding with Ethylenediamine (EDA) with the chemical shift value δ = 351.106 ppm.

Table 1. Chemical shifts for PEIC polymers

% FUNCTIONALIZATION	NMR CHEMICAL SHIFT VALUES (δ)
PEIC 0.25 (25%)	175.00
PEIC 0.50 (50 %)	146.03
PEIC 0.75 (75%)	63.74
PEIC 1.00 (100%)	74.50

Table 2. Chemical shift for PEIP polymers

% FUNCTIONALIZATION	NMR CHEMICAL SHIFT VALUES (δ)
PEIP 0.25 (25 %)	135.96
PEIP 0.50 (50%)	114.12
PEIP 0.75 (100 %)	118.67
UNMODIFIED PEI	305, 320

Table 3. Model compounds Chemical Shifts

MODEL COMPOUNDS	^{113}Cd-Model compd δ (ppm)
Polymethacrylate (PMA)	65.48
Glycine (GLY)	43.17
Succinic Acid (SUC)	45.41
Leucinamide hydrochloride (LEU)	126.3, -357.1
Buthylamide (BTA)	267.87
3-Diamino, 2-hydroxypropane	260, 290
Ethylenediamine (EDA)	351.10

^{113}Cd NMR studies of the Metal-binding characteristics of Polyethylenimine (PEI)

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ABSTRACT

Polyethylenimine (PEI), a water-soluble polymerhas been found to have great affinity to binding with metals, due to its polyelectrolyte character and large macromolecular size. PEI binds readily with Cd (II), Hg (II), etc., and therefore very useful for sequestering metal ions from aqueous streams.

1. INTRODUCTION

The selective removal and/or recovery of harzadous and valuable metal ions and radionuclides from various dilute aqueous streams are major concerns to the United States Government and environmentalists. Heavy metal contamination of the environment is caused by the wide usage of heavy metals in industries to meet the demand of modern society. However, polyethylenimine (PEI) a water-soluble polymer, has been found to have a great affinity to binding with metals, principally due to its polyelectrolyte character as well as their large macromolecular sizes which make them very useful in sequestering metal ions from dilute solutions. Metal-ion NMR is a useful tool in probing specific metal binding sites of macromolecules such as metalloproteins due to the sensitivity of these nuclei to their coordination environments. ^{113}Cd NMR

spectroscopy has been used in studies of the structure and dynamics of inorganic and bio-inorganic molecules[1-4]. The utility of ^{113}Cd NMR as a metallobioprobe is due to the ability of the Cadmium (II) ion to form complexes over a range of conformation and ligand numbers. ^{113}Cd atom has a spin of ½ with no quadrupolar contribution to cause NMR relaxation, which broadens the NMR signals. A chemical shift range of over 900 ppm has been observed for ^{113}Cd, depending on the nature, number and geometric arrangement of the coordinated ligands [5-10]. Freeland et al.[11], have also demonstrated the high affinity of polyethylenimine for mercury. Also there have been several reports of the ability of protein fibers to absorb mercury from aqueous solution [12-14], and the possibility of using them in effluent purification processes or for clinical purposes[15]. Likewise, amine-modified cotton could adsorb mercury (Hg^{2+}) from solutions [16,17]. Hg^{2+} and Cd^{2+} ions have strong affinity for various chemical functional groups such as carboxylate groups, amines, phenolic –OH groups, etc. Therefore, the use of cadmium and mercury NMR is very important in the study of the binding characteristics of PEI to metals.

2. EXPERIMENTAL

Materials: Cadmium perchlorate EDTA, Cadmium oxide, Cadmium sulfate anhydrous and Cadmium chloride were purchased from Alfa Aesar, Deuterium oxide (D_20, 99.9%) deuterium chloride (DCl, 99.5%), Sodium deuteroxide (NaOD, 99.5%) were bought from Cambridge Isotopes, Andover, Massachusetts. Poly(acrylic acid) (PAA, MW = 450.000), Polyethylenimine (PEI, MW = 10,000), Poly(methyacrylic acid, PMAA), Poly(methyacrylamide) PMA, water-soluble, hydrophilic, were purchased from Polysciences, Inc. Mercury (II) nitrate monohydrate, 15.5 N perchloric acid, potassium hydrogen phthalate, picolinic acid, 0.987 N NaOH, 0.953 N HCl, NaOH pellets, 2-propanol, Ethylenediamine, glycine and succinic acid were purchased from Aldrich Chemical Company.

2.1 Sample Preparation:

2.1.1 Preparation of 0.3 M $Cd(ClO_4)_2$ solution: This was done by dissolving 1.251g of $Cd(ClO_4)_2.6H_2O$ in 10 ml of 0.1 M perchloric acid, to give 0.3 M $Cd(ClO_4)_2$ in 0.1 M perchloric acid.

2.1.2 Preparation of $CdCl_2$ solution: This was done by dissolving 65 mg of CdO (12.86% natural abundance) in 2 ml of hot concentrated HCl acid. The aliquot was evaporated on a hot plate until it was dried out and the sediment turned to white powder. The sediment was then dissolved in 3.5 ml of D_2O.

2.1.3 Cdmium-Polymer sample preparation: 60 to 62 mg of polyethylene (PEIC or PEIP) was dissolved in 1 ml of the $CdCl_2$ solution, for the NMR measurements.

2.2 Model Compound Studies

This work is a two-phase project. The first is to measure the chemical shifts of Cd-Polymers (PEIC and PEIP). The second phase is measuring the chemical shifts of well-defined molecular analogs of expected binding sites (Model compounds/structures). Understanding the chemical shift anisotropy of Cd, Hg, Ni and other metals will provide information on the chemical environments of the metals. This is specifically important in chelating environments where the nature of the ligands can change. For example,

-N can become protonated

-N substituents can vary

>C=O becomes >C-O^-

Other complexing moieties may be present; e.g., we may have primary, secondary and even tertiary amines that can bind to metals, all to varying degrees. Other parameters that can and will affect observed resonance positions include, pH, Osmotic strength, (ionic strength), competitive binding with other groups, other metals, temperature, etc. Some of the proposed model compounds and structures include:

1. Ethylenediamine (2 amines)
2. EDTA or PANAM –0.5, containing 4 surface carboxylate groups
3. Bis-diethylenediamine, containing six surface carboxylate groups
4. Cyclam, containing 4 amine groups
5. Glycine, aminocarboxylate

6. Glycolic, gluconic acids, hydroxycarboxylates
7. Succinic acid, dicarboxylate
8. Picolinic acid, carboxylate with neutral N group
9. Starburst dendrimer generation 1.5
10. Poly (acrylic acid) PAA
11. Poly (methylacrylic acid), PMAA
12. Polyacrylamide

Results and Discussion

Table 1and Figure 1 show the chemical shift values for the ^{113}Cd-PEIC complexes. The peaks are broad at low percent functionalization. As the level of carboxyl-modification increases, the peaks become sharper, as can be seen for 75% and 100% functionalized PEIC. The apparent reason for this is related to the number of exposed binding sites for Cadmium. It seems that the binding site for PEIC is the carboxyl group, (>C-O$^-$). At low percent functionalization, the number of binding sites is few. This leads to rapid exchange between free and bound Cd^{2+} ions. This results in the broadening of NMR peaks. As the polymers become more functionalized the rapid exchange reduces drastically, resulting in narrower peaks. $^{113}Cd^{2+}$ ion is an excellent metal ion probe due to its ability to form complexes with many different conformations and ligand numbers[18]. Furthermore, the $^{113}Cd^{2+}$ chemical shift covers a wide range from about 800 to –200 ppm, and the nature of the coordinating ligands and their coordination numbers are strongly reflected in the chemical shift[19-21]. ^{113}Cd chemical shift in solutions of cadmium-containing coordination compounds is reflective of the directly bonded heteroatom of the ligand. In particular, ligands that bind through oxygen cause increased shielding of the Cd nucleus, while ligands that bind through nitrogen produce deshielding of the Cd nucleus. Ligands that bind via sulfur produce very large deshielding (downfield chemical shifts). This might partially explain the chemical shifts of the different levels of functionalization. Since the binding sites of Cadmium to PEIC are through oxygen in the carboxyl moieties, explains while the 75% and 100% modified PEIC are upfield to the 25% and 50% PEIC.

Table 2 and Figure 2 show the chemical shift values of ^{113}Cd-PEIP complexes. As the % functionalization increases from 25% to 75%, the chemical shift values go upfield, as a result of increased shielding by the phosphorus atom. Figure 3 and Table 3 show the binding characteristics of some model compounds. The binding of Cadmium to amine-containing molecules a downfield shift as shown by ^{113}Cd-Ethylenediamine chemical shift at 351.106 ppm.. Ethylenediamine has two amine groups, leading to long downfield shift. Succinic acid has two carboxylic groups and therefore has an upfield shift at 45.41 pp.

The use of Model compounds to investigate metal-binding characteristics of polymers is a standard procedure in NMR spectroscopy. Recently, an investigation of Cd (II)-carboxylate systems (mono- and di-carboxylic acids) in aqueous solution was carried out by Chung and Moon[22], using ^{113}Cd NMR spectroscopy. In this study, they found out that, in Cd(II)-carboxylate systems, an increase in the carboxylate-to-Cadmium ratio caused the chemical shift to move towards an upfield region: the cadmium ion becomes more shielded when coordinated water molecules are displaced by carboxylates. Figure 4 compares the structures of regular PEI, PEIC, and Starburst PANAM Dendrimer 1.5, and shows why a model structure like the dendrimer will be appropriate for the study of the structure and reactions of PEIC.

CONCLUSIONS

Polyethylenimine (PEI), a water-soluble polymerhas been found to have great affinity to binding with metals, due to its polyelectrolyte character and large macromolecular size. PEI binds readily with Cd (II), Hg (II), etc., and therefore very useful for sequestering metal ions from aqueous streams. . ^{113}Cd chemical shift in solutions of cadmium-containing coordination compounds is reflective of the directly bonded heteroatom of the ligand. In particular, ligands that bind through oxygen cause increased shielding of the Cd nucleus, while ligands that bind through nitrogen produce deshielding of the Cd nucleus. Ligands that bind via sulfur produce very large deshielding (downfield chemical shifts).

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