CONFORMATIONAL STUDY OF POLYELECTROLYTES

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by

Chinmaya Dharai

Roll No-409PH2091

&

Pratap Kumar Sahu

Roll No-410PH2145

Under the Academic Autonomy

National Institute of Technology, Rourkela

Under the Guidance of

Dr. Sidhartha Jena

Department of Physics

National Institute of Technology

Rourkela- 769008

DECLARATION

We here by declare that the work carried out in this thesis is entirely original. It was carried out at Department of Physics, National Institute of Technology, Rourkela. We further declare that it has not been formed the basis for the award of any degree, diploma, or similar title of any university or institution.

Chinmaya Dharai   Pratap Kumar Sahu

Department of physics   Department of physics

National Institute of Technology   National Institute of Technology

Rourkela-769008   Rourkela-769008

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National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled "**Conformational Study of Polyelectrolytes**" being submitted by **Chinmaya Dharai and Pratap Kumar Sahu** in partial fulfillment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic experimental work carried out by them under my supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Date:

Dr. Sidhartha Jena
Associate Professor
Department of Physics
NIT, Rourkela ,769008
Odisha, India

ABSTRACT

We have presented the conformational study of anionic polyelectrolyte, sodium sulfonated polystyrene having molecular weight 70kDa with the variation of the added electrolyte concentration. From the zeta potential measurements we found the decrease in particle mobility on increasing the salt concentration from 0M to 0.15M resulting in a decrease in the effective charge on the molecules. A similar decreasing pattern was observed for the viscosity measured by capillary viscometer with increase in the electrolyte concentration. The hydrodynamic radius of the particles obtained from the dynamic light scattering experiments showed significantly lower values with increment in salt concentration. The decreasing values of these parameters with rise in ionic strength indicate the collapsing of the extended polyelectrolyte chains in presence of salt.

Keywords: Conformation, Polyelectrolyte, Sodium Styrene Sulfonate, Dynamic Light Scattering, Zeta Potential, Viscosity.

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1.1 INTRODUCTION

Polyelectrolytes unlike neutral polymers are long chained molecules bearing charges on their backbone which dissociate into polyions and the associated counterions in solutions [1]. They exhibit behavior similar to both the polymers (high molecular weight compounds) as well as the electrolyte (salts) and hence are also known as polysalts. They are highly viscous similar to the polymer solutions also being electrically conductive just as any other salt solution. Figure 1 shows a polyelectrolyte brush and its dissociation in a solvent.
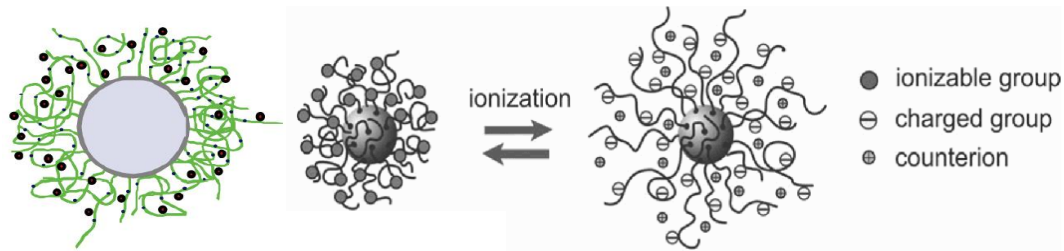

Fig.1 Spherical polyelectrolyte brush

They have been extensively studied for their biological as well as non – biological relevance. Most of the biopolymers known till date are polyelectrolyte in nature with common examples being deoxyribonucleic acid (the genetic material in cells), ribonucleic acid, and proteins. Understanding the functioning of these requires a thorough knowledge of their nature. The polyelectrolytes have been well exploited for their charged nature in different fields such as drug delivery, pharmaceuticals, biomedical applications, cosmetic industries, mineral processing, as thickeners, dispersants, and flavor while other uses include battery applications, paper making, paints, waste water treatment.

Polyelectrolytes have been categorized differently depending on their origin, charges on the backbone, and effective dissociation. The origin of the polyelectrolytes can be natural like biopolyelectrolytes such as DNA, RNA.The synthetic polyelectrolytes are man made and some of its examples are sodium polystyrene sulfonate, Polyacrylic acid poly – L – lysine hydrobromide, poly diallyl dimethyl ammonium chloride etc.

The polyelectrolytes are classified as cationic and anionic polyelectrolytes depending on whether they carry positive and negative charges. Some of the examples of the cationic polyelectrolytes are Poly - L - lysine, Polyallylamine hydrochloride while the sodium sulfonated polystyrene, Polyacrylic acid negatively charged polyelectrolytes. The figure following the text shows the structure of these polyelectrolytes.
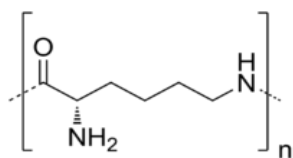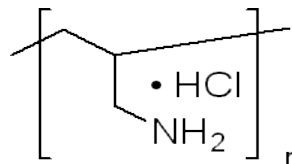
Poly – L – lysine   Polyallylamine hydrochloride

(a)
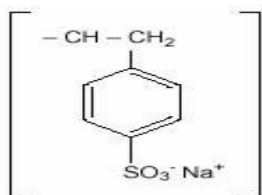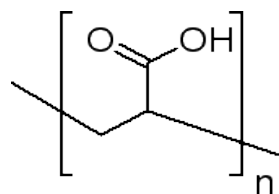
Sodium sulfonated polystyrene   Polyacrylic acid

(b)

Fig. 2 (a) Structures of cationic polyelectrolytes (b) Structures of anionic polyelectrolytes

In case of the poly – L – lysine and Polyallylamine hydrochloride the amine group forms a hydrogen bond with the hydrogen from the hydrobromide/chloride while the bromide/chloride ions are released into solutions thus leaving the positive charges on the polymer chains. In sodium sulfonated polystyrene sodium ions go into the solutions resulting in an anionic nature of the polymer chains. For the Polyacrylic acid the bond between the hydrogen atom and the COO^- is cleaved releasing the hydrogen ions into the solution and leaving behind a negatively charged polyion.

Based on their dissociation at various solution pH the polyelectrolytes are categorized as strong and weak polyelectrolytes. The strong polyelectrolytes are those which remain in a dissociated state for a wide range of the pH range implying they are charged to their full potential for a range of pH values. In contrary the weak

polyelectrolytes dissociate depending on the strength of solution pH. Thus the charges on the weak polyelectrolytes can be tuned by varying the solution pH.

As said earlier polyelectrolytes differ from the conventional polymers by the presence of charges on their backbone. These charges are responsible for giving rise to a range of polyelectrolytes conformations in solutions [1]. An important thing to note here is only the conformation is determined by the charges and not the configuration. Although these terms appear to be similar but there is a significant difference between the two. While change in configuration is associated with bond breaking, rotation of bonds around a fixed axis is sufficient for conformational changes.

The electrostatic repulsion between the backbone charges leads to an extended structures of the polyelectrolytes which contradicts the random – coil like structures of neutral polymers in solutions. The extended structure of the polyelectrolyte in solution is shown in figure 3.
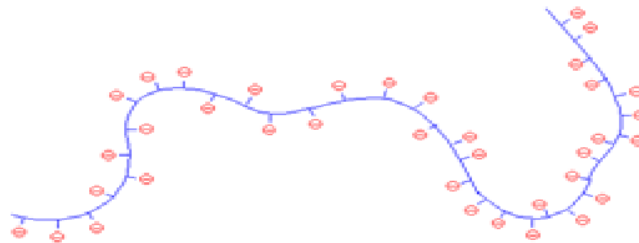
Fig. 3 Stretched polyelectrolyte chains

Polyelectrolytes assume different chain conformations under different conditions. Under fully charged conditions they remain completely extended. If the persistence length of the chains is greater than the chains contour length it will assume a stiff rod – like conformation. However the extended structure collapses on screening of the charges by the external agents leading the chains to adopt a flexible conformation. Certain other polyelectrolytes like DNA adopt a double helix structure in the crowded cells In spite of how simple they appear the conformations of polyelectrolytes are predominantly affected by factors like concentration, charge, ionic strength, solution pH, solvent quality, temperature, polymer architecture to mention a few. In the following text we describe briefly how these factors affect the conformations of polyelectrolytes.

At lower concentrations the linear chain polyelectrolytes assume an extended structure depending on the charges present. But these extended structures tends to collapse (or to say contracts) when the concentration of the polyions is increased as the availability of space for a single molecule decreases due to increasing concentration.

The presence of charges as discussed leads to a stretched conformation of polymer chains due to repulsion between similarly charged units. The extent to which the chain stretches depends on the number of charges present on the polymer chains. More is the number charges the more is the strength of the repulsive interactions that leads to a complete extension of the chains. This results in a larger persistence length (L_p) as compared to the contour length of the polymer chains. The polyelectrolytes therefore assume a rigid rod like structure in solutions on being fully charged.

However the extended structure of the polyelectrolyte collapses in presence of the salt. This is because of the screening of the backbone charges by the ions released by the dissociation of the salt [1]. Because of the presence of intervening oppositely charged ion cloud, the effective repulsive interaction experienced by the similarly charged species on the backbone of the polymer chain reduces considerably. This results in collapsing of the polymer chains. The screening effect and the collapsing of the chains in presence of externally added salt are shown in the figure 4 below.

In presence of

In absence of
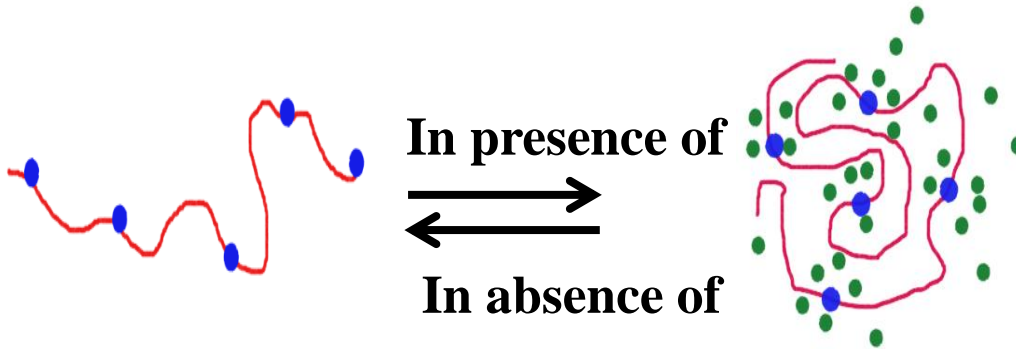
Fig. 4 Collapsing of polyelectrolyte chains in presence of salt

The change in solution pH also results in an appreciable change in the polyelectrolyte conformation especially in the case of weak polyelectrolytes. It is mentioned previously that the conformation shows a strong dependence on the number

of charges. In case of the weak polyelectrolytes this parameter depends on the degree of dissociation which in turn is dependent on the solution pH [1].

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The solvent quality is an essential parameter to tune the conformation from completely extended structures to flexible polymer coils. Polyelectrolytes in good solvent remain extended owing to the strong interactions between the polymer chains and the solvent molecules. A poor solvent on contrary increases the interaction between the polymer – polymer chains resulting in a decreased polymer – solvent interactions. These interactions result in contracting of the polymer chains in the poor solvent. An intermediate condition between the two extreme solvent qualities known as the 'theta condition' also exists where the coils expansion is compensated and the coils assume a random coil conformation.

The temperature tends to reduce the solvent viscosity thus modifying the solvent – polymer interactions. The temperature can therefore play a vital role in tuning the solvent quality from good to poor. Similar behavior of the solvent can be observed on varying the ionic strength. On exceeding the concentration of the added salt beyond certain limit leads to theta conditions [2].

The conformational studies impose a great importance as the conformation of polyelectrolytes is a deciding factor for many of their applications. The functioning of the polyelectrolytes relies heavily on its conformation and a slight variation in the conformation can dramatically affect its regular functioning. For example in biological cells specific function has been assigned to globular protein In case the conformation of the protein is altered due to environmental effects the function is not performed thus affecting the cell functioning.

The adsorption of the polyelectrolytes on solid surface also depends strongly on its conformation. The polyelectrolytes with a flexible conformation exhibit an efficient adsorption on the solid surfaces unlike the chains with rigid rod – like conformation. This adsorption phenomenon is used in various fields with special applications in layer – by – layer technique for making polyelectrolyte thin film. So for a sound knowledge of function and behavior of polyelectrolytes, it becomes highly essential to figure out their exact dependence on conformation.

The dynamics of polyelectrolytes is yet another area where conformation plays a prime role. Polyelectrolyte chains with varying conformation exhibit completely different

dynamics. Also the polyelectrolytes with different conformation present a different environment for diffusing molecules like proteins, other macromolecules thus affecting their diffusion.

Extensive theoretical and experimental work on the polyelectrolyte conformation has been presented by various groups [3-8]. The conformational studies on various polyelectrolytes including both strong and weak ones with variation of the one or more of these factors have been studied for wide range of applications. Adamczyk et al reported conformational studies on a strong polyelectrolyte sodium sulfonated polystyrene of molecular weight 15.8kDa under different ionic conditions [9]. They presented a comparison between the simulated results and the experimental data of DLS studies, dynamic viscosity measurements and electrophoretic mobility measurements. From the simulation results it was found that chains adopted a flexible chains conformation for all the electrolyte concentration but at a higher electrolyte concentration of 0.15M the chains exhibited considerable amount of folding. The experimental results deduced were in good agreement with the theoretical models on including the hydration effects. They also presented similar work on weak polyelectrolytes Polyacrylic acid and Polyallylamine hydrochloride [10, 11]. Wang and Yu studied the conformation in dilute solutions of sodium sulfonated polystyrene of different molecular weight as a function of salt concentration. They found a decreasing value of hydrodynamic radius on increasing the salt concentration from 0.01M – 3M for NaPSS sample with 177kDa molecular weight. Moreover the NaPSS samples exhibited neutral polymer like behavior for 3.1M KCl and 0.15M of NaCl at theta and good solvent conditions respectively [7].

Based on the importance of the conformational studies and the literature we have framed our objectives to **study conformational changes in the anionic polyelectrolyte (sodium sulfonated polystyrene) having molecular weight 70kDa with varying ionic strength.**

CHAPTER – 2

EXPERIMENTAL TECHNIQUES

2.1 Zeta Potential Measurements

The zeta potential measurement was done to determine the effective surface charge on the particles. The zeta potential measurements rely on the electrophoretic mobility measurements. The electrophoretic mobility is measured by applying the potential across the electrodes. On application of potential the charged particles start to move towards oppositely charged electrodes and the velocity of the particles is determined which is related to the Electrophoretic mobility by the relation given by

$$\mu = \frac{v_d}{E}$$

Where μ is the Electrophoretic mobility, v_d is the drift velocity of the particles, E is the electric field [12]. The electrophoretic mobility is related to the surface charge by the relation

$$q = 6\pi\eta R_H \mu$$

Where η is the solution viscosity, R_H is is the hydrodynamic radius of the particles determined from the DLS measurements.

2.2 Viscosity Measurements

The variation in the polyelectrolyte conformation exhibits a profound effect on the solution viscosity. The fully extended polyelectrolyte chains tend to considerably increase the solution viscosity. However in the presence of externally added salt the viscosity comes down because of the collapsing of the polymer chains. We have done the viscosity measurements to see how the conformation of 70kDa sodium sulfonated polystyrene varies with and without any added salt. We have used the Oswald viscometer to measure the solution viscosity. The principle of the viscometer and the method of measurement are discussed below. A typical Oswald viscometer is shown in figure 5. The

liquid is filled in the left arm of the viscometer till it fills up to the bream of the round

flask (mark not shown). The liquid is then suctioned till it reaches the upper mark on the right arm of the U – tube. The suction is then removed and the liquid is allowed to fall by its own weight. The time taken by the liquid to reach the lower mark is noted down [13].
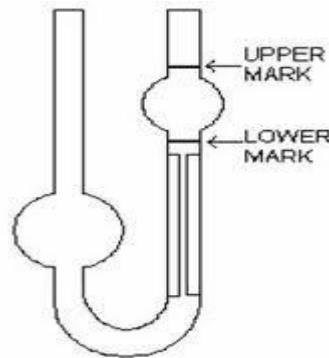
Fig. 5 Schematic of Oswald Viscometer

The time taken by the liquid to fall depends on the viscosity as well as the density of the liquid. The three parameters are related by the following

$$\eta = \rho\, t$$

Where η is the dynamic viscosity of the solution, ρ is the density of the solution, t is the time taken by the liquid to flow down between the two graduation marks.

With water as the reference liquid the viscosity of the solution can be calculated using the relation

$$\frac{\eta_w}{\eta_s} = \frac{\rho_w t_w}{\rho_s t_s}$$

Where the parameters η, ρ, t with suffix w is related to water and those with the suffix s is related to the solution.

The measurements were repeated several times to check the consistency of the values obtained and the average of the measurements were used to calculate the solution viscosity.

2.3 Dynamic Light Scattering

Scattering in general occurs due to the induction of the dipoles in the material by the incident electromagnetic wave. Light scattering is broadly divided as Static and Dynamic scattering depending on the properties determined by the respective experiments. The molecular weight, radius of gyration and other static properties of the system are determined by using the Static Light Scattering. Unlike this the dynamic properties like the diffusion coefficient is determined using the Dynamic Light Scattering (DLS).

Dynamic Light Scattering also known as the Quasielastic Light Scattering or the Photon Correlation Spectroscopy has been broadly used technique for determining the system dynamics [14]. It relies on the fact that the particles undergo a continuous motion in the solution which is better known to us as the Brownian motion. The particles tend to transfer their momentum to other particles on collision thus setting them to motion. The motion of the particles is highly random which can be visualized from the intensity measurements. The figure below shows the schematic of the DLS set – up.
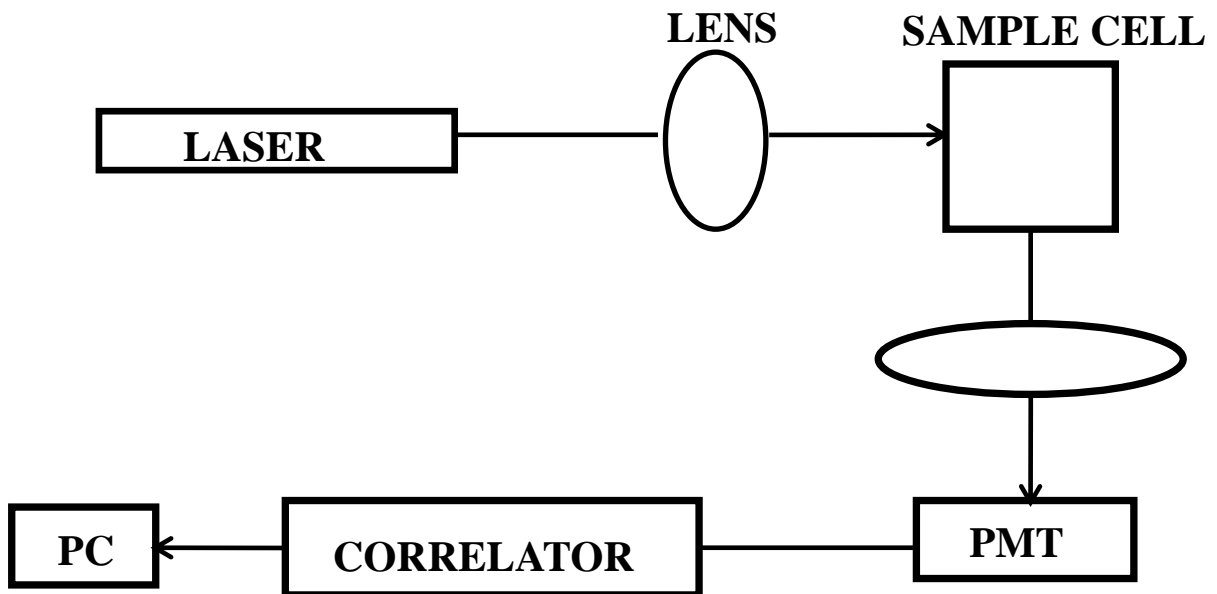
Fig. 6 Schematic of a typical DLS set – up

The particles undergoing the Brownian motion act as the scattering ηcenters scattering the incident laser light in all possible directions. The intensity fluctuations due

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to the motion of the particles are picked up by the photodetector. The amount of fluctuations depends on the size of the particles as smaller particles experience greater scattering as compared to the larger ones. Thus DLS proves to be an excellent technique to determine the size of the particles. The particle size can be determined from the value of the diffusion coefficient. The diffusion coefficient can be determined by the field – field autocorrelation $g_1(q,\tau)$ function given by the relation

$$g_1(q,\tau) = \frac{<E_S(t)E_S^*(t+\tau)>}{<|E_S(t)|^2>}$$

But it is not possible to experimentally determine the field – filed autocorrelation function rather it is the intensity – intensity autocorrelation $g_2(q,\tau)$ function which is experimentally determined parameter. It is given by the relation

$$g_2(q,\tau) = \frac{<I_S(t)I_S^*(t+\tau)>}{<|I_S(t)|^2>}$$

Both the correlation function are related to each other by Siegert's relation given by

$$g_2(q,\tau) = 1 + \beta|g_1(q,\tau)|^2$$

Where β is the coherence factor and whose value depends on the instrumental set-up.

The field – field autocorrelation function is extracted from the intensity – intensity autocorrelation function using the above relation. The field – filed autocorrelation function is related to the decay constant (Γ) by the relation given by

$$g_1(q,\tau) \sim \exp(-\Gamma\tau)$$

The decay constant is related to the particle diffusion coefficient (D) and the scattering vector (q) by the relation

$$\Gamma = Dq^2$$

The scattering vector is related to the wavelength of the incident light by

$$q = \frac{4\pi n \sin\frac{\theta}{2}}{\lambda_0}$$

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Where n is the refractive index of the solution, θ is scattering angle, λ_0 is the wave-length of light in vacuum.

The hydrodynamic radius of the particle can be determined from the diffusion coefficient by using the Stokes – Einstein relation

$$D = \frac{k_B T}{6\pi\eta R_H}$$

where k_B is the Boltzmann constant, η is the viscosity of the solution and R_H is the hydrodynamic radius of the particle.

The Zeta potential and DLS measurements were carried out in Malvern make instrumental set – up Zetasizer Nano 90 (Model# Nano ZS 90). The experimental set – up has been shown in figure 6 below.

Fig 7 Experimental set – up for zeta potential and DLS measurements

CHAPTER – 3

MATERIALS AND METHODS

3.1 Sample preparation for viscosity and Zeta potential measurements

Sodium sulfonated polystyrene of molecular weight 70kDa purchased form Sigma Chemicals Co. was used as the polyelectrolyte. Appropriate amount of the powdered polyelectrolyte was weighed and dissolved in 20 mL of Millipore water for achieving the required sample concentration. Sodium chloride brought from Alfa Aesar was used as the electrolyte to vary the ionic strength. In order to vary the ionic strength different amounts of salt (NaCl) were weighed and the individual solutions were prepared. 4mL of polymer solutions were taken in three different test tubes and 1mL of salt solution of different concentrations were added to them to get a final sample volume of 5mL. The aliquots were mixed thoroughly in vortex mixture for uniform mixing before carrying out the respective measurements on the sample.

For viscosity measurements the final volume of samples was about 20 mL each, maintaining similar concentration of polyelectrolyte and salt. The viscosity of the solutions was measured using a capillary Oswald viscometer.

For Zeta potential measurements sample was prepared in similar way maintaining a final volume of 5mL.

3.2 Sample Preparation for DLS measurements

The crucial part of the sample preparation for DLS measurements lies in the filtration of the solvent as DLS is sensitive to dust particles. The Millipore water was filtered thrice using 0.22 μm syringe filters before preparing the solutions. All the glass apparatus used in sample preparation were thoroughly rinsed with the filtered water before proceeding further. The rest of the procedure was similar to that stated above.

CHAPTER – 4

RESULTS AND DISCUSSIONS

4.1 Zeta potential measurements

The electrophoretic mobility (μ) measurements as obtained from the zeta potential measurements have been tabulated in the table 1.

Table 1: Electrophoretic mobility values as measured for different added salt concentration

Sl#	NaPSS concentration	Salt concentration (M)	μ (X 10^{-8}) m^2/V.s
1		0	-3.30
2		0.001	-2.96
3	0.01wt/wt%	0.005	-2.87
4		0.15	-1.70

The electrophoretic mobility decreased with increasing salt concentration. Using the mobility, hydrodynamic radius (from DLS data), and the viscosity values we have calculated the charges on the polyelectrolyte chains related to these parameters as

$$q = 6\pi\eta R_H \mu$$

The calculated values of charge for different concentrations of added salt are tabulated in table 5. From the table it can be easily inferred that the charges decreases with the addition of salt.

Table 2: Charge on the polyelectrolyte chains as calculated for different added salt concentration

Sl#	NaPSS concentration	Salt concentration (M)	q (X 10^{-17}) C
1		0	-12.4

2		0.001	-8.97
3	0.01wt/wt%	0.005	-6.38
4		0.15	-2.83

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The decreasing values of charge indicate that the charges on the chains have been screened by the ions from the electrolyte. With the decreasing of charges the polyelectrolyte chains are expected to undergo a transition from an extended conformation to a flexible one.

4.2 Viscosity measurements

The viscosity values for the polyelectrolyte solutions with and without salt measured at a temperature of 25°C. The results have been shown in table 3 below.

Table 3: Viscosity of NaPSS solutions with and without salt

Sl#	NaPSS concentration	Salt concentration (M)	Viscosity (cP)
1		0	0.91
2		0.001	0.89
3	0.01wt/wt%	0.005	0.88
4		0.15	0.87

The viscosity values exhibit a monotonic decrease on addition of salt which is expected as the charges are screened. Screening of charges leads to the collapsing of the extended structure in turn reducing the viscosity. However not much variation in the viscosity values is observed because we are in the extremely dilute concentration regime and hence the values are close to the solvent viscosity.

4.3 DLS measurements

The field – filed autocorrelation function as extracted from the intensity – intensity correlation for NaPSS without added salt is shown in figure 7 below.
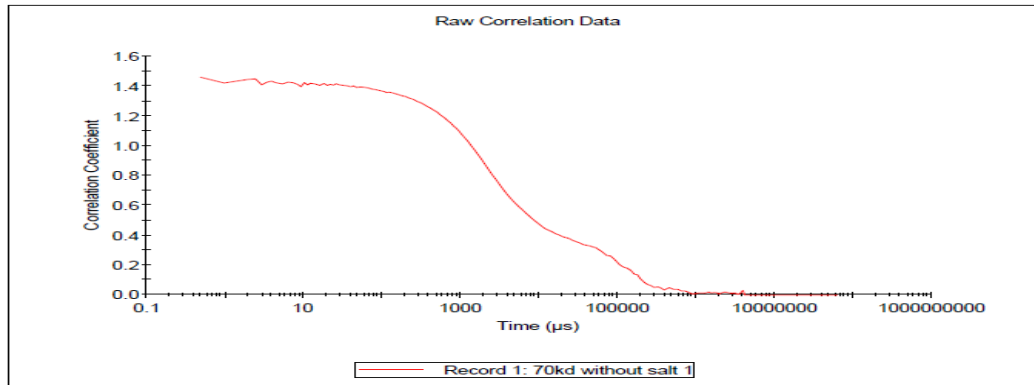
**Fig. 8 Field – Field autocorrelation function**

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The cumulant fit of the field – filed autocorrelation for the same is shown in figure 8. The decay constant Γ is calculated from this fit and further used for calculation of the hydrodynamic radius using the Stokes- Einstein relation.
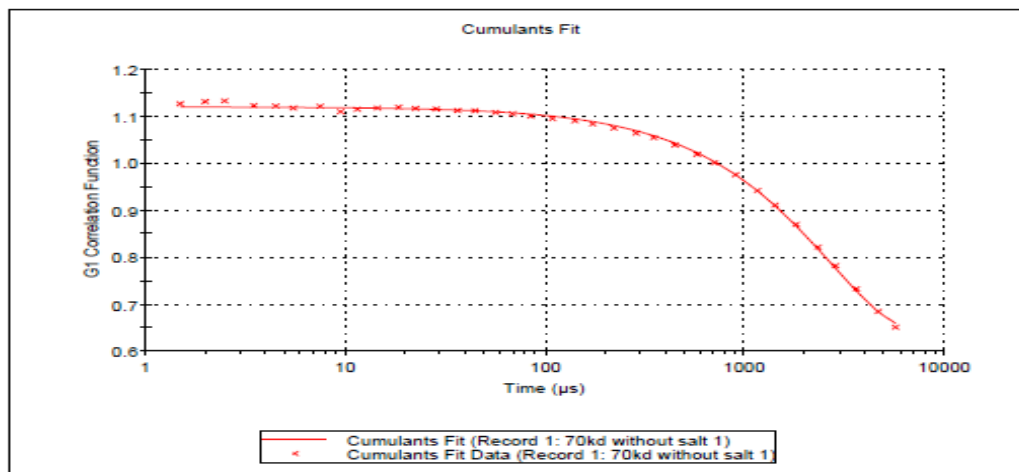
Fig. 9 Cumulant fit to the field – filed autocorrelation function

The hydrodynamic radius obtained from the DLS data for the NaPSS without salt is shown in the figure 9. The hydrodynamic values obtained for the polyelectrolyte chains without added salt was ~ 219.3 nm.
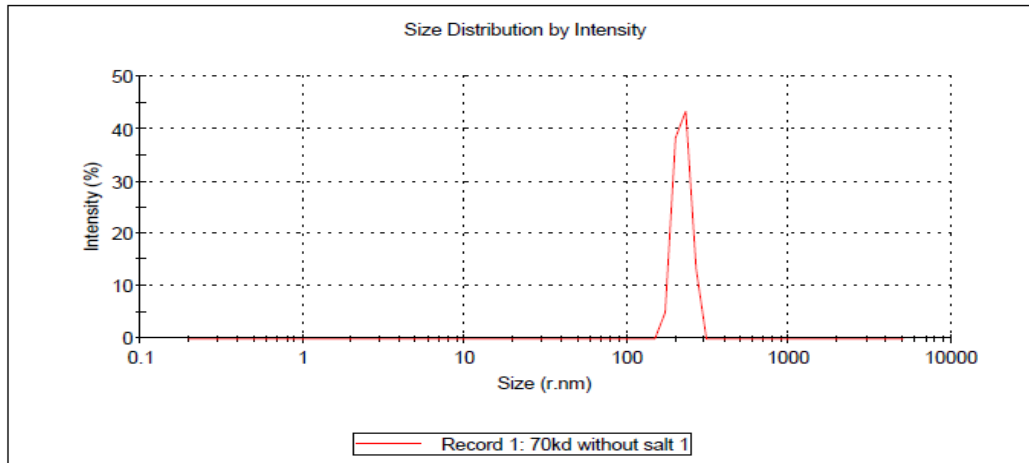
Fig. 10 Hydrodynamic radius for NaPSS without salt

Similar correlation and cumulant fits were obtained for samples with salt and the R_H values obtained are tabulated in table 4.

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Table 4 Hydrodynamic radius for different added salt concentration

Sl#	NaPSS concentration	Salt concentration (M)	R_H (nm)
1		0	219.3
2		0.001	180.6
3	0.01wt/wt%	0.005	134.1
4		0.15	101.5

From the table it is can be easily inferred that the screening of the charges leads to a decreased particle size in support of the argument that the extended structures collapse to a flexible chain conformation.

<u>CONCLUSIONS</u>

From the experimental studies we conclude that the polyelectrolyte conformations can be easily tuned by subjecting them to variation in external factor like electrolyte concentration. On increasing the electrolyte concentration the mobility of the molecules decreased indicating the screening of the backbone charges. As a result the effective charges on the particles reduce. The screening of charges also is responsible for the decrease in the solution viscosity with increasing electrolyte concentration. The hydrodynamic radius obtained from the DLS measurements decreased to a considerable extent on increasing the NaCl concentration. The screening of charges, decrease in viscosity and the hydrodynamic radius with increasing amount of the added electrolyte together indicate the transition of the polyelectrolyte chains from extended to flexible conformations.

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