

# **COIL TO GLOBULE TRANSITION FOR HIGH MOLECULAR WEIGHT SODIUM SULFONATED POLYSTYRENE**

*A Dissertation Submitted in partial fulfillment*

*For the Award of the Degree of **Master of Science in Physics***

*By*

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## **DECLARATION**

I hereby declare that the experimental work presented in this thesis was carried out in Department of Physics at National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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## **CERTIFICATE**

This is to certify that the thesis entitled, “**Coil to Globule Transition for High Molecular Weight Sodium Sulfonated Polystyrene**” submitted by Jiwan Kumar Pandey in partial fulfillment of the requirements for the award of Master of Science in Physics at the National Institute of Technology, Rourkela is an authentic experimental work carried out by him 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:

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## **ABSTRACT**

We have studied the effect of temperature on the conformation of 500 kDa sodium sulfonated polystyrene (NaPSS) in 4.5M salt solution using Dynamic Light Scattering. The measurements were carried out at different solution temperatures from 25°C to 5°C with five degree interval. The solutions were quenched to the desired temperature from 25°C before measurements were carried out on them. The buffer solution of pH 7.0 with 4.5M of salt and at 25 °C acts as a  $\theta$  –solvent for sodium sulfonated polystyrene. A sharp decrease in chain size was observed at 10°C indicating a transition from coil to globular state.

# CONTENTS

## **CHAPTER 1: INTRODUCTION**

1.1.	Definition of polymer	1
1.2.	Electrolyte	2
1.3.	Polyelectrolytes	2
1.4.	Classification of Polyelectrolytes	3
1.5.	Importance of Polyelectrolytes	4
1.6.	Conformation of Polyelectrolytes	5
1.7.	Factors Influencing Conformation of Polyelectrolyte	6
1.8.	Coil to Globule Transition	7
1.8.1.	Cause of CGT	8
1.8.2.	Importance of Coil to Globule Transition	9

## **CHAPTER2: LITERATURE REVIEW** 10

## **CHAPTER 3: EXPERIMENTAL TECHNIQUES**

3.1	Principle and Theory of Dynamic Light Scattering	12
3.2	Principle and Theory of Viscosity Measurement	14

## **CHAPTER4: MATERIALS AND METHODS**

Sample Preparation for Viscosity and DLS Measurements	16
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## **CHAPTER 5: RESULTS AND DISCUSSION** 17

## **CHAPTER 6: CONCLUSION** 21

## **REFERENCES** 22

# CHAPTER - I

## 1. INTRODUCTION

### 1.1 Definition of Polymer

The term “**Polymer**” refers to a high molecular weight chemical compounds that consists of repeating structural units. The repeating structural units are called as “monomers”. Based on its origin the polymers can be broadly classified as natural or synthetic polymers. Some of the common examples of natural and synthetic polymers are:

- a) **Natural polymers:** Wood, wool, silk, natural rubber, etc.

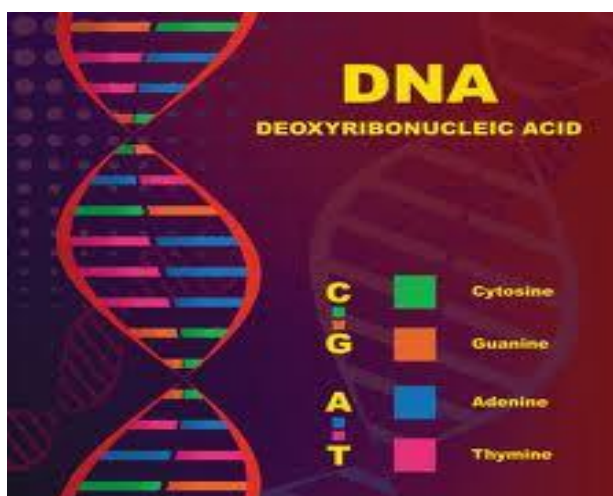


Fig. 1 DNA- a natural polymer

- b) **Synthetic polymers:** Nylon, PVC(Polyvinylchloride), Polypropylene

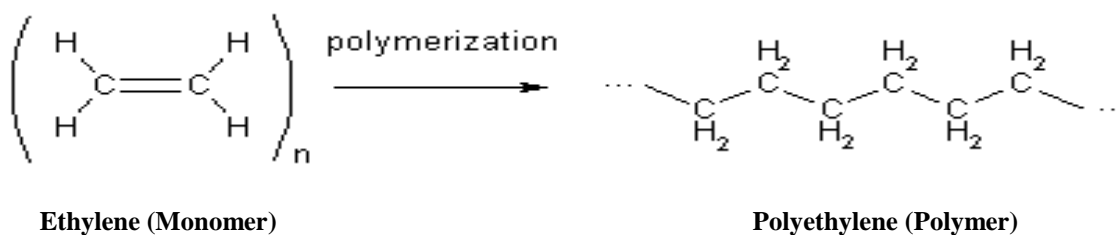


Fig. 2 Polymerization of ethylene molecule to give Polyethylene polymer

## 1.2 Electrolyte

The term “**Electrolyte**” refers to the class of compounds that dissociates into positive and negative ions constituents on being dissolved in suitable solvents. For example, sodium chloride salt dissociates into sodium and chloride ions when dissolved in water.

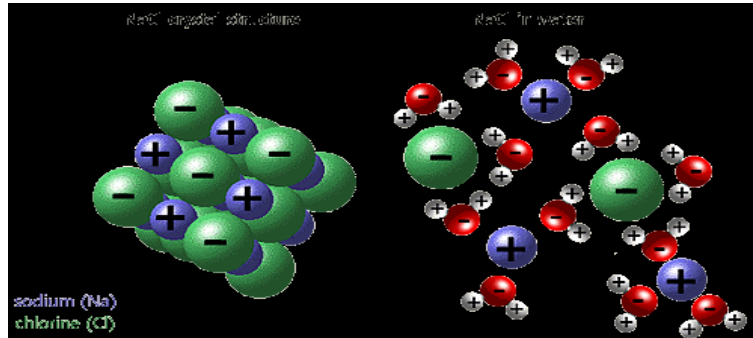
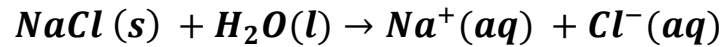


Fig 3: Dissociation of NaCl in Water

## 1.3 Polyelectrolyte

The polyelectrolytes are polymers bearing ionizable groups that dissociate into polyions and counterions when dissolved in polar medium [1]. Some of the common examples of polyelectrolytes are Deoxyribo Nucleic Acid (DNA), Ribo Nucleic Acid (RNA), Sodium Sulfonated Polystyrene (NaPSS), Poly-L-Lysine (PLL), Polyacrylic Acid (PAA).

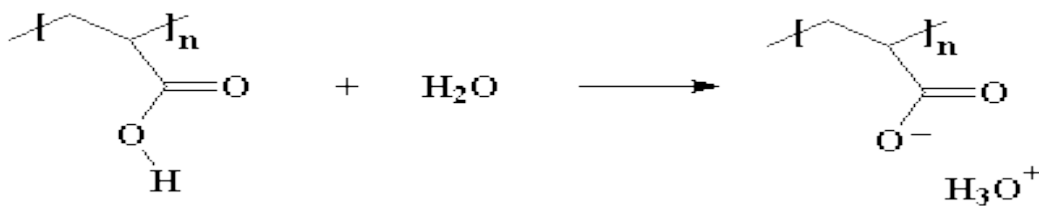
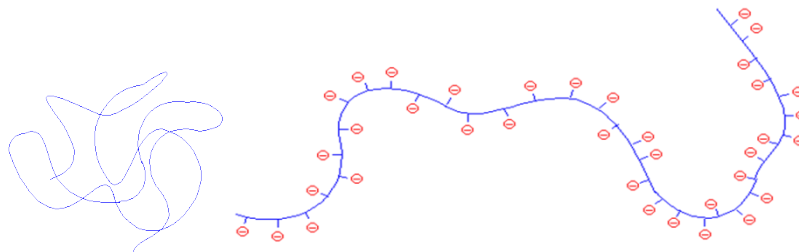


Fig. 4 Dissociation of Polyacrylic acid in water

The polyelectrolytes exhibit significantly different behavior from those of the neutral polymers, because of presence of charges on the backbone of the polymer chains. Some of the features include [2]:



(i) Due to long range Columbic repulsion between the similar charges on monomer units of the polyelectrolytes, it assumes a relatively extended conformation resulting in an increased viscosity and a very small overlap concentration as compared to neutral polymers.



**Fig. 5 Neutral Polymer**

**Polyelectrolyte**

(ii) Due to presence of a large number of counterions, the osmotic pressure of the polyelectrolyte solution is increased, which makes the polymers soluble in solvent.

(iii) For polyelectrolytes, the viscosity varies as square root of its concentration (Fuoss' law) whereas for neutral polymers it varies proportionally with the concentration.

(iv) Because of the increase in entropy due to release of counterions the polyelectrolyte even with hydrophobic backbone gets dissolve in solvent.

## **1.4 Classification of Polyelectrolytes**

The classification of polyelectrolytes is based on sources from which they are derived, the backbone charges, and the strength of dissociation. Below we have discussed the various categories of polyelectrolytes with examples [3].

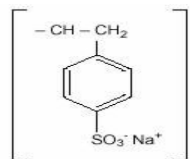
### **i) Natural and Synthetic Polyelectrolyte**

Based on the sources from which the polyelectrolytes are derived they may be classified into natural or synthetic. Examples of natural polyelectrolytes include Nucleic acids, Poly (L-Lysine), Poly (L-glutamic acid), Polypeptides, and Glycosaminoglycans. Some of the well known synthetic polyelectrolytes are Sodium sulfonated polystyrene (NaPSS), Poly Acrylic Acid (PAA), Poly methacrylic acid (PMAA).

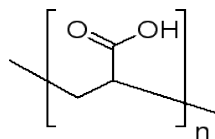
### **ii) Anionic and Cationic Polyelectrolytes**

This classification is based on the type of charge that is present on the backbone of polyelectrolyte chains when dissolved in solvent. Anionic polyelectrolytes acquire a negative charge on backbone in solution while cationic polyelectrolytes acquire positive charges. Some

examples of anionic polyelectrolytes are Nucleic acids, Poly (L-glutamic acid), Poly (sodium styrene sulfonate) and examples of cationic polyelectrolytes are Poly (L-lysine) and Polyallylamine hydrochloride.

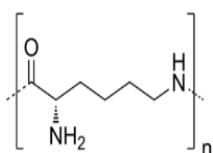


(Sodium Sulfonated Polystyrene)

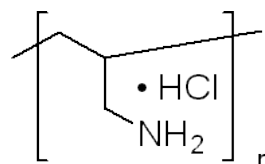


(Polyacrylic acid)

(a)



Poly-L-Lysine



Polyallylamine hydrochloride

(b)

Fig. 6 (a) Anionic Polyelectrolyte (b) Cationic Polyelectrolyte

### iii) Strong and Weak Polyelectrolytes

Based on the degree of dissociation in solution the polyelectrolytes can be classified into strong or weak polyelectrolytes. The polyelectrolytes that dissociate completely in solution within a wide range of pH are called as strong polyelectrolyte. Sodium sulfonated polystyrene and Poly – L – lysine are strong polyelectrolytes. The polyelectrolytes that get partially charged in solution are called as weak polyelectrolyte. Polyacrylic acid and Polyallylamine hydrochloride are categorized as weak polyelectrolytes. The extent of dissociation of a weak polyelectrolyte depends on the solution pH. Thus the charge on weak polyelectrolyte can be controlled by changing the solution pH.

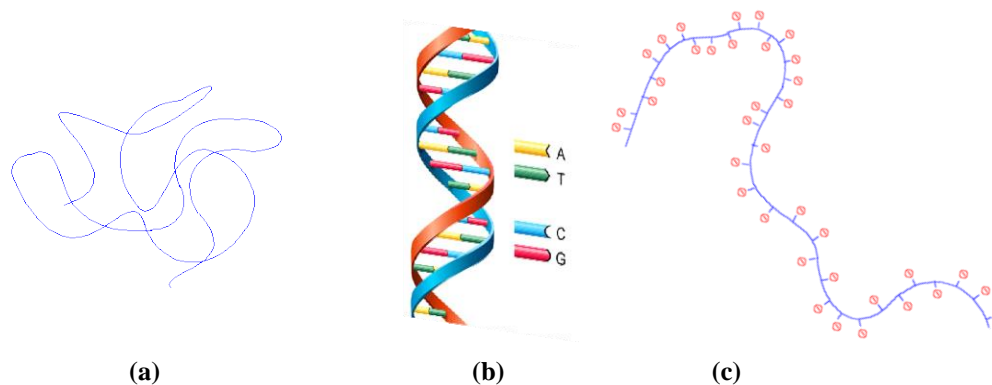
## 1.5 Importance of Polyelectrolyte

The polyelectrolytes have a wide range of biological and non-biological relevance and applications some of which are listed below [2, 4]:

- (i) Most of the known biopolymers for example DNA, RNA are polyelectrolytic in nature. In order to understand their functioning we need to have a thorough knowledge of their nature and properties.
- (ii) The charged nature of polyelectrolyte finds wide applications in various fields such as drug delivery, pharmaceuticals, biomedical applications, cosmetic industries, mineral processing, as thickeners, dispersants and flavor. Other applications include paper making, paints, battery applications, waste water treatment, etc.
- (iii) Recently polyelectrolytes have been used in the formation of polyelectrolyte multilayer (PEM). These thin films are developed using a layer-by-layer deposition technique in which a substrate is repeatedly dipped alternately in baths of positively and negatively charged polyelectrolyte solution. This results in deposition of alternate layers of cationic and anionic species that are electrostatically cross-linked. The advantage of this technique lies in the fact that it is not limited to coating flat objects only [3].

## 1.6 Conformations of Polyelectrolytes

The charges on the monomer unit of polyelectrolyte are responsible for various conformations in solutions. Polyelectrolytes attain varied chain conformations under different external conditions. Under fully charged conditions they assume extended or rod – shaped structure due to the Columbic repulsions between the similarly charged monomer units. However the extended structure collapses due to screening of charges in the presence of external electrolyte. Polyelectrolytes like DNA assume a double helix structure as shown.



**Fig. 7 (a) Random coil, (b) double helix structure of DNA, (c) Extended conformation**

Among the many possible conformations of the polyelectrolyte, one is the **globule conformation** that is attained by polyelectrolytes when the quality of solvent changes from good

to poor. Such conformation may be attained by quenching the polyelectrolyte solution temperature from above  $\theta$  – condition to temperature below it.

The conformation of a polyelectrolyte is a deciding factor for most of its applications. Change in the conformation affects its functioning considerably. Following examples illustrate the importance of conformational study of polyelectrolytes [3, 4, 5].

In biological cells, specific function is assigned to globular protein. In case conformation of protein is altered, say due to changes in external environmental effects, the functioning of the cell is significantly affected.

Adsorption of the polyelectrolytes on solid surfaces shows a substantial dependence on the polyelectrolyte conformation. The polyelectrolytes having flexible conformation get efficiently adsorbed on solid surfaces. This is, however not so in case of chains with rigid rod like conformation. The process of adsorption of polyelectrolytes is used in layer by layer (LBL) deposition technique for making polyelectrolyte thin films.

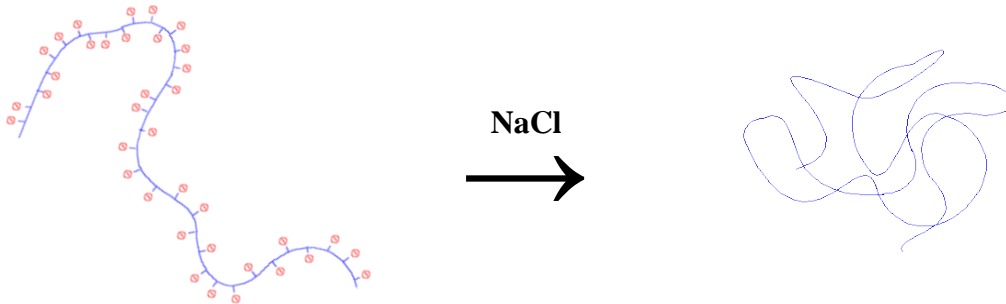
The conformation of a polyelectrolyte also decides its dynamics. The polyelectrolytes with different conformation lead to different diffusing environment for molecules like protein and other macromolecules, thus affecting their diffusion and in process it's functioning.

## **1.7 Factors Influencing Conformations of Polyelectrolyte**

The conformations of polyelectrolytes are significantly affected by factors like polyelectrolyte concentration, charge on its backbone, ionic strength, solution pH, solvent quality and temperature [3].

- (a) *Effect of polyion concentration*: At low concentrations the polyelectrolyte chains assume extended structure, depending on the charge present on their backbone. However with increase in polyelectrolyte concentration the space available to each polyelectrolyte chain is reduced considerably. Thus the charged polymer chain folds onto itself due to volume excluded by other chains.
- (b) *Effect of number of charges on polymer chain*: The more the number of charges on the monomer units of polymer chain, greater is the Columbic repulsion among them. Hence the polyelectrolytes assume a rigid rod like structure in solutions on being fully charged.

(c) Effect of ionic strength: Addition of salt in polyelectrolyte solution results in contraction of polymer chain on account of screening effect due to the oppositely charged ions resulting from the dissociation of salt in solution. This cloud of oppositely charged ions around the polymer chain intervenes and screens the repulsive interactions among the similar charged monomer units of the polymer chain. This results in contraction of the polymer chain with increase in added salt concentration. The figure below shows the contraction of charged polymer chains with the addition of salt.



**Fig. 8 Contraction of polyelectrolyte chains in presence of external electrolyte**

(d) Effect of pH of solution: The effect of pH is more pronounced in case of weak polyelectrolytes. As indicated earlier the extent of dissociation of weak polyelectrolytes can be tuned by varying the pH of the solution. The extent of dissociation determines the charge on the backbone of the polyelectrolyte which in turn decides the conformation of the polyelectrolyte.

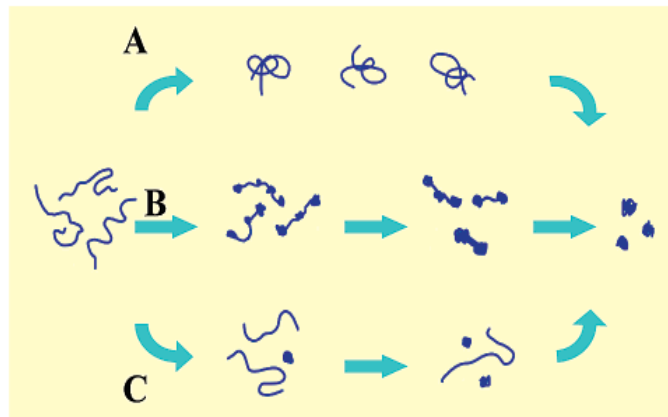
(e) Effect of temperature and solvent quality: With change in temperature the solvent quality changes. In good solvent the polymer – solvent interaction is more and hence the polymer likes to have solvent surrounding. In poor solvent, the solvent –polymer interaction is less and inter-chain and intra-chain interactions dominate. Hence in poor solvent, the polyelectrolyte chains tend to collapse.

## **1.8 Coil to Globule Transition**

In 1960, Stockmayer suggested that a flexible polymer chain can undergo a transition from an expanded state to a collapsed globule. Since then the coil to globule transition or the globule to coil transition is being studied both theoretically and experimentally [1]. The change in conformational state of a polymer chain from random coil conformation to a globular conformation in collapsed state is termed as coil to globule transition or in short CGT [7, 8]. On

the basis of study on statistical conformational properties of single polyelectrolyte chain, it was suggested by Grosberg and Khokhlov that in a poor solvent a polymer chain is compressed and finally attains a globular conformation. The coil to globule transition results when the polymer – solvent interaction decreases that in turn increases the polymer – polymer interaction. The increasing polymer – polymer interaction leads to decreasing size of the polymer coils gradually adopting a globular state. The collapse from coil state to globular state occurs with quenching of the polyelectrolyte solutions below  $\theta$  - temperatures resulting in favorable attractive energy of the polymer to itself.

A polymer chain may be treated based on “necklace” picture to be composed of clusters. The transfer of free energy to the dense phase is the driving free energy and dissipation is due to Stokes drag force. The decrease in the randomly distributed chain segments is largely responsible for the collapse. The various suggested mechanisms for polyelectrolyte in a poor solvent are shown below [9]:



**Fig.9 (A) Continuous phase transition; (B) Cascade of transitions between necklaces (for flexible polyelectrolyte); (C) Abrupt transition (for stiff polyelectrolytes)**

**1.8.1 Cause of CGT:** In the solution there is a finite concentration of the polyelectrolyte chain and on account of the overall electro neutrality of the solution there is also a finite concentration of counterions [6, 7, 13]. We know that on account of Coulomb repulsion the chain assumes an extended structure. At high temperatures, the translational entropy of the counter ions is large as a result of which their interactions with the polyelectrolyte chain will be reduced. However, as the temperature is decreased the translational entropy of the counter ions goes down and hence

they move closer to the oppositely charged polyelectrolyte chain leading to counter ion condensation. This condensation of the counter ions around the chain affects the single chain properties considerably. Thus with decreasing temperature the polyelectrolyte chain begins to collapse. Similarly the multi chain effects come into play resulting in the attraction between two polyelectrolyte chains.

### **1.8.2 Importance of Coil to Globule Transition:**

- 1) Study of such transitions has wide importance in understanding the general and basic concepts in polymer physics and solution dynamics.
- 2) In biological sciences such studies are important due to presence of coil to globule transition in biological macromolecules such as proteins and DNA. It helps to understand the phenomena of protein folding and DNA packing. Moreover this study enables to understand the denaturation of proteins where even a slight change in the environment (like temperature, pH, etc.) may result in abrupt loss of biological activity of proteins and its structure may change dramatically.
- 3) It is analogous with swelling and deswelling behavior of a cross linked polymer and thus its understanding is employed in biomedical engineering for controlled drug delivery.

## CHAPTER – II

### LITERATURE REVIEW

Ersin Serhatli et al studied the coil to globule transition in NaPSS (sodium sulfonated polystyrene) of molecular weight  $1.2 \times 10^6$  Dalton in 4.17M NaCl solution using dynamic light scattering technique. The hydrodynamic radius was found to decrease from 13.1nm at 18°C to 9.1 nm at 10°C. This means that the solvent molecules are expelled almost completely from the globule of polymer chain.

Peter Loh et al utilized conductivity and light scattering measurements on PVP (poly 2-vinylpyridine) to study polyion collapse in isorefractive solvent / non solvent mixtures consisting of 1-propanol and 2-pentanone respectively. The dielectric constant of the solvent remains virtually constant during the chain collapse. Hence the counterion binding is entirely caused by the reduction in polyion chain dimension. Remarkably the counterion binding occurs already well above the theta dimension of polyion which was reported for  $\text{Sr}^{2+}$  induced collapse of sodium polyacrylate in aqueous NaCl solution.

Arindam Kundagrami and M. Muthukumar calculated the phase boundaries and critical point for first order coil – globule transition using a variational theory and considering adsorption of counterions on an isolated polyelectrolyte chain conformation. Phase boundaries for coil to globule transition induced by both Columbic strength (inverse temperature or dielectric constant) and ionic strength (salt) show that the polyelectrolyte chain collapses at a substantially lower Coulomb strength in presence of salt.

Bahattin M. Baysal and Nilhan Kayaman (1998) studied the coil to globule transition for poly (methyl methacrylate) with molecular weight  $2.55 \times 10^6$  in mixed solvent tertbutyl alcohol and water system. Viscometric measurements were used to determine contraction and expansion of molecular chains. A smooth and continuous contraction was observed below the theta temperature (41.5°C) down to 16°C. The viscosity expansion factors were reduced by about 86 % of their theta state dimension, which means that a true collapse was realized in this system.

Wafa Essafi et al. reported the influence of solvent quality on the structure of semi-dilute solution of hydrophobic polyelectrolyte, partially sulfonated polystyrene sulfonate using SAXS and SANS techniques. It was concluded that the solvent quality for hydrophobic polyelectrolyte



in aqueous solution can be improved by adding to water a miscible organic good solvent of the backbone in low proportion or by using an organic polar solvent instead of water.

Nilhan Kayaman et al. used dynamic light scattering technique to study the time dependence of coil to globule collapse in atactic poly(methyl methacrylate) samples having molecular weight  $6.5 \times 10^6$  and  $3.3 \times 10^6$  g/mol dissolved in isoamyl acetate and n-butyl chloride. The transition time from coil to globule state was found to be inversely related to the depth of quench of the process. The transition time also increases with the increase in molecular weight of the polymer chain. Bin Yuan et al. studied the effects of magnetic field on the system composed of polyelectrolyte and oppositely charged magnetic nano-particles by means of Monte Carlo method within the framework of “single-site bond fluctuation model”. For a certain concentration of chains, the coil – globule transition can be induced by the applied magnetic field. Under certain magnetic field, polyelectrolyte chains regularly collapse due to enough adsorption of magnetic particles. For chain length  $N=200$ , the conformation changes from coiled state to globular state with increasing applied magnetic field.

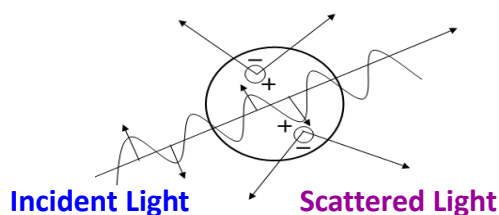
Namykung Lee and D.thirumalai used Langevin simulations and scaling arguments to investigate the collapse kinetics of strongly charged polyelectrolytes in poor solvents. It was reported that the rate of collapse increases sharply as valency ‘z’ of counterions increases from 1 to 4. Upon quenching to low temperature, counterions condense rapidly on a diffusion limited time scale. At intermediate times meta-stable pearl-necklace structures form. The clusters merge at longer times. The structure of globule is controlled by ‘z’ and the solvent quality. For fixed ‘z’ and solvent quality, efficiency of collapse dramatically decreases with increase in size of counterions. Anton kiriy et al. studied the cascade of coil to globule transition of single flexible polyelectrolyte molecules in poor solvent. Hydrophobic flexible polyelectrolyte molecules of poly (2-vinylpyridine) and poly (methacryloyloxyethyl dimethylbenzyl ammonium chloride) are found to be trapped and frozen due to adsorption on mica surface. They reported that increase in ionic strength of the solution induces the cascade of abrupt conformational transitions due to intra chain segregation from elongated coil to compact globule conformation through intermediate pearl necklace globule conformations with different amounts of beads per chain. It was also reported that the length of necklaces and number of beads decreases while the diameter of beads increases with the increase of ionic strength.

## CHAPTER – III

### EXPERIMENTAL TECHNIQUES

#### 3.1 Principle and Theory of Dynamic Light Scattering

Electromagnetic waves incident on a matter induces electric dipole (due to oppositely directed forces on the constituent nuclei and corresponding electron cloud) which oscillates due to oscillating electric field of the electromagnetic waves. These oscillating induced dipoles emit electromagnetic waves in all directions referred to as scattering. In case of a solution the molecules are in continuous translational, rotational or vibrational motion due to thermal interactions and collisions with solvent molecules. As a result the positions of induced charges in the molecules change randomly and the scattered intensity fluctuates in time about the average value which is detected by the detector. The rate at which these spontaneous fluctuations decay to the equilibrium value depends directly on the dynamics of molecules and hence gives information about the relaxation time which in turn is related to diffusion coefficient. The hydrodynamic radius of the molecules can be calculated from the diffusion coefficients.



**Fig. 10 Illustration of the scattering due to induced dipoles**

The Dynamic Light Scattering measures intensity-intensity auto correlation function,  $g_2(\tau)$  is given by

$$g_2(\tau) = \frac{\langle I_s(t)I_s^*(t + \tau) \rangle}{\langle I_s(t)I_s^*(t) \rangle}$$

which is related to field-field auto correlation function,  $g_1(\tau)$  given by

$$g_1(\tau) = \frac{\langle E_s(t)E_s^*(t + \tau) \rangle}{\langle E_s(t)E_s^*(t) \rangle}$$

For a Gaussian distribution,  $g_1(\tau)$  and  $g_2(\tau)$  are related through Siegert equation:

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

where  $\beta$  is the coherence area factor which basically signifies the signal to noise situation.

Since one is mostly interested in mass diffusion behavior hence the correlation function for the scattered field ( $E_s$ ) is:

$$g_1(\tau) \propto e^{(-D_z q^2 \tau)}$$

where,  $D_z$  is the translational diffusion coefficient,  $\tau$  is the relaxation time, and  $q$  is the scattering vector given by

$$q = \left( \frac{4\pi n}{\lambda} \right) \sin \left( \frac{\theta}{2} \right)$$

where  $n$  = refractive index of medium,  $\lambda$  = wavelength of light in vacuum,  $\theta$  = scattering angle. The reciprocal of scattering wave vector signifies the probing length scale.

The translational diffusion coefficient,  $D_z$  is related to the translational frictional coefficient,  $f_T$  by

$$D_z = \frac{k_B T}{f_T}$$

For spherical particles, the translational frictional coefficient is given by the Stokes-Einstein relation,  $f_T = 6\pi\eta R_H$

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

where  $\eta$  and  $R_H$  represent the viscosity of solvent and the hydrodynamic radius of polymer chain respectively. The schematic and the photograph of the DLS setup are given below.

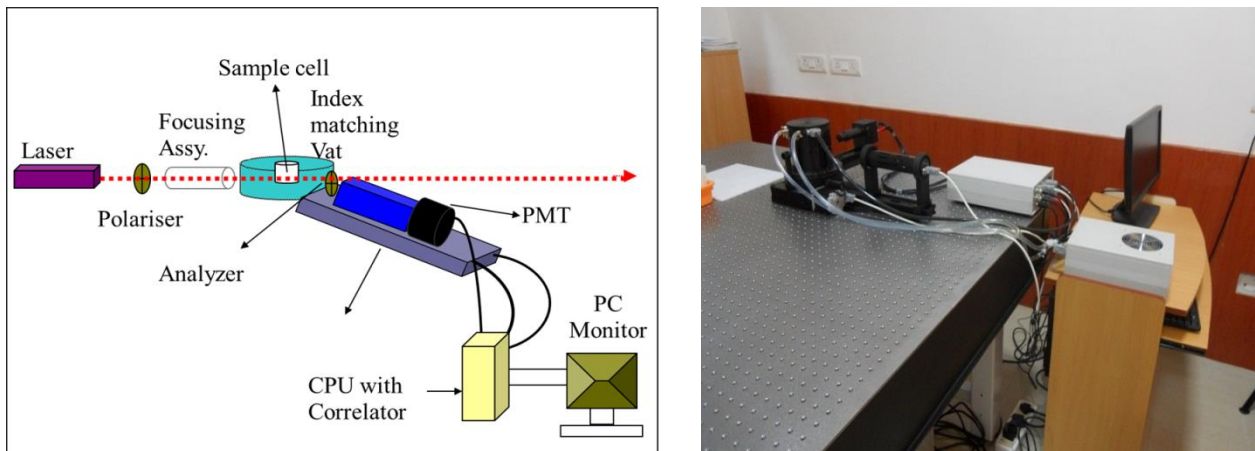
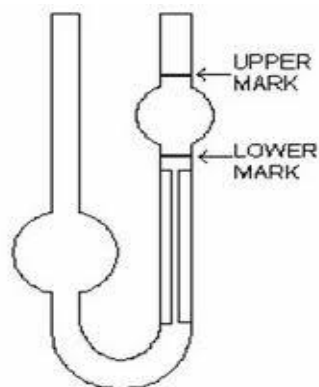


Fig. 11 Schematic and photograph of DLS setup

### **3.2 Principle and Theory of Viscosity Measurement**

The various conformations exhibited by polyelectrolytes considerably affect the solution viscosity. In absence of any added salt the strong polyelectrolytes dissociate fully in solution and are fully charged. As explained earlier this results in extended structure of the polyelectrolyte. The solution in this case is more viscous. However with increase in salt concentration, due to screening effect, the polyelectrolytes no longer remain in extended conformation and start behaving like a neutral polymer. This collapsing of the extended chains leads to a decrease in the solution viscosity. Moreover the viscosity of any solution is expected to decrease with an increase in the temperature. For the determination of particle size from diffusion coefficients that is measured using DLS one needs information about solution viscosity ( $D_z = k_B T / 6\pi\eta R_H$ ). So the viscosity measurements of the sample were done using an Oswald viscometer.

The solution is filled into the viscometer through its left arm of the figure shown below, till the top of the round enclosure. Then by creating suction at the tip of the other (right) arm the liquid is made to rise through the capillary in the right arm of the U-tube till it reaches the upper mark as indicated in the figure below. The suction is then removed and the liquid is allowed to fall under its own weight. The time taken by the liquid to reach to the level of lower mark is noted down.



**Fig. 12 Schematic of Oswald Viscometer**

The time,  $t$  in which the liquid level falls down from the upper to lower mark depends on the viscosity and density of the liquid. These parameters are related as:

$$\eta = \rho t$$

where  $\eta$  = dynamic viscosity of the solution,  $\rho$  = the density of the solution, and  $t$  is the efflux time.

The process is carried out for water (reference) whose viscosity and density are known.

We have

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

Here the subscripts 'w' and 's' refer to water and the solution respectively.

The measurements were carried out at a constant temperature of  $25 \pm 0.5^\circ\text{C}$  for a dilute solution of the sample so that individual properties of the polyelectrolyte could be studied. In dilute solution the effective interaction among the polyelectrolyte chains is negligible. The 'time of fall' was measured three times and its average value was calculated and used for the determination of solution viscosity.

The calculated viscosity value of the sample at  $25 \pm 0.5^\circ\text{C}$  was found to be approximately 1.05 cP which is close to the corresponding value of water, which is 0.89 cP. Since the solution viscosity is close to the water viscosity, we have taken the water viscosity as solution viscosity for all the measurements at different temperatures.

## **CHAPTER – IV**

### **MATERIALS AND METHODS**

#### **Sample Preparation for Viscosity and DLS Measurement**

The elimination of dust from the sample is the most challenging and difficult part of light scattering studies. The presence of impurities, that may enter the sample from surrounding air while preparation, or by contact with the user's fingers, or from the solvent, or from the cuvette itself, or from the tips of micro pipettes can dramatically affect the scattered intensity.

The solvent, water was filtered twice using 0.2 $\mu$ m pore size filter paper and stored in a clean closed glass container. The filtered solvent, were cleaned to the extent that a laser beam focused into a cuvette filled with this solvent in the DLS setup did not reveal any significant bright scatterers. For dynamic light scattering measurements first of all the cuvettes were thoroughly rinsed in clean water and then with filtered Millipore water. After filtration the water was stored in a clean closed glass container.

About 500ml of 0.01M phosphate buffer solution of pH 7.0 was prepared by using 0.1M stock solution of Na<sub>2</sub>HPO<sub>4</sub> and 0.25M stock solution of NaH<sub>2</sub>PO<sub>4</sub>. 35 ml of 4.5M NaCl solution in buffer was then prepared and filtered again through filter paper of 0.22  $\mu$ m pore diameter. The NaPSS solution of concentration, 2mg/ml was prepared by adding appropriate amount of NaPSS to the solvent and left over night and then mixed thoroughly using a vortex mixer. The sample is further centrifuged for removal of large particulates. The sample thus prepared was used for viscosity and DLS measurements.

## CHAPTER - V

### RESULTS AND DISCUSSION

In Oswald viscometer the efflux times for water and the sample of NaPSS solution were recorded three times and their respective mean were taken.

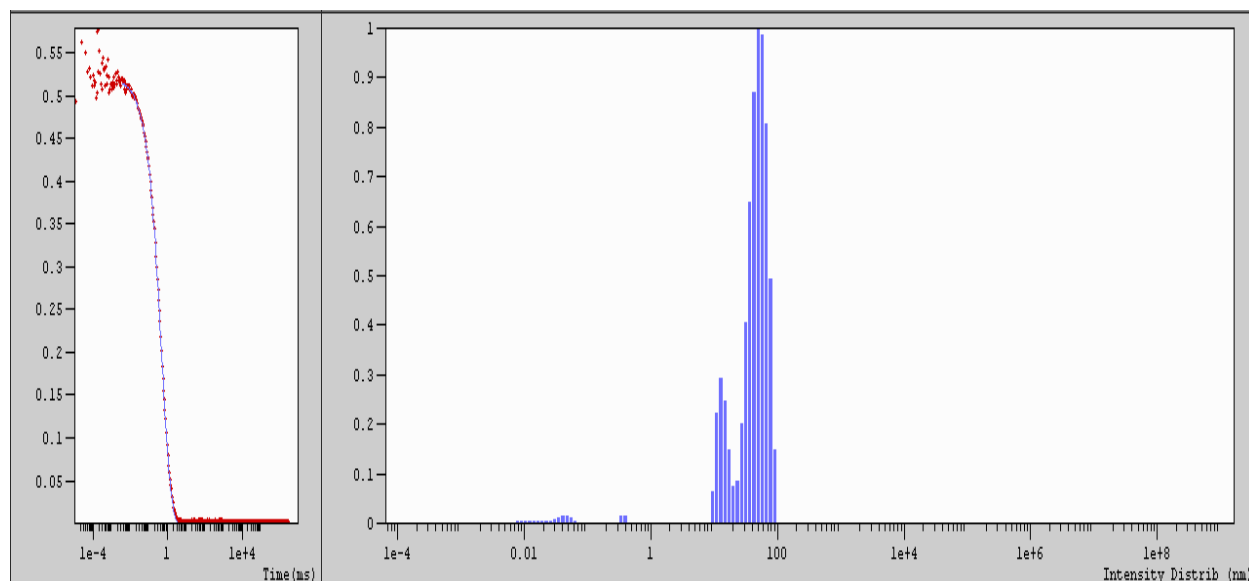
Efflux time for water,  $t_w = 78.00s$

Efflux time for the sample,  $t_s = 125.15s$

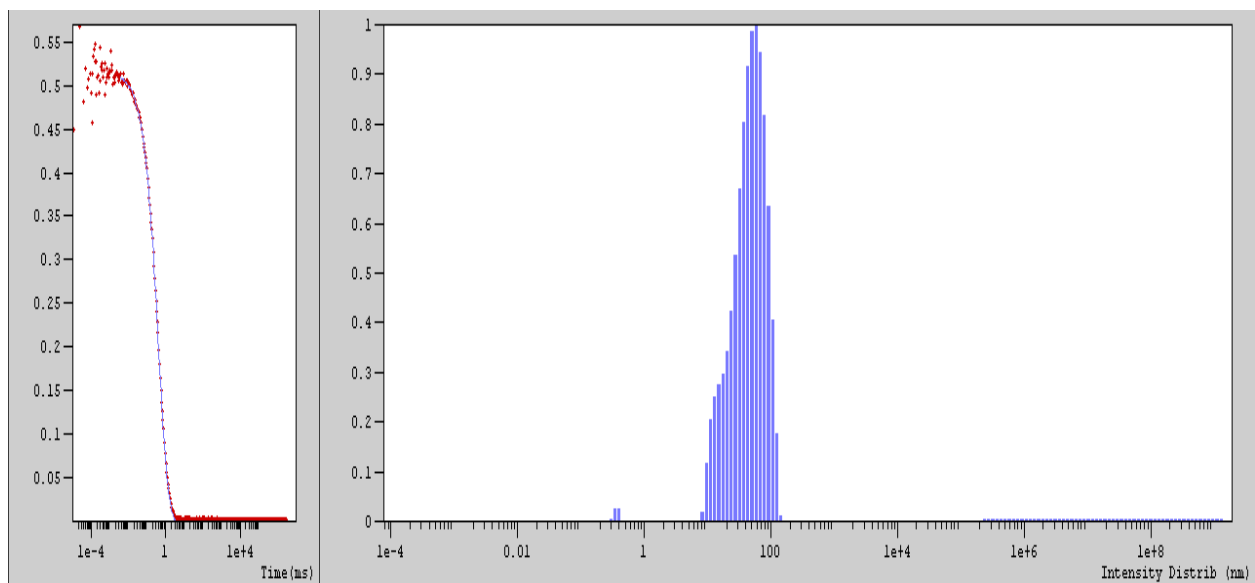
$$\eta_s = \frac{\eta_w * t_s * d_s}{t_w * d_w}$$

Putting the values in above equation we found  $\eta_s = 1.05cP$ .

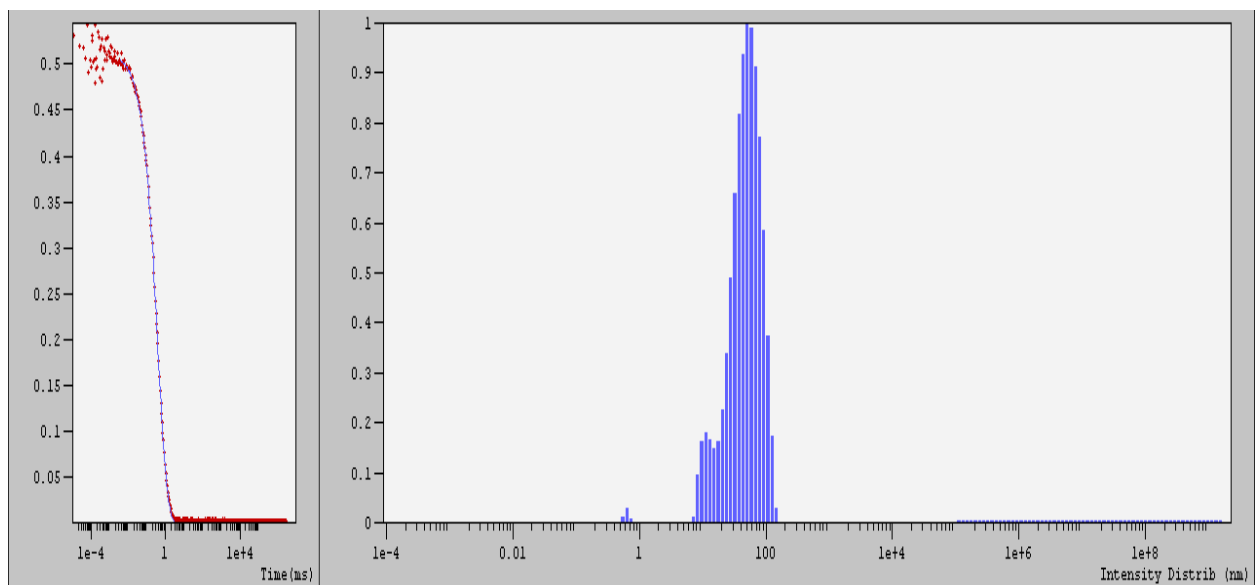
**Dynamic Light Scattering** measurements were carried out using freshly prepared clean sample. The reference temperature was taken to be 25°C. The sample was quenched from the reference temperature to the desired temperature before the DLS measurements were performed. The plots obtained for the auto correlation function versus time and the corresponding intensity distribution of particle size curves at different temperatures for the 2mg/ml concentration of NaPSS in 4.5M salt(NaCl) solution are shown below:



**Fig. 13 Auto correlation function versus time and intensity distribution of particle size curves at 5°C**

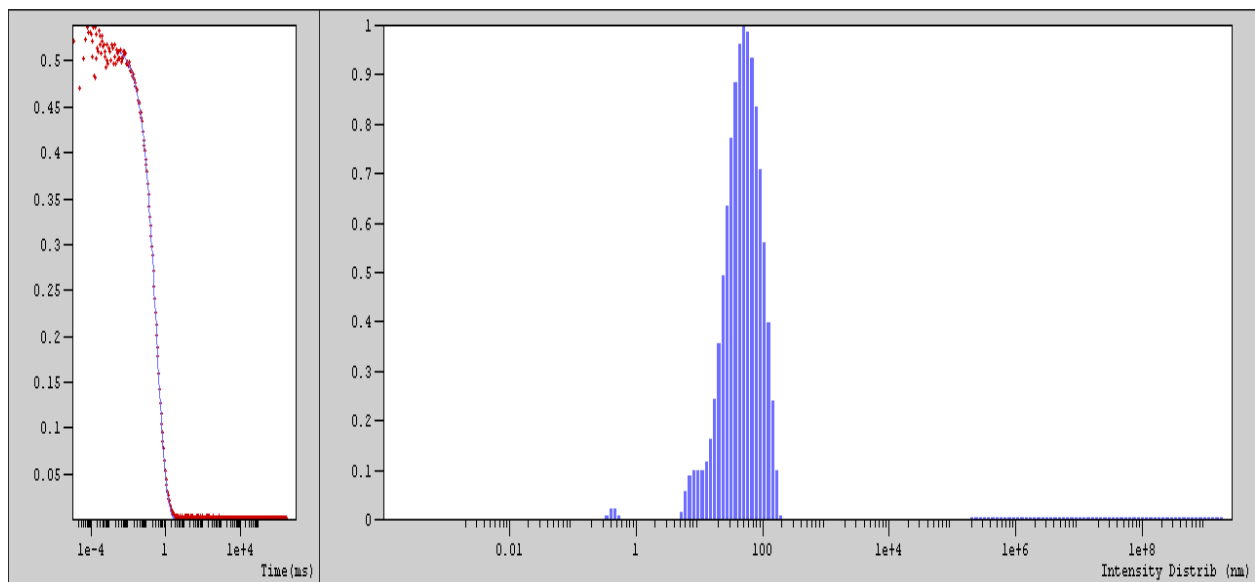


**Fig. 14 Auto correlation function versus time and intensity distribution of particle size curves at 10°C**

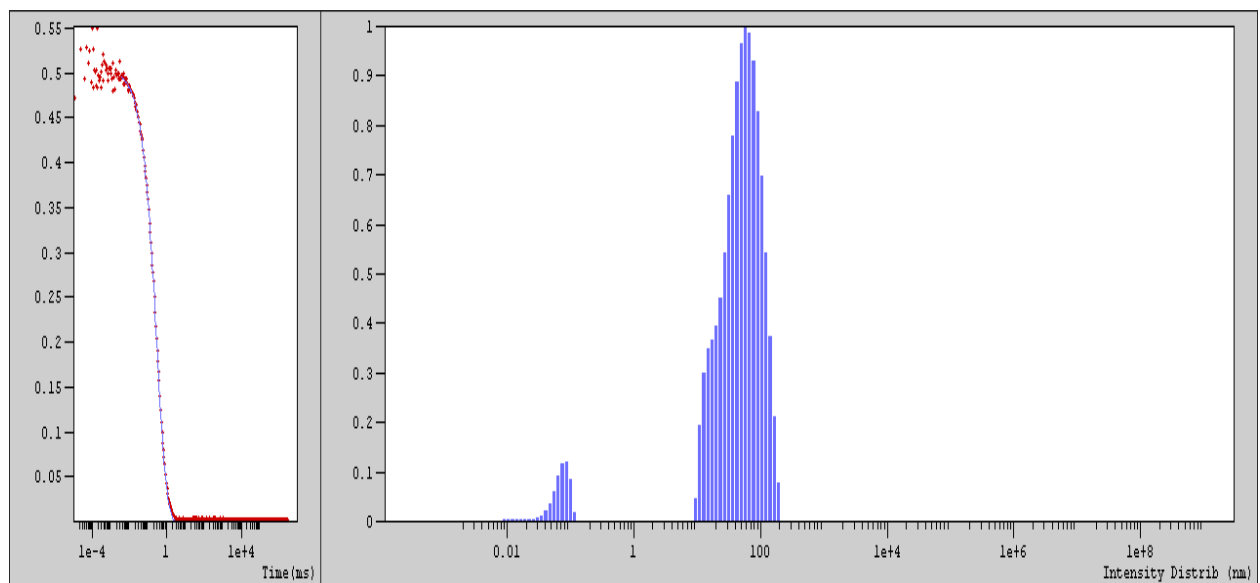


**Fig. 15 Auto correlation function versus time and intensity distribution of particle size curves at 15°C**





**Fig. 16 Auto correlation function versus time and intensity distribution of particle size curves at 20°C**



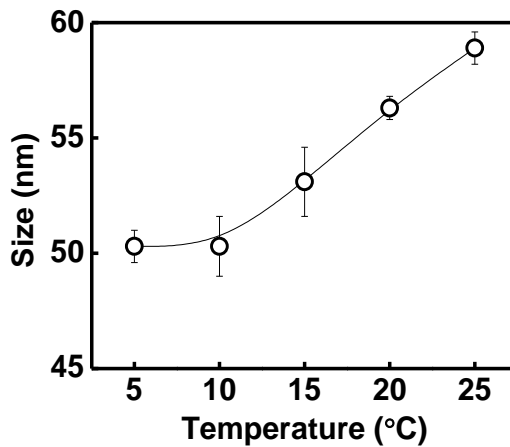
**Fig. 17 Auto correlation function versus time and intensity distribution of particle size curves at 25°C**

The summary of the experimental results are given in the table below.

**Table 5.1 values of particle size and viscosity at different temperatures**

SI #	Temperature (°C)	Viscosity (cP)	Particle size (nm)
1	25	0.89	58.9 ± 0.7
2	20	1.01	56.3 ± 0.5
3	15	1.14	53.1 ± 1.5
4	10	1.31	50.3 ± 1.3
5	05	1.52	50.3 ± 0.7

The buffer solution of pH 7.0 with 4.5M of salt and at 25 °C acts as a  $\theta$  –solvent for sodium sulfonated polystyrene. As the sample is quenched from 25 °C to lower temperatures the solvent quality turns poor, where the polymer – polymer interaction increases and polymer – solvent interaction decreases resulting in the collapse of the polyelectrolyte chain. The variation in the hydrodynamic radius of 500 kDa NaPSS particles with temperature is shown in the graph below:



**Fig. 18 Plot of particle size with temperature**

The results obtained suggest that the hydrodynamic radius of the 500 kDa NaPSS sample in 4.5M NaCl solution decreases gradually from  $\sim 59.0$  nm to 50.0 nm with decrease in temperature. The reduction in size was found to be about  $\sim 9.0$  nm on quenching from  $25^{\circ}\text{C}$  to  $10^{\circ}\text{C}$ . Below  $10^{\circ}\text{C}$ , the particle size remains almost constant. The reduction in particle size with decrease in temperature may be attributed to the counterion condensation around the polyelectrolyte chain. At high temperatures the translational entropy of the counter ions is more and hence their interaction with the polyelectrolyte chain may be considered negligible. As the temperature is reduced the translational entropy of the counter ions decreases and they come close to the oppositely charged polyelectrolyte chain, thereby screening the repulsion between the like charges. This results in the collapse of the chain to a globular state when the sample was quenched to about  $10^{\circ}\text{C}$ .

Moreover the collapse seems not to very sharp but gradual. The nature of the coil to globule transition depends on the stiffness of the chain. For stiff polymer chains the transition is very sharp. For flexible chains, the transition is rather smooth. The onset of particle size reduction first involves the formation of dense phase. Secondly, the state of collapsed stage is achieved as the collapse proceeds through intermediate states [10]. The first process of formation of the dense phase is a relatively faster process. These droplets then grow by linking the monomers from the bridges connecting them. Finally the droplets come into close contact and hence coalesce into a single globular state.

## **CHAPTER - VI**

### **CONCLUSIONS**

In this project we have studied the effect of temperature on a dilute solution of highly charged polyelectrolyte solution of Sodium Sulfonated Polystyrene of molecular weight, 500 kDa by using Dynamic Light Scattering. The prepared sample of 500kDa was seen to show a conformational transition from a random coil at 25<sup>0</sup>C to globule conformation at 10<sup>0</sup>C, when it was quenched from the reference temperature to the desired temperature. At high temperature the interactions of the counterions with the polyelectrolyte chain is negligible on account of high translational entropy of the small counterions. As temperature is reduced, the counterion condensation around the polyelectrolyte chain results in strong interaction between the counterions and the chain resulting in the collapse mechanism. The presence of counterions significantly reduces the solvent quality on account of the short ranged dipole-monomer and dipole-dipole interactions. Thus,  $\theta$  –solvent becomes effectively poor at sufficiently low temperature resulting in the coil to globule transition.

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