Determination of effective charge of flexible Polyelectrolytes by Light Scattering

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Sanjib Saha

geboren in Kalkutta, Indien

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Abstract

The most important property controlling the physicochemical behaviour of polyelectrolytes and their applicability in different fields is the charge density on the macromolecular chain. A polyelectrolyte molecule in solution may have an effective charge density which is smaller than the actual charge density determined from its chemical structure. In the present work an attempt has been made to quantitatively determine this effective charge density of a model polyelectrolyte by using light scattering techniques. Flexible linear polyelectrolytes with a Poly(2-Vinylpyridine) (2-PVP) backbone are used in the present study. The polyelectrolytes are synthesized by quaternizing the pyridine groups of 2-PVP by ethyl bromide to different quaternization degrees. The effect of the molar mass, degree of quaternization and solvent polarity on the effective charge is studied. The results show that the effective charge does not vary much with the polymer molar mass or the degree of quaternization. But a significant increase in the effective charge is observed when the solvent polarity is increased. The results do not obey the counterion condensation theory proposed by Manning. Based on the very low effective charges determined in this study, a new mechanism for the counterion condensation phenomena from a specific polyelectrolyte-counterion interaction is proposed.

Zusammenfassung

Die wichtigste Eigenschaft zur Kontrolle des physikalisch-chemischen Verhaltens von Polyelektrolyten und ihrer Anwendbarkeit in verschiedenen Gebieten ist die Ladungsdichte in der makromolekularen Kette. Ein polyelektrolytisches Molekül in Lösung kann eine effektive Ladungsdichte kleiner als die aktuelle Ladungsdichte haben, welche sich aus der chemischen Struktur ableiten lässt. In der vorliegenden Arbeit wurde die quantitative Bestimmung der Ladungsdichte eines Polyelektrolyt-Modells unter Anwendung von Lichtstreutechniken untersucht. Bewegliche lineare Polyelektrolyte mit einem Poly(2-Vinylpyridine) (2-PVP) "Backbone" wurden für diese Untersuchung verwendet. Die Polyelektrolyte wurden durch Quaternisierung der Pyridingruppen von 2-PVP in Ethylbromid mit unterschiedlichen Quaternisationsgraden Die synthetisiert. Auswirkung von Molmasse. Quaternisierungsgrad sowie der Lösungsmittelpolarität auf die effektive Ladung wurde untersucht. Die Ergebnisse zeigen, dass es kaum eine Abhängigkeit der effektiven Ladung von der Polymermolmasse oder dem Quaternisierungsgrad gibt. Allerdings, ist eine signifikante Erhörung der effektiven Ladung zu beobachten, wenn die Lösungsmittelpolarität erhöht wird. Die Ergebnisse sind nicht durch die Gegenionenkondensation nach Manning zu erklären. Basierend auf den vorliegenden Ergebnissen kann die niedrige effektive Ladung nur durch spezifische wechselwirkung zwischen Polyelektrolyte und Gegenionen verursacht werden.

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1 General introduction and Motivation

Polyelectrolytes, as the name implies, combines two important classes of scientific concepts; polymer and electrolyte. Structurally, these are long chain molecules bearing chemical groups which are capable of ionization in suitable polar solvents. Depending on the nature of the ionizing groups on the chain, polyelectrolytes may be categorized in two broad classes: (i) **Strong polyelectrolytes** – where the ionizing groups resemble small molar mass salts and dissociate completely when placed in a polar solvent. (ii) **Weak polyelectrolytes** - where the ionizing groups are made of weak acids or bases and shows variability in terms of degree of dissociation depending on the pH of the solution.



Figure 1.1 Examples of strong and weak polyelectrolytes

Polyelectrolytes find a wide variety of applications as biological building blocks (nucleic acids, protein, cellulose), in industries (paper, paint, cosmetics, pharmacy etc.) and is an active field of interdisciplinary research in many areas like interpolyelectrolyte complexes ¹, polyelectrolyte adsorption on charged surfaces ², fabrication of novel nanomaterials (multicomponent films³) etc. So, it is not surprising that the study of the physicochemical behaviour of these systems attracted an increased interest in the scientific community over last few decades. Historically, only highly charged water soluble polymers were mainly used as model systems both in theory and experiments mainly due to the presence of aqueous environments in most of the practically important applications of these polymers. Low solubility of these polymers in organic solvents might have been another reason. The insolubility problem can be solved when a very low amount of charges are given

to the polymer (sometimes also referred as ionomers when the fraction of charged groups on the polymer is < 15%) and then it is dispersed in a polar organic solvent (alcohols, DMF etc.). Studies have shown that the typical polyelectrolyte behaviour is a general property of the charged chains and not confined to aqueous solutions of highly charged polyelectrolytes only^{4,5,6,7}.

Despite of their huge application, the fundamental understanding of the charged polymer systems is still far from being complete when compared to the neutral polymers, and it is a well-accepted fact that they remain the least understood system in soft matter science^{8,9}. Along with the hydrodynamic interactions, short range interactions and chain flexibility which are also present in neutral polymers, the charged counterparts brings in long range electrostatic forces into the picture which makes the system even more complex both theoretically (straight forward application of modern polymer theories like renormalisation group theory, scaling ideas are not possible) and experimentally. The long range coulomb interactions in polyelectrolyte solutions leads to many fascinating and counter-intuitive phenomena^{10,11}. Especially light scattering, which is a routine analysis technique for neutral polymers, is still very poorly understood in polyelectrolyte solutions.

The most important factor which makes polyelectrolytes different from other uncharged polymers is the linear charge density on the macromolecular chain. Virtually all the macroscopic properties of polyelectrolyte systems are critically dependent on its charge density. Albeit its huge implication on polyelectrolyte behaviour, we lack a basic quantitative understanding of the charge density both from theoretical and experimental point of view. It is now well accepted that the effective charge density of a polyelectrolyte molecule in solution is smaller than the actual value and there is a great deal of literature supporting this general conclusion^{12,13,14,15,16,17,18,19}, although the results normally do not coincide with each other. From a theoretical point of view, the polyelectrolyte system constitutes a multibody interaction problem. Various levels of approximations have to be involved to answer specific queries,^{20,21,22,37} which is the main reason of disconformities between the results.

From an experimental point of view, the difficulties arises mainly because of long range coulumbic interactions between the charged groups on the same chain or on different chains and also with the small ions which are present in the solution. At high added salt concentration, polyelectrolyte solutions behave similar to the neutral polymers because of extensive screening of the electrostatic interactions, which may obscure the correct determination of the effective charge. At low added salt concentration or in salt free solutions the effect of the polymer charges on the experimentally measured properties are strongest and may provide a way to determine the charge density. The problem with measurements at low added salt concentration or salt free solutions is that the single molecular properties of the polyelectrolyte chains are overwhelmed by ensemble properties due to long range intermolecular correlations which often exceed single chain dimensions. To study the properties of polyelectrolyte solution at this low ionic strength limit, working with low polymer concentrations is preferable which will make experiments (for determination of charge density) like conductivity, electrophoresis, and osmosis difficult because of very low measured signal. In this regard, light scattering may have edge over other techniques especially for high molar mass polymers because the measured quantity in this technique (intensity) is proportional to the square of the molar mass and the contrast can also be controlled by controlling dn/dc.

Light (along with neutron and x-ray) scattering techniques have been used for quite a long time now to study the structure and dynamics of polyelectrolyte solutions at low ionic strength. A great deal of work has been done elucidating the conformational transitions of single chains and intermolecular interactions with static light scattering measurements. Both of these properties are obtained from the angular dependence of the scattered light intensity. Surprisingly, in most of those studies, a quantitative analysis of the scattering intensity at 0 scattering angle (I₀) is avoided. The molecular property that is obtained from I₀ is the molar mass of the polymers. To this end, the use of light scattering is mainly limited to characterize polyelectrolytes²³ or to test some new experimental setup (like GPC²⁴) by measuring the molar mass at high added salt concentration which, as discussed in the last paragraph obscures any effect arising due to charges on polyelectrolyte chains.

At low ionic strength, the molar mass of a polyelectrolyte obtained by static light scattering is smaller than the actual molar mass. The relative discrepancy between the measured molar mass and the actual molar mass as a function of the polymer and added salt concentration can be correlated to the charge on the polymer chains. Such correlation is possible because of the intimate relationship of I_0 with the osmotic pressure of the solution which in turn depends upon the equivalent concentration of the charges on the polyelectrolyte chain.^{78,83,87}

In this thesis, the molar mass of quaternized poly(2-vinylpyridine) (QPVP) polymers are systematically measured as function of the polymer concentration and an added small molar mass salt concentration, and the experimental results are compared with the suitable theory to obtain the effective charge of the polymers in solution. Polymers with different molar masses and charge densities are used for a comparative study. Effect of the solvent polarity on the effective charge is also tested by using two different solvents namely water and 1-propanol. The results for the QPVP polymers is compared with that of salt free aqueous solution of sodium poly(styrenesulphonate) (NaPSS) polymer for which extensive literature data measuring the effective charge is available.^{25,26,27}

2 Background/Theory

2.1 Terminologies

When dissolved in a polar solvent, ionization of the monomers of a polyelectrolyte molecule produces electrically charged groups on the polymer molecule. This charge containing polymer molecule is known as **polyion or macroion**. The ionization process also releases smaller ions in the solution which have charges opposite in sign to that of the chain and makes the solution electro neutral on macroscopic scale. These small ionic species are named as **counterions**. For flexible polyion chains (which are able to undergo conformational transitions) electrostatic repulsion of the charged groups on the polyion chain gives the complexity and richness of the solutions.^{28,29} Moreover, because of the strong electric field around the polyion, these solutions also show different thermodynamic properties compared to small electrolytes.^{30,31} Addition of low molar mass salt to the polyelectrolyte solutions, which leads to the "normal" behavior of polyelectrolyte solutions.



Figure 2.1 Schematic representation of the charge distribution on a single flexible polyions surrounded by its own counterions

2.2 Linear charge density, Bjerrum length and screening length

The electrostatic interactions in a polyelectrolyte solution are dependent on various length scales characteristic both to the polyion chain and the surrounding solvent. The most basic term being the distance between two successive charged monomers along the backbone (A). This distance depends on the fraction of the total monomers that carries electrical charges. If the fraction is given as α , then for a polyion with N monomers:

$$A = \frac{b}{\alpha}$$
 Equation 2.1

where b is the distance between two successive monomers (charged or uncharged). Here it is assumed that the charged monomers are smeared homogeneously along the chain backbone.

The solvent molecules surrounding the polymer chain are assumed to be a continuous medium which modulates the electrostatic interactions through its constant dielectric constant. There exists a length scale at which the electrostatic interaction energy between two charges becomes same as the thermal energy available (k_BT). This characteristic length scale specific to the solvent is known as the Bjerrum length (l_B):

$$l_{\rm B} = \frac{e^2}{4\pi\epsilon\epsilon_0 k_{\rm B}T}$$
 Equation 2.2

where e is the elementary charge and ε_0 is the permittivity of vacuum.

Like in any electrolyte solution, each polyion is surrounded by an ionic atmosphere of the small ions (counterions and small salt ions) which reduces the electric field created by the polyion. The radius of the ionic atmosphere is known as the Debye screening length³² and given as:

$$r_D = \kappa_D^{-1} = \left(4\pi l_B \sum z_i^2 c_i\right)^{-1/2}$$
 Equation 2.3

where κ_D is the screening constant, c_i and z_i are the concentration and valence of the ith small ion in the ionic atmosphere. Although the expression shown in Equation 2.3 was actually derived for small spherical ions, it is also used as a good approximation in many theoretical works on polyelectrolyte solutions.^{33,34,35}

2.3 Counterion condensation: Manning theory

Close proximity of the equal charges on a polyion gives rise to a very strong electrical potential around the chain that controls the distribution of the counterions in the solution. Till date, all thermodynamic calculations and predictions about polyelectrolyte solution behavior are based on this simple qualitative picture. Most of the theoretical works have been done assuming a rod like geometry of the polyion chain which enables analytical solution of the Poisson-Boltzmann equation ³⁶. The concept known as the counterion condensation came to existence mainly through the works of Oosawa²⁸ and Manning.^{37,38,39,40} According to this concept, there will be situations when the linear charge density of a rod like polyion in solution is reduced from its actual value because of "binding" of oppositely charged counterions on the chain. The condensation or binding of the counterions commences only when the linear charge density exceeds a limiting value.

The condensation is governed by a balance between strong electrostatic attraction and loss of translational entropy for the counter ions when they bind to the chain. Simply, the phenomenon can be understood by considering a charged rod (polyion) and an oppositely charged ion (counterion) near to the rod as shown below,



Figure 2.2 Schematic representation of counterion-polyion interaction leading to the condensation of the counterion on the chain

The rod has a sequence of charges e at distance A from each other. The linear charge density is given by e/A. By moving the small ion from distance r_1 to r_2 , the entropic gain in energy will be,

$$|F_{entropy}| \sim k_B T ln\left(\frac{r_2}{r_1}\right)$$
 Equation 2.4

and the loss of electrostatic attraction energy will be given by,

$$|F_{\text{elect.}}| \sim \frac{e^2}{4\pi\epsilon_0 \epsilon A} \ln\left(\frac{r_2}{r_1}\right)$$
 Equation 2.5

Comparing Equation2.4 and Equation2.5, the entropic gain will dominate if,

$$\frac{e^2}{4\pi\varepsilon_0\varepsilon AK_BT} < 1$$
 Equation 2.6

And the small ion will escape to the bulk. On the other hand, the electrostatic attraction energy will dominate when,

$$\frac{e^2}{4\pi\epsilon_0\epsilon AK_BT} > 1$$
 Equation 2.7

In this case the small ion will bind to the rod (condensed). The quantity

$$\frac{e^2}{4\pi\epsilon_0\epsilon AK_BT}$$
 or, $\frac{l_B}{A}$

is known as the Manning parameter (ξ_M) and the value of this quantity dictates whether or not a counterion will be condensed on the chain. For $\xi_M \leq 1$ (weak coupling), all counterions are free to move to the bulk of the solution and for $\xi_M >1$, (strong coupling) a fraction of the counterions will bind to the chain until $\xi_M =1$. The fraction bound to the chain can be shown to be⁴¹ (1-1/ ξ_M). The remaining fraction (1/ ξ_M) of the counterion interacts with the reduced charge of the polyion chain through Debye-Hückel potential.

Though Manning's theory is at least qualitatively supported by some experimental results^{42,43,44}, it is still highly controversial in the polyelectrolyte research field^{45,46,47,48,49,50}. Besides neglecting the correlation between the condensed counterions, there are basically two open questions regarding the applicability of this theory. Firstly, the "state" of condensed counterions is still not yet fully understood. There is no direct experimental proof

that says whether the condensed counterions are still mobile along the chain contour (also known as territorial binding⁵¹) or form immobile stern layer due to specific site bindings (ion pair)^{52,53}. Because in either case those condensed counterions would be an integral part of the chain itself and will not "show up" in experiments. The second problem with Manning's theory is the approximation of the polyion conformation as an infinite rod which is not a good model for flexible polyions. A highly charged flexible polyion is believed⁵⁴ to be rod shaped in a salt free infinitely diluted solution (which is the reason why Manning's theory is also known as the limiting law). Comparison of the theory to experiments may then be limited by the difficulties in measuring the so called infinite dilute solution.

2.4 Polyelectrolyte single chain conformation

The flexibility of the polyion may be addressed by describing the polyion chain with the worm like chain model⁵⁵ used for semi flexible neutral chains. The polymer chain in this model is pictured as a continuous elastic curve, and the extent of coiling or bending of this curve is characterized by the so called persistence length (l_p). A section of the polymer contour having a length smaller then l_p will behave almost like an elastic rod. This concept was extended to the case of polyions by introducing the effect of the charges on the intrinsic conformational behavior of the neutral backbone^{56,57}. Persistence length for the charged polyion is described as the sum of two contributions, (i) the bare persistence length ($l_{p,0}$) of the uncharged chain and (ii) an electrostatic contribution ($l_{p,e}$) due to the repulsion between the charges on the chain:

$$l_{p} = l_{p,0} + l_{p,e}$$
 Equation 2.8

The radius of gyration from the persistence length is obtained as⁵⁸

$$\langle R_g^2 \rangle = \frac{l_p l_c}{3} - l_p^2 + \frac{2l_p^3}{l_c} - \frac{2l_p^4}{l_c^2} \left(1 - \exp\left(-\frac{l_c}{l_p}\right)\right)$$
 Equation 2.9

 l_c is the contour length of the chain. The electrostatic persistence length ($l_{p,e}$) is calculated from the screened electrostatic interaction of the charges, and it's value depends on the screening length. Taking account for counterion condensation the following relations of $l_{p,e}$ is predicted:

$$l_{p,e} = \frac{l_B r_D^2}{4A^2} \qquad \text{for, } l_B \le A \qquad \text{Equation 2.10}$$
$$l_{p,e} = \frac{r_D^2}{4l_B} \qquad \text{for, } l_B > A$$

In the absence of any added salt, only the free counterions contribute to the screening length r_D which will then have very high value making the value of $l_{p,e}$ also very large according to Equation 2.10. So, even if the backbone of the polyion is very flexible $(l_{p,0}<<l_c)$, at salt free conditions the contribution of $l_{p,e}$ alone will produce very large total persistence length (see Equation 2.8). If $l_{p,e}$ (or l_p) is much bigger than the contour length (l_c) of the polyion, then the whole chain will have a rod conformation. The radius of gyration of the chain is obtained from Equation 2.9 as¹⁴:

$$\langle R_g^2 \rangle = \frac{l_c^2}{12}$$
 for $l_c << l_p$ Equation 2.11

2.5 Concentration regions

The solution property of both charged and uncharged polymers depends upon the relative distances of the chains from each other. At very low concentrations chains are well separated and single chain properties like molar mass, size and/or shape can be determined by experiments. The conformation of the chains in this regime can be understood by the single chain conformation described in the previous section. With increasing concentration, individual chains start to overlap with each other to produce a network or mesh like structure. So, the polymer (or polyelectrolyte) solutions are classified in two distinct regimes: **dilute** and **semi dilute**. The crossover between the two concentration regimes are characterized by the **overlap concentration** (c_p *) when the monomer density inside a volume occupied by a single chain is equal to the total average monomer density in whole solution. Depending

upon the chain architecture, measurement method etc. different expressions are used to calculate the overlap concentration for neutral polymer solution⁵⁹:

$$c^* \left(\frac{4\pi}{3} R_g^3\right) = \frac{M}{N_A}$$
 Equation 2.12
 $c^* \left(\sqrt{2} R_g\right)^3 = \frac{M}{N_A}$ Equation 2.13

$$c^*[\eta] = 1$$
 Equation 2.14

where M is the molar mass and N_A is Avogadro's number.

In the semi dilute concentration regime, the solution property is independent of the individual chains and is governed by the so called **correlation length** (ξ)⁶⁰, which is the segment length of a chain between two successive entanglements with other chains. Although such classification of concentration regions is found to be satisfactory for neutral polymer solution, for polyelectrolyte solutions with long range interactions the above equations for calculation of c* may not be completely correct. Different scaling approaches have been proposed^{61,62} for the overlap concentration of the polyelectrolyte solution.

2.6 Osmotic pressure

Osmotic pressure of a salt free polyelectrolyte solution is much higher compare to the neutral polymer solution at same concentrations. In a dilute, salt free solution of a polyelectrolyte, the osmotic pressure of the solution is given as the sum of the contributions from the polyions and the counterions. Assuming that all the counterions are free from the polyion and that the solution behaves ideally with respect to all the components (polyion and counterion), the osmotic pressure can be written as:

$$\Pi_{id} = (1+z) \frac{C_p}{M} RT$$
 Equation 2.15

where Π_{id} represents the ideal solution osmotic pressure. C_p and M are respectively the concentration (mass / volume) and molar mass of the polyion chains. Each polyion chain has z charges, which makes the molar concentration of the free counterions to be zC_p/M . Since a single polyion carries many charges along their backbone, z>>1 or,

$$\Pi_{id} = \frac{C_p}{M} zRT$$
 Equation 2.16

The osmotic pressure of a salt free polyelectrolyte solution is dominated by the counterions, the contribution from the larger polyions being a negligible fraction. Counterion condensation and/or counterion-polyion correlation reduces counterion activity and makes the measured osmotic pressure lower than what it should be according to Equation 2.16. This disparity is taken care of by introducing so called osmotic coefficient (ϕ_p) which is obtained as the ratio between the measured and ideal osmotic pressure:

$$\phi_{\rm p} = \frac{\Pi_{\rm exp}}{\Pi_{\rm id.}}$$
 Equation 2.17

where Π_{exp} is the experimentally measured value. So, the measured osmotic pressure (Π_{exp}) is related to the polyion properties through:

$$\Pi_{exp} = \frac{C_p}{M} \phi_p z RT$$
 Equation 2.18

 Φ_p is found to be considerably smaller than 1, and inversely proportional to the charge on the polymer $z^{63,64}$. From a osmotic pressure measurement point of view the quantity $\Phi_p z$ is regarded as the effective charge of the polyion in the solution. A systematic measurement of the osmotic pressure as a function of the polyion in salt free condition will give M/(Φ_p .z) as the apparent molar mass of the polyion. Even if the value of z is known, it is not possible to obtain the true molar mass (M) from this apparent value due to the unknown value of Φ_p which is also found to be a function of the polyion concentration⁶⁵.

Addition of a neutral salt to the polyelectrolyte solution reduces the osmotic pressure. To calculate the osmotic pressure for a polyelectrolyte solution with added salt, one has to consider the effect of Donnan equilibrium⁶⁶⁻⁶⁷ which sets up between the polymer and salt compartment due to the expulsion of neutral salt by the polymer. The osmotic pressure measured in this case is more commonly known as the Donnan pressure or oncotic pressure which can be shown to be^{68·69}:

$$\Pi_{\text{donnan}} = C_{\text{p}} \text{RT} \left(\frac{1}{M} + \frac{z^2}{4M^2 C_{\text{s}}} C_{\text{p}} + \cdots \right)$$
 Equation 2.19

where, C_s is the initial salt concentration (mass/vol.) in the salt chamber. All other symbols are same as in Equation 2.16. In analogy to the virial expression of the osmotic pressure of neutral polymer solution, the Donnan second virial coefficient is given as:

$$A_{2,donnan} = \frac{z^2}{4M^2C_s}$$
 Equation 2.20

Experimentally measured values of the second virial coefficient is found to be smaller than what is shown in Equation 2.20 due to the screening of the polyion charge by the salt ions to a smaller ($z_{eff} < z$) value⁷⁰.

2.7 Symbols and constants used in this chapter

ξ _M	Manning charge condensation parameter
ξ	correlation length in semi dilute polymer solution
Φ_p	osmotic coefficient
А	contour distance between two consecutive charges on polyion chain
α	degree of dissociation of a polyion
κ _D	Debye screening constant
l _B	Bjerrum length
$\Pi_{\rm id} / \Pi_{\rm exp/} \Pi_{\rm donnan}$	ideal/ measured / donnan osmotic pressure
r _D	Debye screening length
l _c	chain contour length
$l_{p,0} / l_{p,e} / l_p$	bare / electrostatic / total persistence length
Z	charge on a polymer chain

3 Light scattering: Techniques and Theory

The origin of light scattering from a polyelectrolyte (or polymer in general) solution is the existence of microscopic inhomogeneities of the refractive index in the scattering medium. For the particular case of the scattering geometry shown in Figure 3.1, the intensity of the scattered light at a scattering angle θ can be shown to be⁷¹,

$$R(\theta, t) = \frac{I(\theta, t) r^2}{I_0} = \frac{4\pi^2 n_0^2 v}{\lambda^4} \Delta n(\theta, t)^2$$
 Equation 3.1

where,

 $R(\theta,t)$ is the Rayleigh ratio which is nothing but a normalized scattered intensity.

r is the distance of the detector from the solution.

 I_0 and λ are respectively the intensity and wavelength of the incident light.

v is the volume of very small region in the solution sustaining the fluctuation of refractive index.

n₀ is the refractive index of pure solvent.

 $\Delta n(\theta,t)$ is the Fourier transform of the refractive index fluctuation $\Delta n(\mathbf{r},t)$ at a position \mathbf{r} in the space.

The dependence of the scattered intensity both on scattering angle (θ) and time (t) leads to two major variations of the experimental light scattering techniques namely **static light scattering (SLS)** and **dynamic light scattering (DLS)**. The general principles and theories behind these two techniques and the relevant informations obtained are discussed below in detail.



Figure 3.1 Schematic representation of an experimental setup for light scattering measurement. The incident electric field vector (E_0) is polarized along z-axis of an arbitrary reference system. The polymer solution is in a cylindrical container which is shown in the origin of the reference system. The direction of propagation of the incident light and scattered light is shown with the initial (K_0) and scattered (K_s) wave vectors respectively. Scattered light intensity is detected on x-y plane at a distance r from the origin and at an angle of θ from K_0

3.1 Static light scattering

In static light scattering experiment the time averaged scattered intensity from a polymer solution is evaluated. The absolute value of this average intensity at 0 scattering angle (R(0)) is controlled by the thermodynamics of the solution and under certain conditions can be used to extract important parameters such as the molar mass (M) and the second virial coefficient (A₂). On the other hand, the angular dependence of the scattered intensity R(θ) results from interference of light waves scattered from different parts of the solution and gives information about the structure of the solution. Depending upon the value of λ and θ , different length scales of this structure, starting from a single polyion chain (R_g) to the interchain distances, can be probed.

3.1.1 Scattering intensity at $\theta=0$: two component system

The fluctuation theory of light scattering developed for small particles describe the relation of R(0) with the thermodynamic properties of the solution. Fluctuation in two component (polymer and solvent) systems arises due to density and concentration fluctuations. For small concentrations, these two effects can be assumed to be independent of each other. Using the concepts of the fluctuation theory in statistical thermodynamics⁷², R(0) can be written as^{73,74,75},

$$R(0) = \frac{4\pi^2 n_0^2}{\lambda^4 N_A} \left\{ \left(\frac{\partial n}{\partial \rho} \right)^2 RT\beta\rho + \left(\frac{\partial n}{\partial C} \right)^2 \frac{RTC}{\left(\frac{\partial \Pi}{\partial C} \right)} \right\}$$
 Equation 3.2

Where,

as:

 ρ and β are respectively the density and the isothermal compressibility of the solvent.

- C is the mass concentration of polymer.
- R is the universal gas constant.
- Π is the osmotic pressure of the solution
- T is the absolute temperature

The first term in the bracket in Equation 3.2 denotes the contribution due to density fluctuation of the solvent and it is normally subtracted from the measured R(0) which leaves only the contribution from the polymer due to its concentration fluctuation (see Equation 3.3):

$$R(0)_{polymer} = K \frac{RTC}{\left(\frac{\partial \Pi}{\partial C}\right)}$$
 Equation 3.3

where K is known as the optical contrast between the polymer and solvent and given

$$K = \frac{4\pi^2}{\lambda^4 N_A} n_0^2 \left(\frac{\partial n}{\partial C}\right)^2$$
 Equation 3.4

Equation 3.3 shows direct relation of the intensity of the scattered light to the important thermodynamic property of the solution known as the osmotic modulus ($\partial \Pi/\partial C$), which is related to the free energy change of the solution with the change in solute concentration. When the expression for osmotic pressure for a polymer solution (see section 2.6) is introduced in Equation 3.3 the apparent molar mass of the polyions chains can be determined from the light scattering data using,

$$M_{app} = \frac{KC}{R(0)^*}$$
 Equation 3.5

3.1.2 Scattering intensity at $\theta=0$: multi component system

Fluctuation theory for light scattering as described in the previous section is only applicable for a two component system like a polymer in a pure solvent. For polyelectrolytes, only at very high added salt concentrations does the solution behave like pseudo two component system and Equation 3.5 gives the correct (or true) molar mass. For salt free or low added salt concentration, a polyelectrolyte solution has to be treated has multicomponent system^{76,77,78}. Even if the scattering intensity from the small ions are neglected compared to the intensity of very high molar mass polyion chains, concentration fluctuation of the latter will be modified through electrostatic interactions between with the smaller ions. The general light scattering properties from a multicomponent system was first considered by Zernike⁷⁹ and later a complete statistical mechanical treatment by many others^{80,81,82} gives the excess scattering intensity for a volume V at 0 scattering angle as,

$$R(0) = \frac{4\pi^2 n_0^2 V k_B T}{\lambda^4} \sum_{j=1}^{2} \sum_{i=1}^{2} \Psi_i \Psi_j \frac{A_{ij}}{a_{ij}}$$
 Equation 3.6

Where,

i, j represents individual components except the one with the maximum amount in the mixture (solvent), which is represented as subscript 0.

 $\Psi_i = (dn/dm_i)_{T,P,m}$ is the increase of refractive index due to the ith component which has mass m_i in the solution

^{*} This is the excess scattering intensity of the solution; the subscript polymer is dropped for convenient representation. From now on, the symbol R(0) or $R(\theta)$ will be used only for the contribution of the polymer (excluding the solvent intensity).

Aij and aij are the co-factor and determinant having elements,

$$a_{ij} = \left(\frac{d\mu_i}{dm_j}\right)_{P,T,m_{k\neq j}}$$
 Equation 3.7

This shows the change in the chemical potential of one component due to the change in concentration of all other components. For a two component system Equation 3.7 reduces to the equation derived by Einstein.

The concept of scattering from multicomponent system is used by Prins and Hermans⁸³ to describe the scattering properties of charged colloidal particles in ideal solution conditions assuming the colloidal particle with its dissociated counterions as one component and the added neutral salt as the other component. Their result can also be used for polyelectrolyte solutions with low amount of added salt assuming a fix charge on the polyions chains. The final result can be shown to be,

$$\frac{\partial \left(\frac{\pi}{K_{\rm B}T} \right)}{\partial c_{\rm p}} = \frac{1}{N_{\rm true}} + \frac{\alpha}{1 + \frac{2c_{\rm s}}{\alpha c_{\rm p}}}$$
 Equation 3.8

where,

N_{true} is the true degree of polymerization of the polyion

c_s is the salt concentration in mol/L

 $c_{\mbox{\scriptsize p}}$ is the monomolar concentration of the polyion

 α is the effective degree of ionization of the polyion

The apparent degree of polymerization N_{app} is the reciprocal of the osmotic compressibility as defined by Equation 3.8. So, measuring the N_{app} as a function of c_s and c_p will enable one to get the degree of ionization α using:

$$\frac{1}{N_{app}} = \frac{1}{N} + \frac{\alpha}{1 + \frac{2c_s}{\alpha c_p}}$$
 Equation 3.9

3.1.3 Scattering intensity at $\theta=0$: effect of Donnan equilibrium

It was proposed^{84,85} that a true determination of the molar mass from Equation 3.5 is only possible when the dn/dc value in the contrast factor K is measured in a Donnan equilibrium where the polyion solution is first dialyzed against the salt solution. dn/dC of the polyion solution should then be measured using the equilibrated salt solution as the background solvent. Because of the dialysis process the diffusible small salt should be in same chemical potential in both the solution and the refractive index obtained is by this procedure might be different than the value that is measured at a constant salt concentration. The relation between the apparent and true molar masses is given by⁸⁴:

$$M_{app} = M_{true} \left[1 + \frac{\left(\frac{\partial n}{\partial C_s}\right)}{\left(\frac{\partial n}{\partial C_p}\right)} \left(\frac{dC_s}{dC_p}\right)_{\mu_{salt}} \right]^2$$
 Equation 3.10

where C_s is the salt concentration in g/L, μ_{salt} is the constant chemical potential of the salt at Donnan equilibrium. It will be shown later in this thesis that the polyions used in this work does not show any significant effect from using non dialyzed value of dn/dC. This is in agreement with the finding of Eisenberg⁸⁶, who suggested that for strong polyions, the small change in the salt concentration due to the dialysis process will have very little effect on the light scattering properties of the polyion. Moreover, the applicability of Equation 3.9 over Equation 3.10 to get the true molar mass from the apparent one is supported from the theoretical calculation of Mysels⁸⁷.

3.1.4 Scattering intensity for $\theta > 0$

Fluctuation theory is only applicable for small ($R_g < \lambda / 20$; where Rg is the radius of gyration of polymer) polymer chains. For big polymer chains, light scattered from different parts of the chain interfere with each other which reduces the scattering intensity for $\theta > 0$. The scattering intensity now becomes a function of the measuring angle. Calculation of the scattering intensity for such system is mathematically very difficult and its only been solved for spherical particles by Mie^{88,89}. However, analytical expressions for the scattering intensity for given as,

$$2x(m-1) \ll 1$$
 Equation 3.11

Where, x is relative size of the particles compare to the wavelength of the incident light ($\sim R/\lambda$)and m is the relative refractive index of the polymer compare to the solvent ($n_{polymer}/n_{solvent}$). When this condition is fulfilled, the polymer chain can be imagined as a linear array of small scatterers as shown in Figure 3.2.



Figure 3.2 Scattering scheme from a polymer coil. The scattered light $E_{s,i}$ and $E_{s,j}$ from two different positions of the chain shown at \mathbf{r}_i and \mathbf{r}_j has a phase difference of $\mathbf{q}.\mathbf{r}_{i,j}$ and interferes at the detector

Summing the contributions of all scattering centers, the scattering intensity of a single chain can be shown⁹⁰ to be,

$$R(\theta) \approx b^2 \sum_{i,j=1}^{N} \left[\exp\{i, \mathbf{q}, \mathbf{r}_{i,j}\} \right]$$
 Equation 3.12

Where b is called the scattering length and is proportional to the polarizability of a single scattering center. q is the scattering vector which determines the scattering geometry (Figure 3.2). For a scattering angle θ , q is given as,

$$|\mathbf{q}| = |\mathbf{k}_{i} - \mathbf{k}_{s}| = \frac{4\pi n_{0}}{\lambda} \sin\left(\frac{\theta}{2}\right)$$
 Equation 3.13

The quantity $\mathbf{q}.\mathbf{r}_{i,j}$ gives the phase difference of scattered lights from two parts of the polymer at position \mathbf{r}_i and \mathbf{r}_j . The summation in Equation 3.12 runs over the degree of polymerization N of the polymer. The single chain interference is expressed as the **form** factor P(q) which is given by,

$$P(q) = \frac{1}{N^2} \langle \sum_{i,j=1}^{N} \exp\left(i\mathbf{q} \cdot \mathbf{r}_{ij}\right) \rangle$$
 Equation 3.14

where the average is done over all possible conformation of the chain.

For polyelectrolyte solutions at low ionic strengths, monomers from different chains are correlated to each other due to long range coulombic interactions. Along with single chain interference (P(q)), scattering intensity from polyelectrolyte solution is also affected by interchain interference. In this case, Equation 3.12 has to be replaced by a fourfold sum:

$$R(\theta) = b^{2} \langle \sum_{\alpha,\beta=1}^{n_{p}} \sum_{i,j=1}^{N} \left[\exp\{i. \mathbf{q}. \left| \mathbf{r}_{i}^{\alpha} - \mathbf{r}_{j}^{\beta} \right| \} \right] \rangle$$
 Equation 3.15

where n_p is the number of polyion chains in the scattering volume. \mathbf{r}_i^{α} is the i-th segment of the α -th chain. The average is a taken over all possible chain conformation and all possible distribution of different chains. The summand in Equation 3.15 includes both intra and inter particle interferences. For a distribution of homogenous spherical polyions, the two contributions can be separated, and the scattering intensity can be written as⁹¹,

$$R(\theta) = KCMP(q)S(q)$$
 Equation 3.16

Where S(q) is known as the intermolecular structure factor which depends upon the distribution of the polyions in the solution. The distribution is given by g(r), which is the probability of finding the centre of masses two chains within a distance r. S(q) is for a isotropic solution, is related to g(r) by the equation:

$$S(q) = \left(1 + \frac{4\pi n_p}{V} \int_0^\infty (g(r) - 1) \frac{\sin qr}{qr} r^2 dr\right)$$
 Equation 3.17

The importance of Equation 3.16 can be apprehended in the following two cases:

<u>Case1</u>: In the absence of intermolecular correlation (for example, polyelectrolyte solution with high concentration of added salt), g(r)=1 and S(q) =1. Then the angular dependence of scattered intensity S(q) depends solely on the single chain form factor, which is given (for homogenous distribution of the scattering centers within the chain volume) as,

$$P(q) = \frac{4\pi}{N^2} \int_{V} P(r) \frac{\sin qr}{qr} r^2 dr$$
Equation 3.18

The integration is done over the chain volume v. P(r) is the radial distribution function of the scatterers within the chain. P(r) and hence P(q) depends on the topology of polyion chain. For an ideal coil like chain, P(r) is a Gaussian function of r. For small sized chains (qR_g<<1, where R_g is the radius of gyration), form factor can be expressed as a taylor series in q⁹²,

$$P(q) = 1 - \frac{1}{3}R_g^2 q^2 + ...$$
 Equation 3.19

Inserting Equation 3.19 in Equation 3.16 and using S(q)=1, we get

$$\frac{\text{KC}}{\text{R}(\theta)} = \frac{1}{M} (1 + \frac{1}{3} \text{ R}_g^2 q^2)$$
 Equation 3.20

Equation 3.20 is used to evaluate the radius of gyration from the scattering data from the slope of KC/R(θ) vs q².

Case2:

If the conformation of the polyion chain is known, theoretical equations can be used for P(q), which enables one to get the distribution of the polyion chains (which is also known as the structure of the polyion solution) g(r) from the angular dependence scattered intensity $R(\theta)^{93}$. A detailed description of this topic is out of the scope of this thesis.

3.1.5 Effect of polydispersity

In the derivation of the theoretical expressions for molar mass (section 3.1.1-section 3.1.3 or radius of gyration (3.1.4), the polymer chains are explicitly assumed to be monodisperse. Any synthetic polyelectrolyte sample would have a distribution of molar masses and chain sizes. If the polydispersity index (M_W/M_n) is not very high, the important equations used to get the molar mass or size of polyion chain would still be useful without any correction, but the results obtained would only be an average value of the of the quantities in question. For the molar mass, light scattering measurements yield a weight average value given as:

$$M_{W} = \sum_{i} \frac{C_{i}M_{i}}{C_{i}}$$
 Equation 3.21

Whereas the radius of gyration is given as a z-average of all the polyion chains in the sample:

$$\langle R_g^2 \rangle_z = \sum_i \frac{C_i M_i R_{g,i}^2}{C_i M_i}$$

Equation 3.22

3.2 Dynamic light scattering

Temporal fluctuation of the refractive index gives rise to time dependent fluctuation in the scattering intensity (see Equation 3.1). A typical trace of the measured intensity is shown already in Figure 3.1. Temporal fluctuation of the refractive index originates from molecular motion, mainly diffusion of the polyion chains in the solution. The aim of a DLS measurement is to quantify this fluctuation of the scattered intensity, which enables us to determine the diffusion coefficient.

3.2.1 Intensity correlation function (I.C.F)



Figure 3.3 Fluctuating scattered intensity with time and the corresponding Intensity correlation function

The quantification of the intensity fluctuation is achieved by comparing the measured intensity at any given time t to the intensity at a later time $(t+\tau)$. This process is continued for all values of t starting from 0 to the maximum time T (duration of the intensity data collection). The average of all these multiplication results gives the so called intensity correlation function:

$$G^{(2)}(q,\tau) = \langle I(q,t) * I(q,t+\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T I(q,t) I(q,t+\tau) dt$$
 Equation 3.23

where, q is the scattering vector and τ is the delay time. The quantity $\langle I(t)*I(t+\tau) \rangle$ is a monotonically decaying function in τ (see **Figure 3.3**) which is directly related to the molecular motion that creates the intensity fluctuation. At $\tau=0$, the system is almost unchanged (polymer chains does not move very far)and it produce maximum correlation $\langle I(q)^2 \rangle$, and when τ is very large compared with the characteristic time of the fluctuation of I(q,t), the signal at I(q,t) and $I(q,t+\tau)$ become essentially uncorrected, and $G^{(2)}(t)$ decays to a value of $\langle I(q) \rangle^2$. The characteristic time τ_c of this decay is a measure of the typical fluctuation time of the intensity. For a large number of monodisperse polymers in Brownian motion, the correlation function is an exponential decaying function of the correlation time delay τ . The normalized time correlation function of the scattered intensity is defined by:

$$g^{(2)}(q,\tau) = \frac{\langle I(q,t) * I(q,t+\tau) \rangle}{\langle I(q) \rangle^2}$$
 Equation 3.24

Similarly, the normalized time correlation function of the scattered field is defined by:

$$g^{(1)}(\tau) = \frac{\langle E^*(q,t) * E(q,t+\tau) \rangle}{\langle I(q) \rangle}$$
 Equation 3.25

The scattered field E can be regarded as a sum of independent random variables $(E = \sum_i E_i)$ where E_i is the contribution from the i-th subregion of the scattering volume. The central limit theorem implies that E_s , must be distributed according to a Gaussian distribution, which is characterized its average and standard deviation. On this assumption, two time correlation functions are connected via the Siegert relation⁹⁴

$$g^{(1)}(q,\tau) = 1 + C_{coh} \{g^{(1)}(q,\tau)\}^2$$
 Equation 3.26

where C_{coh} represents the degree of spatial coherence of the scattered light over the detector and is determined by the ratio of the detector area to the area of one speckle ($0 < \beta < 1$). A is a baseline. The detector aperture can be chosen in a way so that, about one speckle is allowed to the detector. For this condition, $C_{coh} \sim 1$ the best signal to noise ratio is obtained.

3.2.2 Density correlation function and its relation with $g^{(1)}(q,t)$

Due to random movement of the scattering particles, the density of a very small volume in the solution fluctuates with time. Quantitatively this fluctuation is given as the van Hoff self correlation function:

$$G_{s}(r,\tau) = \langle n(0,t)n(r,t+\tau) \rangle$$
 Equation 3.27

where n stands for number density of scattering particles. Principally Equation 3.27 gives the conditional probability that a particle will be found in position r at time $t+\tau$, if the same particle was in the origin (r=0) at some previous time t. The choice of r or t is not significant to describe the density correlation; it's only the distance vector (**r**-**0**) or the time lag τ which are important. For undergoing absolute random movement in the solution due to diffusive motion, the expression for the density correlation function is given by a Gaussian distribution function:

$$G_{s}(r,\tau) = \left[\frac{2\pi}{3}\langle\Delta R(\tau)^{2}\rangle\right]^{-3/2} \exp\left(-\frac{3r(\tau)^{2}}{2\langle\Delta R(\tau)^{2}\rangle}\right)$$
 Equation 3.28

where $\langle \Delta R \rangle^2$ is the mean square displacement of one particle undergoing Browninan motion and is given by,

$$\langle \Delta R(\tau)^2 \rangle = 6D_s \tau$$
 Equation 3.29

where D_s is the self diffusion coefficient. The electric field time correlation function introduced in the last section is just Fourier transform of the density correlation function:

$$g^{(1)}(q,\tau) = \int G_s(r,\tau) \exp(iqr) dr$$
 Equation 3.30

Inserting Equation 3.28 and Equation 3.29 into Equation 3.30, the relation between the measured correlation function and the particle self diffusion coefficient is found to be,

$$g^{(1)}(q,\tau) = B \exp(-D_s q^2 \tau)$$
 Equation 3.31

where B is signal to noise ratio. For bigger particles, the effect of form factor (P(q)) has to be taken into account. So, for solution of big, polydisperse particles $g^{(1)}$ is given as:

$$g^{(1)}(q,\tau) = B \frac{\sum N_i M_i^2 P_i(q) \exp(-q^2 D_i \tau)}{\sum N_i M_i^2 P_i(q)}$$
 Equation 3.32

So, for polydisperse systems, $g^{(1)}(\tau)$ is not monoexponential anymore. The deviation from this monoexponential decay for very small polydispersity can be accounted for with cumulant expansion of $g^{(1)}(\tau)$ as a function of different moments of the distribution of diffusion coefficients:

ln (g⁽¹⁾(q,
$$\tau$$
)) = -constant - $\Gamma_1 \tau + \frac{1}{2!} \Gamma_2 \tau^2 - \cdots$. Equation 3.33

The initial slope or the first cumulant Γ_1 is given as,

$$\Gamma_{1} = q^{2} \left\{ \frac{\sum N_{i} M_{i}^{2} P_{i}(q) D_{i}}{\sum N_{i} M_{i}^{2} P_{i}(q)} \right\} = q^{2} D_{app}(q)$$
 Equation 3.34

Dapp is an angular dependent average diffusion coefficient. The q=0 extrapolated value of Dapp gives the "true" z-average diffusion coefficient:

$$\langle D \rangle_z = \frac{\sum N_i M_i^2 D_i}{\sum N_i M_i^2}$$
 Equation 3.35

And finally, with knowledge of the solvent viscosity and temperature, the hydrodynamic radius of the particle is calculated using Stokes-Einstein equation:

$$R_{h} = \langle 1/R_{h} \rangle_{z}^{-1} = \frac{K_{B}T}{6\pi\eta_{0} \langle D \rangle_{z}}$$
 Equation 3.36

3.3 Symbols and constants used in this chapter

*	complex conjugate
<>z	z- average properties
b	scattering length $\left(=\frac{4\pi^2\alpha}{\lambda^2}\right)$
β	isothermal compressibility
С	mass concentration (mass / volume)
c _p	monomolar concentration of polymer
E_0/I_0	electric field/intensity of incident light
ϵ_0/ϵ	dielectric constant of pure solvent/solution
Κ	optical contrast
k _B	Boltzmann's constant
k_i / k_s	wave vectors for incident/ scattered radiations
λ	wavelength of light
П	osmotic pressure
n ₀ /n	refractive index of solvent/solution
ρ	density of solvent
M_{W}	weight average molar mass of a polymer
Ν	degree of polymerization
n ₀ /n	refractive index of solvent/solution
η_0	viscosity of solvent
q	scattering vector
R or $R(\theta)$	Rayleigh ratio
R _g	radius of gyration of polymer molecule
R_h	hydrodynamic radius
Γ_{i}	moments of the distribution of decay rates of electric field correlation
function	
v	volume of fluctuating volume elements

4 Materials and Methods

4.1 Characterization of the neutral poly (2-vinylpyridine) (2-PVP) polymers by G.P.C

All neutral poly (2-vinylpyridine) (2-PVP) standards were bought from PSS Mainz who also provided the nominal molar mass of the polymer according to G.P.C measurements of done in THF with 0.1 vol.% Diethylaminoethylamine. Two different molar masses of 2-PVP are used in this work as the backbone precursor for the charged polyelectrolytes. The molar masses of these neutral backbones are 65,000 g/mol, and 850,000 g/mol. The polymers are designated throughout this work as 2-PVP_65KD, and 2-PVP_850KD, respectively. The original G.P.C measurements for the 2-PVP_850KD backbone done by the manufacturer is shown in Figure 4.1 and the summary of all the G.P.C results are given in Table 4.1.



Figure 4.1 Molar mass distribution of the neutral 2-PVP_850 KD polymer in T.H.F with 0.1 vol. % Diethylaminoethylamine as provided by the manufacturer
polymer / lot no.	M _w (gmol ⁻¹)	Weight average degree of polymerization(N _W)	M _n (gmol ⁻¹)	P.D.I
2-PVP_850_KD/vp13058	8.51*10 ⁵	8105	7.84*10 ⁵	1.1
2-PVP_65KD/vp29072	6.43*10 ⁴	612	6.28*10 ⁴	1.02

Table 4.1 Summery of the G.P.C results for all neutral 2-PVP polymers in THF[†]

4.2 Quaternization of poly (2-vinylpyridine)

The neutral 2-PVP backbones are given positive charges by quaternizing the N-atom in the aromatic ring with ethyl bromide. In each case, ~ 1 g of the uncharged polymer is dissolved in nitro-methane (~100 ml) under argon. After complete dissolution of the polymer an excess amount of ethyl bromide is added in the solution. The mixture is then stirred continuously at 60°C. The reaction is stopped at different times to get different degrees of quaternization (Table 4.2).



Figure 4.2 Quaternization reaction of the 2-PVP backbones

[†]Provided by the manufacturer.

The reaction mixture is then added to 1 Liter of petroleum ether previously cooled to -30°C. The precipitate is filtered, washed thoroughly with petroleum ether to remove excess ethyl bromide and dried in room temperature. The product is re-dissolved in benzene and few drops of methanol and then lyophilized to get rid of the solvent. The dried sample is stored in a nitrogen atmosphere. The degree of quaternization is calculated by the Br/N ratio obtained by a double elemental analysis of N and Br atoms by Mikroanalytische labor Pascher in Germany. For the quaternized polymers the symbols used are self-explanatory and the same representation is followed throughout the thesis.

Degree of quaternization / designation Polymer backbone Reaction time of the product. 2-PVP_65KD 48 hrs. 23% / QPVP_65KD_20% 4.3% / QPVP 850KD 4%¹⁰⁰ 2-PVP 850KD 54 hrs. 2-PVP_850KD 1 week 20% / OPVP 850KD 20%¹⁰⁰ 35% / QPVP_850KD_ 35%¹⁰⁰ 2-PVP_850KD 2 weeks

Table 4.2 Quaternization products from the various neutral poly (2-vinylpyridine)

4.3 Molar mass and the monomolar concentrations of the quaternized polymers from average monomer molar mass

The molar mass of the 2-PVP polymers should increase after quaternization process due to the additional ethyl bromide units attached to the chain. The quaternized polymers are assumed to be statistical co-polymers of charged and uncharged pyridine units. The monomer molar mass of the quaternized polymer is calculated as a weight average of the charged and uncharged monomers which are given in Table 4.3.

Table 4.3 Molar mass of uncharged and charged pyridine monomers in the QPVP polymers

Uncharged monomer mass / gmol ⁻¹	Charged monomer mass / g/mol ⁻¹
105	214

For a specific quaternized polymer with a degree of quaternization α , the average monomer molar mass is given by Equation 4.1 and a complete list for all the polymers used is shown in Table 4.4

$$m_0 = 214 * \alpha + 105 * (1 - \alpha)$$
 Equation 4.1

Table	4.4	Average	monomer	molar	mass	for	QPVP	polymers	for	different	degrees	of
quaterr	nizati	ion										

Degree Of quaternization	Average monomer mass / g/mol
4.3%	110
20%	126.8
35%	143.2

The expected average molar mass of the quaternized polymer is calculated as,

$$M_W = N_W * m_0$$
 Equation 4.2

where $N_{\rm w}$ is the weight degree of polymerization of the uncharged precursor 2-PVP molecule.

In some places in the discussion of light scattering results for the quaternized 2-PVP polymers, monomolar concentrations (moles of monomers per unit volume; c_p) for the polymer are used instead of the mass concentrations (C_p). Conversion between these two concentrations units also depend upon the monomer molar mass as shown below.

$$c_{\rm p} = \frac{C_{\rm p}}{m_0}$$
 Equation 4.3

 m_0 is given by Equation 4.1.

4.4 Sodium polystyrene sulfonate

A highly purified sodium salt of poly (styrene sulfonate) is bought from Sigma-Aldrich (Lot no. pss9029n) with weight average molar mass of 64,000 g/mol with very small polydispersity (P.D.I <1.2) and is used for light scattering measurements in aqueous solution. Normally the polymer contains some amount of sodium sulfate and the usual practice⁹⁵ is to dialyse an acidic aqueous solution of the polymer against high purity water to remove ionic impurities and then titrate the dialyzed solution with NaOH. This procedure is not followed for the measurements in this work as according to the manufacturer the synthesis and post synthesis of the polymer is done in a way to remove even trace amounts of sodium sulphate, also the light scattering measurements does not show any effect which could be ascribed to the presence of high ionic impurities.

4.5 Solvents

HPLC grade 1-propanol was purchased from Sigma Aldrich. The solvent was dried with molecular sieves (3Å) at least for two weeks, and then distilled under nitrogen and stored in a water free atmosphere. The conductivity measured after the purification of the solvent was in the range of 0.01-0.024 μ S/cm which is comparatively higher than 0.001-0.009 μ S/cm reported in the literature.^{96,97}The higher conductivity of the solvent may indicate small amount of ionic impurity present even after distillation which may have significant effect on the polyelectrolyte solutions especially for the low polymer concentrations used in this work.

For aqueous solution measurements, highly pure water from a Millipore filter unit (Millipore Milli-Q) is used as solvent. The details of the solvent properties are given in Table 4.5.

Dielectric	Viscosity (n)	Refractive	Conductivity	Bjerrum length
aonstant	(a)	index		(l _B) @ 20 °C /
constant		mdex	$/ \mu S \text{ cm}^{-1} (20 \text{ °C})$	nm
20.1	2.204^{98}	1.3850	0.01-0.024	2.84
80	1	1.3330	0.05-0.07	0.7

Table 4.5 Solvents

4.6 Small molar mass salt

For the light scattering measurements of the polyelectrolytes solution in 1-propanol, tetrabutylammonium bromide is used as the screening salt (Figure 4.3). Light scattering intensity of the salt solution is almost same to that of the solvent (1-propanol) itself at least to a concentration of 10^{-3} M which is the maximum salt concentration used in this thesis. Also conductivity measurement of TBAB in 1-propanol shows that the equivalent conductivity decreases linearly with the square root of the concentration (dissociation of the salt is 100% as the equivalent conductivity (Figure 4.3). This indicates the salt dissociates completely in 1-propanol and the solution behaves ideally (no association of the salt ions). Although at higher concentrations (c>10⁻³ M) the linearity is lost but this high concentration region is not important for the work in this thesis. For aqueous solutions, both TBAB and NaBr are used as the screening salt. The salts were bought from Sigma Aldrich and used without any further purification.



Figure 4.3 tetrabutylammonium bromide (TBAB) salt: chemical structure and equivalent conductivity in 1-propanol. The squares shown in the conductivity plot are taken from literature (where the measurements were done at 25° compared to 20° in this thesis)⁹⁶

4.7 The differential increment of refractive index:

All dn/dc measurements were done with a home built Michelson interferometer⁹⁹, for different solvents and salt compositions. It is to be emphasized here that all the measurements were done without establishing any Donnan equilibrium between the polymer solution and the background solvent/ salt solution, which is also a common practice followed in literature to nullify the so called Donnan effect of charged polymer solutions. It is assumed here that the effect is very small especially at high added salt concentrations, which is also supported by almost same value of dn/dc at salt free and added salt solutions for few of the samples as shown in Table 4.6.

Polymer	Solvent	Added salt	dn/dc (mL/g)
		concentration (M)	
2-PVP_850KD	1-propanol	10^{-5} (TBAB)	0.1902^{100}
2-QPVP_850KD_4.3%	1-propanol	10^{-5} (TBAB)	0.1894^{100}
2-QPVP_850KD_4.3%	1-propanol	10^{-1} (TBAB)	0.1891 ¹⁰⁰
2-QPVP_850KD_20%	1-propanol	10 ⁻⁴ (TBAB)	0.1889
2-QPVP_850KD_35%	1-propanol	10 ⁻⁵ (TBAB)	0.2024
2-QPVP_850KD_35%	water	0	0.2400
2-QPVP_850KD_35%	water	5e-3(TBAB)	0.2388
2-PVP_65_KD	1-propanol	0	0.19 [‡]
2-PVP(H) backbone	1-propanol	0	0.1901
NaPSS65K	water	0	0.198 ¹⁰¹

Table 4.6 Differential refractive index increment for all polymers used

4.8 Light scattering apparatus

The static light scattering measurements were done with high precision ($\pm 0.5^{\circ}$) SP86 goniometer (ALV) with capability to measure an angular range of 12° to 152°. A HeNe (Uniphase) Laser, with 25 mW power output is at $\lambda = 632.8$ nm, is used as the light source. The scattered light is detected with a high QE Avalanche photodiode fiber optic detection unit (ALV) mounted on the goniometer arm. Most of the measurements in this thesis are

[‡]The value is taken as average of the values for PVP_850KD backbone and PVP(H)backbone

done for an angular range of 30° to 150° in steps or 3 or 5° unless otherwise specified. The temperature was controlled with a thermostat to a value of 20 °C. The length scales (~ q⁻¹) probed with the specifications given above for the case of the two solvents are shown below.

Solvent	Angular range of	Range in q-space	Length scales
Solvent	measurement	(cm^{-1})	probed $(2\pi/q)/$ nm
1-propanol	30-150°	$7.1*10^4$ -2.7*10 ⁵	880-240
water	30-150°	$6.8*10^4$ -2.6*10 ⁵	920-245
water	20 120	0.0 10 2.0 10	20 210

Table 4.7 Length scales probed by the static light scattering measurements

The dynamic light scattering measurements were performed with ALV/CGS-8F DLS/SLS 5022F goniometer equipped with 8 APD avalanche photodiode optic detection units 17° apart from each other. A Uniphase HeNe ion laser (21 mV output power at $\lambda = 632.8$ nm wavelength) was used as the light source. The measured intensity signal is fed to a multi tau digital correlator (ALV-7004) where the autocorrelation functions are calculated and displayed in real time. The minimum sampling time for the correlation function is 100 ns. For very low scattering solutions, the equipment also provides with a possibility of measuring the correlation function in a cross correlation mode (the scattered intensity is divided in two parts and detected by two photomultipliers placed at the same scattering angle, the two signals are then cross correlated which eliminates non- random detector self correlation at correlation times < 1 µs). All measurements are performed in homodyne detection mode.

Cuvettes:

The measured solutions were contained in cylindrical quartz glass cuvette (Hellma) with 15 mm inner diameter closed at the top with an air tight Teflon cap to prevent from atmospheric humidity. Before every use, the cuvettes are thoroughly cleaned first with piranha solution (H_2SO_4/H_2O_2 75/25 vol. %) and then with distilled water. Then they are rinsed with freshly distilled acetone for at least 40 minutes. The cuvettes with solution are introduced to the light scattering instrument embedded within a glass bath filled with toluene. The cuvettes are hold in place with a cuvette holder in a way that the incoming laser light is focused at center of the cuvette. Some measurements (especially dls for solutions with very low polymer and added salt concentrations) took very long time (at most24 hrs.) to get a

better signal to noise ratio, so it is compulsory to check that the positively charged QPVP polymers are not removed from the solution with time due to electrostatic attraction with the negatively charged glass surface of the cuvette. Intensity measured at 90° scattering angle with the QPVP_850_20% polymer in salt free 1-propanol for two different polymer concentrations shows a decrease of around 3% over a period of time of about 36 Hrs (Figure 4.4).



Figure 4.4 Change in the scattering intensity with time for the QPVP_850KD_20% polymer in salt free 1-propanol. The Polymer concentrations are ~ 300 mg/L (\Box) and 14 mg/L (\blacksquare)

4.9 Preparation of the solutions for light scattering measurements

All solutions for measurements in 1-propanol are prepared and stored inside a glove box under nitrogen atmosphere. A primary stock solution is prepared for each polyion by weighing in required amount of the solid sample in pure 1-propanol and kept for at least 24 hours with continuous stirring for complete dissolution. The polymer concentrations in the primary stock solutions are 1 g/L (for QPVP_850KD) and 5 g/L (for QPVP_65KD). These primary stock solutions are used for salt free measurements at high polymer concentrations (C_p > 200 mg/L for QPVP_850KD and C_p > 500 mg/L for QPVP_65KD).

For measurements with lower polymer concentrations, secondary polymer stocks are prepared by diluting the primary stock solutions with 1-propanol to a concentration of 200 mg/L (QPVP_850KD) and 500 mg/L (QPVP_65KD). These secondary stocks are also used for the salt concentration dependent measurements where the polymer concentration is kept fixed to very low value. A series of stock solutions of tetrabutylammonium bromide is prepared with concentrations ranging from 10^{-5} - 10^{-2} M. The desired polymer and/or salt concentration within the light scattering cuvette is achieved by filtering precalculated volumes of the respective polymer stock, salt stock and 1-propanol through small pore size membrane filters (Millex LG 0.2 µm, Millipore). Concentration loss due to filtration process is found to be \leq 5% by UV absorption measurements (see appendix Table A2).

For aqueous solution measurements the same scheme for solution preparations are followed as described above for measurements in 1-propanol. The filter used in this case is Millex-GV 0.2 μ m filters from Millipore. The preparation and handling of the solutions are done in ambient conditions.

4.10 Static and dynamic light scattering data evaluation

4.10.1 SLS data evaluation

Before every measurement with the polymer solution, the instrument is calibrated by measuring scattering intensity of pure toluene. A constant average scattered intensity for toluene within $\pm 3\%$ deviation over the whole angular range is regarded to be the ideal condition to continue with the experiment. The measured raw scattering intensity I(q) of the polymer solution as a function of scattering angle is converted to the absolute Rayleigh ratio (R(q)) using Equation 4.4 to exclude the effects from the scattering geometry.

$$R(q) = \frac{I(q)_{solution} - I(q)_{solvent}}{I(q)_{Toluene}} * 1.39 * 10^{-5}$$
 Equation 4.4

where the subscripts represent the scattering intensities from the polymer solution, the solvent (1-propanol or water) and Toluene. A value of $1.39*10^{-5}$ cm⁻¹ is used as the absolute scattering intensity for toluene. The angular dependence of R(q) is then demonstrated by plotting KC/R(q) as a function of q² (Zimm representation), where C is the polymer concentration and k is the optical constant.

4.10.2 DLS data evaluation

Typical electric field correlation functions measured at low (30°) and high (90°) scattering angles are shown in Figure 4.5 for the quaternized PVP polymers in 1-propanol for 3 representative polymer and/or added salt concentrations regimes.

For high added salt solutions with low polymer concentrations (low c_p/c_s) the scattered intensity signal is correlated with itself (autocorrelation). The electric field correlation functions for such solutions looks similar to what is shown in plot A of Figure 4.5, where at very small correlation time ($\tau < 10^{-3}$ ms) a sharp decay is observed due to self correlation of the detector. This decay is observed for all scattering angles. At higher τ ($\sim 10^{-3} < \tau < \sim 10^{-1}$) another relaxation process could be seen in g₁ specially for lower scattering angles, which is most probably due to density fluctuation of the solvent ¹⁰² and/ or the diffusion of added salt which is visible only because of very low excess scattering of the polymer solution over that of the solvent.

For salt free solutions (plot B and plot C in Figure 4.5) the measurements are performed in cross correlation mode which eliminates the initial sharp decay due to the detector electronics. Decay due the solvent is still present at low scattering angles. In all the cases only the long time decay (shown within the blue vertical lines in Figure 4.5) of g_1 is evaluated to study the cooperative diffusion of polymer chains. The measured data within these limits are fitted as a combination of two exponentials as shown in Equation 4.5 using simplex algorithm¹⁰³.

$$g_1(\tau) = A_0 + A_1 * \exp(-\tau/b) + A_2 * \exp(-\tau/c)$$
 Equation 4.5

where A_1 and A_2 are the amplitudes of the two exponentials and b and c are the corresponding decay rates. A_0 is the baseline which is manually set to 0 by subtracting a small value (generally of the order of 10^{-3}) from the measured g_1 . The measured data points fit pretty well with the fitting function and the fitting quality can be seen by the residuals which are shown as red lines in Figure 4.5. Only for the salt free high polymer concentration solutions the residual line shows some systematic deviation within the fitted range especially at long correlation times (see plot C in Figure 4.5). But these deviations are very small and fluctuate between ± 0.01 which accounts for only ~ 3% of the total amplitude of g_1 and can be neglected.



Figure 4.5 Electric field correlation functions for QPVP_850KD_4% polymer in 1propanol.(**A**) $C_p = 10 \text{ mg/L}$, $c_s = 10^{-3}\text{M}$; (**B**) $C_p = 10 \text{ mg/L}$, $c_s = 0 \text{ M}$; (**C**) $C_p = 200 \text{ mg/L}$, $c_s = 0 \text{ M}$. The fitted lines are shown in green and the residuals are shown as red line

In the limit of very low $c_{p,e}/c_s$ (plot A) the solution is believed to be monomodal with respect to the relaxation processes that give rise to the fluctuating intensity signal. For such cases, only the initial decay of g_1 or the initial slope of lng_1 is relevant which is given by,

$$\frac{1}{A_1 + A_2} \left(\frac{A_1}{b} + \frac{A_2}{c} \right)$$
 Equation 4.6

This initial decay is equivalent to the first cumulant Γ_1 which gives the average apparent diffusion coefficient of a polydisperse polymer solution (see section 3.2.2; Equation 3.33 and Equation 3.34).

$$\Gamma_1 = q^2 \langle D_{app} \rangle = \frac{1}{A_1 + A_2} \left(\frac{A_1}{b} + \frac{A_2}{c} \right)$$
 Equation 4.7

or,

$$\langle D_{app.} \rangle = \frac{1}{q^2} \left\{ \frac{1}{A_1 + A_2} \left(\frac{A_1}{b} + \frac{A_2}{c} \right) \right\}$$
 Equation 4.8

In the other limit of very high $c_{p,e}/c_s$ (plot C) distinct bimodal character of g1 is seen within the fitted range. For such cases, the dynamics of the solution is described by at least two separate components having their own diffusion characteristics. The diffusion coefficients for the two components (D₁ and D₂) are obtained (assuming each component is monomodal) from the individual exponentials shown in Equation 4.5. In chapter 5 these components are described as fast (fast decaying) and slow (slow decaying) modes and the diffusion coefficients are represented as D_f and D_s respectively.

$$D_1 = D_f = \frac{1}{q^2 b}$$
 Equation 4.9

And,

$$D_2 = D_s = \frac{1}{q^2 c}$$

For solutions where both c_p and c_s is small (plot B), decay of g_1 is spread over a large range of τ although different modes are not apparent as in the case of plot C. For such

solutions, either $\langle D_{app} \rangle$ as shown in Equation 4.8 or D_1/D_2 as shown in Equation4.9 is evaluated depending upon the specific conditions which will be discussed in detail in chapter 5. For solutions which does not manifest any specific angular dependence of the measured $\langle D_{app} \rangle / D_1 / D_2$, an average value over the whole angular range is used for the determination of the hydrodynamic radius. If the diffusion coefficients differ depending upon the scattering angle, only the q=0 extrapolated values are used to calculate the corresponding hydrodynamic radii.

4.11 Characterization of all neutral and charged 2-PVP polymers in 1-propanol by light scattering measurement

4.11.1 Neutral 2-PVP polymers

Molar masses for the neutral 2-PVP polymers by G.P.C measurements (Table 4.1) may be biased with the choice of the standards. Moreover, information about other important molecular (radius of gyration, hydrodynamic radius, chain conformations etc.) and thermo dynamical (second virial co-efficient) properties of the neutral chains before quaternization are absolutely prerequisite before even starting measurements with the charged polymers. The single chain properties of these neutral polymers in 1-proapnol are obtained by static and dynamic light scattering. Because of the nitrogen atoms on the chain, the neutral polymer may obtain some residual charges in the solution or even in the solid state. Because of this reason, light scattering measurements are done in presence of a very low concentration of tetrabutylammonium bromide dissolved in the solution. Static light scattering data is analysed by conventional Zimm plot¹⁰⁴. The plots for the two polymers are shown in Figure 4.6 and all the results are summarized in Table 4.8.



Figure 4.6 Static and dynamic light scattering measurements with the neutral 2-PVP polymers in 1-propanol. (A) 2-PVP_65KD polymer; $C_p = 1.5 \text{ g/L}$ with 10^{-4} M TBAB. Only two solutions (with $C_p = 5 \text{ g/L}$ and 3 g/L) were used to measure dynamic light scattering as the resulting hydrodynamic radius does not change considerably with polymer concentration; (B) 2-PVP_850KD polymer; $C_p = 0.1-0.5 \text{ g/L}$ with 10^{-5} M TBAB

4.11.2 Quaternized 2-PVP polymers

There is a possibility that during the quaternization reaction or the following workup (like, lyophilization), the neutral polymer chain may undergo some degradation (specially for the case of high degrees of quaternization which requires longer time of reaction) giving charged polymers with lower degree of polymerization compare to that of the neutral precursor molecule. Infarct, G.P.C measurements with the quaternized polymers in a mix solvent of water and acetonitrile show some indications of chain degradation (see appendix Figure A1 and Table A1). For the sole purpose of this thesis, a quantitative knowledge of the molar mass or the degree of polymerization of all the quaternized polymers is inevitable. For this reason, it is necessary to investigate the molecular properties of the quaternized polymers with the help of light scattering experiments (Figure 4.7A,B,C). For all the measurements shown in Figure 4.7, high concentrations of added TBAB is used depending upon the polymer concentration to make $c_{p,e}/c_s <<1$ to be sure that intermolecular correlation between different polymer chains is negligible. The results of these measurements are summarized in Table 4.8 along with the corresponding values obtained for the neutral precursor molecules.



Figure 4.7A. Static and dynamic light scattering measurements with QPVP_65KD_20%_polymer in 1-propanol with 0.1 M TBAB concentration. The polymer concentrations used for static measurements are 2, 3, 4, and 5 g/L ($0.01 < c_{p,e}/c_s < 0.08$). For dynamic light scattering only the two solutions with polymer concentration of 2 and 4 g/L are used



Figure 4.7B. Static and dynamic light scattering measurements with QPVP_850KD_20%_polymer in 1-propanol with 10^{-3} M TBAB concentration. The polymer concentrations are varied from 8 mg/L to 40 mg/L ($0.01 < c_{p,e}/c_s < 0.06$)



Figure 4.7C.Static and dynamic light scattering measurements with QPVP_850KD_35%_polymer in 1-propanol with 10^{-2} M TBAB concentration. The polymer concentrations are varied from 8 mg/L to 40 mg/L ($0.02 < c_{p,e}/c_s < 0.1$)

For both high and low molar mass samples, the values M_W , R_g and R_h are higher for the charged polymer than the corresponding neutral precursor until a degree of quaternization of 20% (see Table 4.8). Only for the 35% quaternized polymer, decrease of all 3 of these values after quaternization strongly supports the polymer chain degradation in qualitative agreement with the G.P.C measurement results (see appendix Figure A1 and Table A1).

Polymer	$\mathbf{M}_{\mathbf{W}}$	$\mathbf{R_g}^{\$}$	N**	$\mathbf{R_{h}}^{\dagger\dagger}$	\mathbf{A}_2	o - ratio
Tolymer	g/mol.	nm	IW	nm	mol.L.g ⁻²	p - 1400
2-PVP_65KD	8.51*10 ⁴	9.97	810	6.3	6.41*10 ⁻⁷	1.58
QPVP_65KD-20%	9.2*10 ⁴	13.4	705	8.2	3.11*10 ⁻⁷	1.63
2-PVP_850KD	8.88*10 ⁵	46.3	8460	30.6	3.52*10 ⁻⁷	1.51
QPVP_850KD_20%	9.25 [*] 10 ⁵	77.6	7300	37.6	1.47 *10-6	2.065
QPVP_850KD_35%	$4.62*10^5$	29.8	3230	21.3	1.21*10 ⁻⁷	1.4

Table 4.8 Molecular parameters for neutral and charged poly (2-vinylpyridine) polymers in

 1-propanol as obtained by static and dynamic light scattering measurements

The values of the degree of polymerization (NW) as shown in Table 4.8 are calculated on the basis of the measured molar mass and the corresponding molar mass of a single monomer. For the charged polymers, an average molar mass of the monomers are used as described in section 4.3. An apparent difference is found between values of N_W measured with light scattering and with G.P.C in THF. The values used in the next chapter for these polymers are obtained by averaging the two values from two different measurements, which results in $N_W = 711$ for the smaller molar mass and $N_W = 8300$ for the bigger molar mass polymers. For the quaternized polymers until a degree of quaternization of 20% the same values of N_W are used as the corresponding precursors. Only for the 35%

[§] This is actually the z-average value

^{***} Average degree of polymerization

^{††} Is calculated as $R_h = (\langle 1/R_h \rangle_z)^{-1}$

quaternized high molar mass polymer the calculated value of 3230 from the light scattering measurements (Table 4.8) is used as the "true" N_W .

A ₂	osmotic second virial coefficient
C _p	polymer mass concentration
c _{p,e}	molar concentration of charged monomers.
C _s	molar salt concentration
$M_w\!\!\!\!/M_n$	weight / number average molar mass
m ₀	(average) molar mass of monomer
N_{w}	weight average degree of polymerization

4.12 Symbols and constants used in this chapter

5 Result and discussion (I): Effect of the nominal charge and molar mass of a polyelectrolyte on its degree of dissociation

One of the most important properties determining the molecular as well as the ensemble properties of solution of charged polymer is the amount of electrical charges on the chain. Two equivalent procedures are followed in literature to indicate this quantity; (1) the fraction of the total monomers bearing charges, and (2) the distance between two consecutive charges along the chain (A). In a solution, strong electrostatic interaction limits the extent to which the charges on the polymer dissociate, making the effective charge on the polyion much less than the nominal charge^{37,38,39} (actual number of ionizable units on the polymer chain). According to the condensation theory, renormalization of the polymer charges will depend upon the actual nominal charge density on the chain, and only when this value exceeds certain limit, the counterions start to bind with the polyion resulting in a lower effective charge. The effective charge also depends on the stiffness of the polymer chain and the predictions of condensation theory are actually based upon the assumption that in infinitely dilute solution single polyelectrolyte molecule has a long rod like conformation. The solvent polarity may also affect the charge condensation and hence the effective charge.

In this chapter (section 5.1–section 5.7) the discussion is aimed mainly to investigate the influence of the nominal charge and molar mass on the effective charge of polyelectrolytes with a poly(2-vinylpyridine) backbone. A detailed account of the characteristic light scattering properties of polyelectrolyte solutions will also be given in this chapter. The effect of the solvent on the effective polyion charge will be examined in the next chapter. The two terms, effective charge and effective degree of ionization/dissociation are used interchangeably in this thesis. Both of them mean the same thing that is the fraction of charged monomers on the polymer chain and is denoted by the symbol α .

5.1 Objective and polymers

The goal of the present work is to quantify the effective charge of a model polyelectrolyte to test the prediction of the charge condensation theory in a low polarity organic solvent with the help of light scattering measurement. Well characterized polymers with small polydispersity are a prerequisite for producing good quality light scattering data. Quaternized poly (2-vinyl pyridine) polymers dissolved in 1-proapanol are measured with static and dynamic light scattering. The three polymers used in the present work are shown in Table 5.1 along with the characteristic properties of the chain itself and the solvent 1-propanol.

Polymer sample	Degree of polymerization	Distance between two charges along contour length (A) / nm	Bjerrum length in 1- propanol (nm)	Manning's charge density parameter ξ_M = l_B/A
QPVP_850KD_4%	8300	5.81		~0.5
QPVP_850KD_20%	8300	1.25	2.84	~2.3
QPVP_65KD_20%	726	1.25		~2.3

 Table 5.1 Quaternized 2-PVP polymers used (QPVP)

The idea behind using these three specific polymers was 2-fold. The first being the Manning charge density parameter (ξ_M) for the first two polymers with the same degree of polymerization. The values of ξ_M are shown in Table 5.1. According to the limiting law of charge condensation³⁷, in a very dilute salt free solution in 1-propanol, the 4.3% quaternized polymer is expected to be fully ionized whereas the 20% quaternized sample should undergo charge renormalization until A=l_B which corresponds to an effective degree of quaternization of 9%.

On the other hand, the effect of molar mass on the effective charge at a constant nominal charge density can be studied by comparing the last two polymers listed in Table 5.1.

5.2 Range of polymer and salt concentrations used in the light scattering experiments

In presence of salt: A series of solutions in 1-propanol with salt was prepared and measured by light scattering for all three polymers. For any one series, the polymer concentration was kept fixed to a very low value and the ionic strength of the solution was varied by adding tetrabutyl ammonium bromide to the solution. The fixed polymer concentration was deliberately chosen to be very small but care was taken that the difference

of scattering intensities between the polymer solution and the solvent was high enough compared to the noise produced by thermal fluctuations. The lowest polymer concentration (C_p) used in this work is 10 mg/L for the bigger molar mass polymer, which at zero added salt limit gave a scattering intensity at least 1 KHz higher than that of the solvent in the angular range studied. For the smaller molar mass polymer, the lowest polymer concentration measured was 75 mg/L and the concentration of added tetrabutyl ammonium bromide (c_s) was varied between zero and 10^{-2} M.

<u>Salt free solutions:</u> Another series of solutions was prepared in pure 1-propanol with polymer concentrations varying over one or two decades in magnitude. It is to be remembered that, although no salt is added, these so called salt free solutions may contain very small residual ionic strength which is probably not removed by the distillation of 1-propanol as indicated by the measured conductivity of the solvent (see section 4.5). For such low polymer concentrations studied here, even the small residual ionic strength may have significant effect on the properties of the solution which is after all, governed by the ratio $c_{p,e}/c_s^{105}$ as will be discussed later. The final point to make here is that each concentration is prepared independently of others (i.e. not adjusting in the same cuvette) and both static and dynamic light scattering is measured with the same solution. The details of the polymer and salt concentration range measured are given below.

Polymer sample	Polymer concentration (C _p)	Added salt concentration (c_s)
	(mg/L)	(M)
	<u>Constant C_p; different c_s</u>	
QPVP_850 KD_4%	10	
	20	
	40	$0 \le c_s \le 10^{-3}$
QPVP_850 KD_20%	10	
QPVP_65 KD_20%	75	$0 \le c_s \le 10^{-2}$
	100	
	Salt free ; different C_p	
QPVP_850 KD_4%	$10 \le C_p \le 10^3$	
QPVP_850 KD_20%	$10 \le C_p \le 5*10^3$	0
QPVP_65 KD_20%	$75 \le C_p \le 5*10^3$	

Table 5.2 Polymer and salt concentration ranges measured

5.3 Static and dynamic light scattering

Molecular properties obtained from light scattering measurements of the quaternized polymers will depend both on the added salt concentration as well as the polymer concentration. Changing the salt concentration will change the extent of electrostatic screening which is manifested by the Debye screening length. Whereas, a change in the polymer concentration will change the average distances between the polymer chains in the solution. Both of these effects control the extent of intermolecular interaction. Hence, the characteristic average chain properties like weight average molar mass (M_w), z-average radius of gyration ($R_g = \langle R_g^2 \rangle_z^{0.5}$), z-average hydrodynamic radius ($R_h = (\langle 1/R_h \rangle_z)^{-1}$) etc. depend strongly on both polymer and added salt concentration. The "interaction free" condition is achieved with some finite low concentration of polymer along with relatively higher added salt in terms of equivalent concentrations. As long as the polymer concentration is not high enough that individual chains start to overlap with each other, the concentration of the added salt needed to nullify intermolecular interactions increases proportionally with the equivalent concentration of polymer. In other words, the ratio of $c_{p,e}/c_s$ determines the extent of interactions in a polyelectrolyte solution. For $c_{p,e}/c_s \ll 1$ the solution properties of polyelectrolyte is qualitatively similar to that of uncharged polymers. In the following experiments, this ratio is varied over a wide range by keeping one of the concentrations (polymer or salt) fixed and then changing the other concentration.

The main aim of this work is to systematically measure the scattering intensity of the polymer solutions as function of polymer and added salt concentration for all three polymers. From the extrapolation of scattering intensity to zero scattering angles, the molar mass is to be calculated as,

$$M_{app} = \frac{R(0)}{KC_p}$$
 Equation 5.1

where the symbols have usual meanings. Before going in to the discussion on the measured values of this quantity, it's sensible to mention the effects and typical manifestation of strong intermolecular interaction for a polyelectrolyte solution at larger scattering angles (q>0), and the method of extrapolation of the angular dependent R(q) to get the value R(0).

5.4 Angular dependence of the scattering intensity & radius of gyration ($R_g = \langle R_g^2 \rangle_z^{0.5}$)

The R_g values are obtained from the slope of the reduced inverse scattering intensity vs. q² plots. The values of R_g at different c_s and C_p ranges are shown in Figure 5.1 to Figure 5.3 for all the polymer samples measured (see appendix Table A3 to Table A5 for complete list of measurement results). For some low added salt solutions and salt free solutions, the initial slope of KC/R is found to be negative. In these cases calculation of R_g is not possible and only the absolute values of the initial slopes are shown in the same graph with R_g values. The reason for the negative slope will be discussed in detail in section 5.4.2. The subscript app (stands for apparent) indicates that all the values shown are only apparent values as they are obtained from a solution of finite polymer concentration (i.e. extrapolation to infinitely dilute solution is not done). From the distinct nature of both the structure and dynamics of the solution, different regimes with respect to polymer and salt concentrations can be identified, which will be discussed in the following sections with the particular characteristics of each regions.



Figure 5.1 Radius of gyration (scale: right axis) for the QPVP_850KD_4% polymer in 1propanol; (**A**) constant polymer concentration of (**■**) 10 mg/L, (Δ) 20 mg/L and (o) 40 mg/L with added TBAB concentration varying from 0-10⁻³ M. The solid line shows the trend of R_g for few high added salt concentrations and is extrapolated to 0 added salt concentration (**B**) salt free solutions with polymer concentration ranging from 10–10³ mg/L. Negative slopes of inverse scattering intensity with scattering angle for solutions with specific c_s and c_p are shown with red points (scale: left axis)



Figure 5.2 Radius of gyration (scale: right axis) for the QPVP_850KD_20% polymer in 1propanol; (**A**) constant polymer concentration of 10 mg/L with added TBAB concentration varying from 0-10⁻³ M. The solid line shows the trend of R_g for few high added salt concentrations and is extrapolated to 0 added salt concentration (**B**) salt free solutions with polymer concentration ranging from $10 - 5*10^3$ mg/L. Negative slopes of inverse scattering intensity with scattering angle for solutions with specific c_s and c_p are shown with red points (scale: left axis)



Figure 5.3 Radius of gyration (scale: right axis) for the QPVP_65KD_20% polymer in 1propanol; (A) constant polymer concentration of (\Box) 75 mg/L and (\blacksquare) 100 mg/L with TBAB concentration varying from 0-10⁻² M. (**B**) salt free solutions with polymer concentration ranging from 10 – 5*10³ mg/L. Negative slopes of inverse scattering intensity with scattering angle obtained for solutions with specific c_s and c_p are shown with red points (scale: left axis)

The angular dependence of the scattered light intensity measured experimentally depends on both intra (form factor) and inter (structure factor) molecular correlations and the resulting scattering intensity is given as:¹⁰⁶

$$R(q) = Nb^2 P(q)S(q)$$
 Equation 5.2

where N is the number density of scattering particles, b is the scattering length, P(q) and S(q) correspond to intra and intermolecular interferences respectively. Changing the salt concentration changes both P(q) and S(q) and hence changes the nature of the angular dependence of the scattered light intensity.

5.4.1 High added salt ($c_s \ge 10^{-4}$ M) with low polymer concentrations: conformational transition of a single chain

At the high added salt limit, intermolecular interaction is very weak and each chain is assumed to be isolated from each other (S(q) = 1 for all values of q). The scattered intensity depends mainly on the particle scattering function or form factor P(q). For a coil like conformation of the chain, in the regime where q^{-1} >>R_g,(Guinier regime) P(q) is given as \approx (1-q²R_g²/3) or, 1/P(q) \approx (1+ q²R_g²/3). So, if the inverse reduced scattered intensity is plotted as a function of q² a straight is obtained with a positive slope as shown in Figure 5.4 for the highest added salt concentration used for each polymer sample (complete set of plots can be found in appendix Figure A6– Figure A8). The slope of the straight line is determined by average size of single, isolated polymer chains.



Figure 5.4 Angular dependence of the reduced inverse scattered intensity in presence of high added salt concentration. (**A**) QPVP_850KD polymer with 4.3% (\Box) and 20% (**■**) quaternization with $C_p = 10 \text{ mg/L}$ and $c_s = 10^{-3} \text{ M}$. (**B**) QPVP_65KD_20% polymer with $C_p = 100 \text{ mg/L}$ and $c_s = 10^{-2} \text{ M}$

At this high added salt concentration limit, the molar mass and radius of gyration is obtained with linear fitting of the reduced inverse scattering intensity data with the usual Zimm formula,

$$\frac{\mathrm{KC}_{\mathrm{p}}}{\mathrm{R}(\mathrm{q})} = \frac{1}{\mathrm{M}_{\mathrm{app}}} \left(1 + \frac{1}{3} \mathrm{R}_{\mathrm{app}}^2 \mathrm{q}^2 \right)$$
 Equation 5.3

As seen in Figure 5.1 and Figure 5.2 (plot A) with the bigger molar mass polymer, R_g increases with decreasing added salt content, a trend which is previously reported both by experiments and theoretical results¹⁰⁷. An increase in the electrostatic persistence length of the polymer at low ionic strength was proposed to be the reason for this behaviour. A comparison of the 4% and 20% quaternized samples indicates a smaller Rg for the higher quaternized polymer. Even if a Manning type condensation of the counterions for the 20% polymer is considered, it should still have a higher charge than the 4.3% polymer. So the 20% sample is expected to be bigger if not equal in size compare to the 4.3% quaternized polymer. A possible explanation for this behaviour could be the attraction between the dipoles formed by the backbone charges and condensed counterions¹⁰⁸. The R_g values for the highest added salt concentration solutions were still very large (79 nm and 70 nm for the 4% and 20% quaternized polymers respectively) compared to the neutral precursor backbone (46 nm). A previous study¹⁴⁵ with similar polymers in water showed that at very high salt concentration (much higher than the highest salt concentration shown in Figure 5.1 and Figure 5.2) the R_g values of the charged polymers reduce to that of their neutral precursors. That implies that a salt concentration of 10^{-3} M was still not high enough to completely screen the expansion of the polyion chains due to repulsive intramolecular interactions. A test measurement with the 4% quaternized polymer at 0.1 M. TBAB concentration gave $R_g = 53$ nm (see appendix Table A3 and Figure A6) which is almost similar to the value obtained for the neutral precursor 2-PVP. For this thesis work though, measurements with salt concentration higher than 10⁻³ M was not important. Because the single chain 'true' molar mass of the charged polymers, which were the main interest of this work, could be determined with 10⁻³ M salt concentration and does not vary much by further increasing the salt amount (see section 5.6).

For the smaller molar mass polymer in this high added salt region, R_g values scatters too much (see Figure 5.3) because of the very small size of the polymer which introduces relatively high uncertainties in determining the slope. An average value of 13 nm with an uncertainty of ± 2 nm can be assigned to this polymer which is similar to what is obtained by a complete Zimm analysis done independently from these measurements (see section 4.11.2).

5.4.2 Low added salt ($c_s < 10^{-4}$ M): Intermolecular interaction & structure peak

When the salt concentration is lower than 10^{-4} M, different chains start to interact with each other through long range columbic forces. The bigger molar mass polymers still show a positive slope when the inverse scattering intensity is plotted against q² (plot A in Figure 5.5) but the R_g values obtained seems to be lower than the actual R_g value for a single polymer chain obtained at high added salt. The smaller molar mass polymer shows a strong negative slope. For all of the plots, linear fits are performed to get the apparent molar mass from KC_p/R (0).



Figure 5.5 Reduced inverse scattered intensity as a function of scattering angle for (A) 10 mg/L solution for the QPVP_850KD polymers with 4.3% (\Box) and 20% (**\blacksquare**) degree of quaternization and (B) QPVP_65KD_20% polymer with two different polymer concentrations of (\Box) 75 and (**\blacksquare**) 100 mg/L. Added salt concentration is 10⁻⁵ M for all the measurements shown

The angular dependence of the scattering intensity results from both P (q) and S(q). For $qR_g <<1$ the Debye¹⁰⁹ formula for P(q) is given as,

$$P(q) = 1 - \frac{1}{3}q^2 R_g^2$$
 Equation 5.4

whereas S(q) for an isotropic solution is given as⁹¹,

$$S(q) = 1 + 4\pi N \int_0^\infty [g(r) - 1] r^2 \frac{\sin qr}{qr} dr$$
 Equation 5.5

where g(r) is the radial density distribution function which gives the probability to find a molecule at r when there is already another molecule at r=0. g(r) is given as,

$$g(r) = \exp\left(-\frac{U(r)}{K_BT}\right)$$
 Equation 5.6

where U(r) is the interaction energy between two particles. Knowledge of U(r) enables determination of S(q). Assuming very weak interaction energy between molecules, an approximate analytical solution for S(q) is given by Bodycomb and Hara¹¹⁰where the final equation is given as an extended Zimm formula,

$$\frac{KC_{p}}{R(q)} = \frac{1}{M_{app}} \left[1 + q^{2} \left\{ \frac{R_{g}^{2}}{3} - \frac{\xi_{g}^{2}}{6} \left(1 - \frac{M_{app}}{M} \right) \right\} \right]$$
 Equation 5.7

where ξ_g indicates a length scale around a particle from where other particles are excluded due to strong repulsive interactions ($\xi_g^3 \sim$ exclusion volume). Equation 5.7 shows that the experimental slope of the KC/R with q^2 will give an apparent $R_{g,app}$ which is smaller than the true R_g .

$$R_{g,app} = \left\{ \frac{R_g^2}{3} - \frac{{\xi_g}^2}{6} \left(1 - \frac{M_{app}}{M} \right) \right\}^{\frac{1}{2}}$$
 Equation 5.8

With decreasing ionic strength, ξ_g increases and the experimental $R_{g,app}$ becomes even smaller than the true $R_{g.}$. This is the reason why a maximum is shown for the bigger molar mass polymers when the experimental R_g values are plotted against added salt concentration (see plot A in Figure 5.1, Figure 5.2). The negative contribution of the structure factor on the experimentally measured slope is more obvious for the smaller molar mass for which R_g is very small compared to the term containing ξ_g in Equation 5.7 and the increasing negative slope with lower salt concentrations (plot B Figure 5.3) indicates increasing intermolecular interaction or higher electrostatic exclusion zone around one polymer molecule.

For the two high molar mass polymers studied here, at very low added salt concentrations, the scattering property is characterized with appearance of a broad minimum in the inverse scattering intensity profile at a certain value of q which is represented as q_m. For the given polymer concentration used, only few low added salt concentration solutions showed this particular behaviour (see Table 5.5). Typical scattering profiles with the minimum are shown in Figure 5.6 along with those at higher salt concentration where the minimum disappears. This phenomenon is actually the continuation of what is discussed in the previous paragraph about the effect of an electrostatic exclusion zone. It is clear from Equation 5.7, that with decreasing c_s (which in turn increases the exclusion volume) there will be one point when the term containing ξ_g would eventually overcompensate the R_g term which will produce a negative slope of KC/R. For the bigger molar mass polymer though, due to its high R_g value, one can expect to find some conditions (with respect to C_p and c_s) where the two terms inside the curly brackets in Equation 5.6 would be comparable to each other and depending upon the relative contributions of the individual terms, a positive or negative slope may result. The minimum in the plot then qualitatively be understood when those two terms cancels each other. That is also the reason why no peak is observed for the small molar mass polymer because in this case the $R_{\rm g}$ is very small. At $c_{\rm s}\!<\,10^{-4}$ M the interaction term is already higher than the R_g^2 term and only a negative slope of KC/R was measured. There is no analytical expression which can fit the scattering curves with its minima. A simple polynomial fit is performed for these data sets, as shown in Figure 5.6 to get the q=0 extrapolated intensity and hence the apparent molar mass.



Figure 5.6 Reduced inverse scattering curve as function of q^2 : (A) QPVP_850KD_4% (A) and (B) QPVP_850KD_20% with added salt concentration of 0 M (**n**), 10^{-6} M (**n**), 10^{-5} M (**n**) and (B) 0 M (**n**), 10^{-6} M (**n**), $5*10^{-6}$ M (**n**), $7.5*10^{-6}$ M (**n**). The polymer concentration is fixed at 10 mg/L. The solid lines are the least square fits of the respective data sets

The minimum in the inverse scattering intensity is equivalent to an intensity maximum which is reported frequently for low salt polyelectrolyte and charged colloid solutions in small angle neutron ^{111,112}, X-ray ¹¹³ and light scattering experiments ^{114,115}. Different length scales and polymer concentrations are measured with these techniques; light scattering measurements are suitable for low polymer concentrations (large intermolecular distance-> small q) and low range of q values. The appearance of an intensity peak in dilute solutions of charged molecules is mainly the result of intermolecular correlations and is explained either via a liquid like structure formation in solution¹¹⁶ or by a correlation hole concept¹¹⁷. The difference between the two models is the nature of the radial distribution function g(r) of the scattering molecules in solution since the structure factor S(q) is the Fourier transform of g(r). The variation of g(r) and S(q) is shown¹¹⁸ in Figure 5.7 as function of the respective variables.



Figure 5.7 Radial distribution function and corresponding structure factor for the liquid like structure (left) and correlation hole (right)

For liquid like structure formation, the peak in S(q) is a result of a peak in g(r) at a certain value of r, which represents the position of the nearest neighbour from a central molecule. From the experimental peak position of S(q), the average distance between the particles can be calculated as,

$$d_{exp.} = \frac{2\pi}{q_m}$$
 Equation 5.9

where q_m is the value of q where the maximum of the scattering intensity occurs, the subscript exp. stands for experimentally obtained quantity.

Assuming a homogenous distribution of molecules in the solution, the average distance between polymer chains can be calculated from the concentration and molar mass as,

$$d_{cal.} = \left(\frac{M}{N_A C_p}\right)^{1/3}$$
 Equation 5.10

where the subscript cal. stands for calculated values. A comparison of d_{cal} and d_{exp} values is given in Table 5.3.for the measurements that showed such intensity peak.

Polymer	Polymer concentration (mg/L)	Added salt concentration (M)	q _m (cm ⁻¹)	d _{exp} (nm)	d _{cal} (nm)
QPVP_850KD_4%	10	10 ⁻⁶	$1.577*10^5$	398.4	535
	10	0	$1.695*10^5$	370.8	535
QPVP_850KD_20%	10	5*10 ⁻⁶	9.876*10 ⁴	636.2	561
	10	10-6	$1.418*10^5$	443.2	561
	10	0	$1.591*10^5$	395	561

Table 5.3 q_m and intermolecular distances for very low added salt solutions of the QPVP polymers with higher molar mass

As seen in Table 5.3, the calculated and experimentally measured values of the intermolecular distances do not correlate with each other. Also the position of the intensity peak q_m and hence the experimentally obtained intermolecular distance d_{exp} varies with added salt concentration as shown in Figure 5.8. The effect of the addition of salt to the position of the intensity peak is a matter of contradictions and debates in the literature. Some reports showed¹¹⁹ that the peak position does changes with added salt, and there are also reports which claim¹²⁰ that the salt does not have any effect in the position of the peak and it merely decreases the scattering intensity at q_m .



Figure 5.8 The Intermolecular distances obtained from the q_m values for QPVP_850KD polymer with 4.3% and 20% quaternization degree at low added salt concentrations for a fixed polymer concentration of 10 mg/L

From the framework of correlation whole concept, g(r) or S(q) do not have any peak itself (there is no preferential "ordering") and both of them behave more like a sigmoidal curve. S(q) for such systems monotonically increases with q and asymptotically reaches 1 when $q \rightarrow \infty$ (see Figure 5.7). On the other hand P(q) decreases with increasing q. The product of these two quantities gives a peak in scattering intensity at q_m where P(q)~S(q) (see Figure 5.9).



Figure 5.9 Schematic explanation of the appearance of an intensity peak as a product of P(q) and S(q). The P(q) shown here is calculated for an ideal coil polymer

A change in polymer concentration at constant salt concentration would also affect the intermolecular interaction. For salt free solution, the average distance between two chains decreases with increasing polymer concentration which results in a decrease of the reduced scattering intensity (I_0/c) and gives smaller molar masses. Also variation of the polymer concentration changes the position of the intensity peak. The variation of the normalized intensity with q^2 for the two bigger molar mass polymers is shown in Figure 5.10.


Figure 5.10 Reduced scattering intensity plotted as a function of q^2 ; (A) QPVP_850KD_4% and (B) QPVP_850KD_20% in salt free 1-propanol. The polymer concentrations for both polymers are 10 (**n**), 20 (**n**), 50 (**n**), 100 (**n**), 200 (**n**) and 500 (**n**) mg/L

The behaviour of salt free solutions for these polymers are qualitatively same for both quaternization degrees for 10 mg/L < C_p < 1g/L. There is an intensity peak for few low polymer concentrations. The position of the peak moves to higher q with increasing polymer concentration and ultimately moves out of the measured q range which is in accord with neutron scattering experiments (higher q value) at high polymer concentrations. The intermolecular distance is calculated from the peak position by using Equation 5.9 for the lowest polymer concentrations and the values are plotted against the polymer concentration (c_p) in a log-log plot (Figure 5.11). A slope of ~ 0.48 for the 4.3% quaternized polymer and ~0.46 for the 20% quaternized polymer is obtained from linear fitting of the data. A slope ~ 0.5 is predicted ¹²¹ for semi dilute polymer solutions in the salt free limit because of intersegment interaction in a polymer chain network, and is also validated by experiments¹²². For dilute polymer solutions a slope of ~ 0.33 is expected and also measured by light scattering¹²³.Only one report is found where very low polymer concentrations (similar to the concentration measured here) of NaPSS in water shows a slope of 0.5 and it is explained as an ordered structure of long rod like polymers according to the cell model¹²⁴.



Figure 5.11 Variation of the intermolecular distances obtained from the positions of the intensity maximum with polymer concentration in salt free 1-propanol for QPVP_850KD_4% (Δ) and QPVP_850KD_20%(\bullet) polymers. The slope of a linear fit of the log-log data is equal to 0.48 and 0.46 for the 4% and 20% quaternizations respectively

For the measurements in the present work neither a rod like conformation nor a polymer concentration to be high enough to already enter the semi dilute regime seem plausible. So the slope of 0.5 measured with this polymer is not understood completely. It might be due to the origin of the peak as discussed for the few low added salt concentration measurements, but it cannot be confirmed as there is still no knowledge about how a intensity peak, which is a product of two monotonic functions, should change with the polymer concentration. Because the change in C_p will change both P(q) and S(q) in a complex manner. A rough estimation of the transition concentration from dilute to semi dilute region can be worked out from the Rg value obtained by extrapolating few high added salt measurement values to $c_s=0$ (see Figure 5.1, plot A) and using,

$$C^* = \begin{pmatrix} M \\ \frac{4}{3} N_A \pi R^3 \end{pmatrix}$$
 Equation 5.11

There is no consensus as to which value (R_g or R_h) should one use for R in Equation 5.11. The values for C* for the measurements done here are calculated using both radii and shown in Table 5.4.

For the 20% quaternized sample with a calculated value of M $\sim 10^6$ g/mol, lower limit of C^{*}(using R_g as R_h) is found to be ~ 0.5 gm/L which is almost 15 times higher than the highest C_p (~30 mg/L) which shows a peak in the scattering intensity as shown in Figure 5.11. So the reason for a slope of ~ 0.5 logd vs logc_p plot could not be due to measurements in semi dilute concentration regime.

Polymer	$R_g (c_s=0) / nm$	$R_h (c_s=0) / nm$	C*(R _g) / gm/L	C*(R _h) / gm/L
QPVP_850KD_4%	105.5	55	0.3	2
QPVP_850KD_20%	96	48.7	0.5	3.6
QPVP_65KD_20%	13	8.7	18	62

Table 5.4 Calculation of overlap concentration

For polymer concentrations > 50 mg/L all three polymers show a negative slope in KC/R vs. q^2 plot. In the dynamics section later, it will be shown that all these solutions contain large aggregates (slow modes) having hydrodynamic radii higher than 100 nm. But due to the effect of very strong electrostatic interactions in salt free solutions even these large aggregates could not be seen. However, with increasing polymer concentration the size of the aggregates increases. So the magnitudes of the negative slope decreases and at very high polymer concentration the size of the aggregates are big enough to overshadow the structure factor effect and produces a positive slope in the static light scattering measurements. The behaviour of the negative slope with increasing polymer concentrations higher than 1 gm/L do not contain any physical information. Moreover, for the bigger molar mass polymer, such high polymer concentration is probably in the semi dilute region (Table 5.4) and a discussion about these high concentration solutions is beyond the scope of the present work.

Polymer	Polymer concentration (mg/L	Salt concentration (M)	Nature of the KC/R plotted against q ²
	10	10 ⁻⁶	Structure peak
OPVP 850 KD 4%	10	$6*10^{-6} \le c_s \le 8*10^{-4}$	+ve slope
QI VI _630 KD_470	$10 \le C_p \le 30$	0	Structure peak
	$50 \leq C_p \leq 10^3$	0	-ve slope
	10	10 ⁻⁶ , 5*10 ⁻⁶	Structure peak
	10	$7.5*10^{-6} \le c_s \le 10^{-3}$	+ve slope
QPVP_850KD_20%	10≤C _p ≤27	0	-Structure peak
	$50 \le C_p \le 10^3$	0	-ve slope
	$2*10^3, 5*10^3$	0	+ve slope
QPVP_65KD_20%	75	$10^{-5} \le c_s \le 10^{-2}$	~0
	100	$10^{-5} \le c_s \le 10^{-4}$	~0
	100	$2*10^{-4} \le c_s \le 10^{-2}$	~0
	$75 \le C_p < 10^3$	0	-ve slope
	$10^3 \le C_p \le 5*10^3$	0	+ve slope

 Table 5.5 Qualitative feature of the angular dependency of the scattered light at various polymer/added salt concentrations

5.5 Dynamics

Intermolecular interactions in charged polymer solutions do not only effect the time average properties like average radius of the polymers or the nature of angular dependence of average scattering intensity as discussed in the previous section. The dynamics or the time evolution of the system properties is also affected. So, it is quite expected that fundamental dynamic variables such as diffusion coefficient which is measured with dynamic light scattering will also show different transition regions in terms of polymer and/or added salt concentration (Figure 5.12 to Figure 5.14). Following the same sequence as in the discussion of the angular dependency and radius of gyration in the previous section, the characteristic behavior of the diffusion coefficient respectively the hydrodynamic radius at different added salt and polymer concentrations is discussed below.



Figure 5.12 Hydrodynamic radius for the QPVP_850KD_4% polymer in 1-propanol; (A) constant polymer concentration of (**n**) 10 mg/L, (Δ) 20 mg/L and (o) 40 mg/L with added TBAB concentration varying from 0-10⁻³ M. (**B**) salt free solutions with polymer concentration ranging from 10–10³ mg/L. The vertical line in plot A shows the onset of coupled diffusion region (see text). Red points indicate measurements where a slow diffusion mode is observed. (The hydrodynamic radii of the slow diffusion mode are not included here)



Figure 5.13 Hydrodynamic radius for the QPVP_850KDKD_20% polymer in 1-propanol; (A) constant polymer concentration of 10 mg/L with TBAB concentration varying from $0-10^{-3}$ M. (B) salt free solutions with polymer concentration ranging from $10-5*10^{3}$ mg/L. The vertical line in plot A shows the onset of coupled diffusion region (see text). Red points indicate measurements where a slow diffusion mode is observed. (The hydrodynamic radii of the slow diffusion mode are not included here)



Figure 5.14 Hydrodynamic radius for the QPVP_65KD_20% polymer in 1-propanol; (A) constant polymer concentration of (\Box) 75 mg/L and (\blacksquare) 100 mg/L with TBAB concentration varying from 0-10⁻² M. (**B**) salt free solutions with polymer concentration ranging from 75–5*10³ mg/L. The vertical line in plot A shows the onset of coupled diffusion region (see text). Red points indicate measurements where a slow diffusion mode is observed. (The hydrodynamic radii of the slow diffusion mode are not included here)

5.5.1 Dynamics of the polyions in presence of high added salt concentration ($c_s \ge 10^{-4}$ M)

In the presence of an excess amount of added salt, each polymer chain migrates independently of other chains. From the initial decay of the electric field correlation function the self diffusion coefficient for a single polymer chain is obtained. Like the inverse scattering intensity, the apparent diffusion co-efficient D_{app} also scales linearly with square of the scattering vector q (Figure 5.15). The z- average diffusion coefficient and respectively the hydrodynamic radius (R_h) are obtained by extrapolating the D_{app} values to zero scattering angle.

The hydrodynamic radii obtained for all three polymers as a function of added salt concentration are shown in Figure 5.12 to Figure 5.14 (Plot A). The behaviour is similar to the variation of R_g with c_s in the same salt concentration regime. Comparison of the behaviour of the hydrodynamic radii between small and big molar mass polymers actually supports that in this region of added salt concentration the polyions get more extended with decreasing amount of salt content. For the small molar mass polymer the determination of the radius of gyration as discussed, may contain big errors because of very small R_g , whereas hydrodynamic radius measurement is not biased with this condition. While the R_g values in this high c_s range were only scattered about an average, the R_h values show a definite increase with decreasing salt similar to the higher molar mass polymers, but of course the extent of changes in R_h for the small molar mass is not as big as in the case of the high molar mass polymer.



Figure 5.15 Angular dependence of the apparent diffusion coefficient in presence of high added salt concentration. (A) QPVP_850KD polymer with 4.3% (\Box) and 20% (\blacksquare) quaternization with $C_p = 10 \text{ mg/L}$ and $c_s = 10^{-3} \text{ M}$. (B) QPVP_65KD_20% polymer with $C_p = 100 \text{ mg/L}$ and $c_s = 10^{-2} \text{ M}$

5.5.2 Dynamics in low salt/ salt free solution

5.5.2.1 Fast mode/coupled mode / D_f/D_s

Like the radius of gyration, the hydrodynamic radius of all three polymer samples also starts decreasing with decreasing c_s when $c_s < 10^{-4}$ M. (see Figure 5.12 to Figure 5.14 (plot A).The explanation for such behaviour of the hydrodynamic radius is that for solutions where long range interactions exits, motion of any molecule may be coupled to other molecules in the neighbourhood (i.e. two oppositely charged small ions). For the present case where screening of the long range electrostatic interactions is not that strong the polyion motion in the solution is coupled with the very fast moving small ions which in effect drag the slow moving polyion chains which increases the diffusion coefficient of the polymer molecules. To denote this faster diffusion of the polymer chains the sign D_f is used, where f stands for fast. A higher diffusion coefficient results in a low value of calculated hydrodynamic radius (R_f). With decreasing ionic strength the extent of the electrostatic coupling between the polyions and small ions increases which lowers the measured hydrodynamic radius.

In salt free solutions, the polyion and small ions coupling are strongest. The nature of the variation of R_f with polymer concentration is shown in Figure 5.12 to Figure 5.14 (Plot B). Increase in the polymer concentration in salt free conditions also decreases the R_f values for the bigger molar mass polymer until a low plateau ~ 2-3 nm is reached. This behaviour indicates that with increasing polymer concentration the effective screening of electrostatic interactions between the polyion and small ions are weaker. The small molar mass polyion does not show any significant variation with increasing polymer concentration and the value of R_f for this polymer remains almost constant around the same plateau value as the bigger molar mass polyion.

Fast diffusion coefficients (D_f) measured both for added salt and salt free solutions with different polymer concentrations are shown in Figure 5.16 as a function of the ratio of salt concentration (c_s') to monomolar concentration (c_p). To put the salt free data together with the added salt measurement data, a small contribution from the solvent in terms of salt concentration is assumed which is ~ $1.5*10^{-6}$ M and the total salt concentration is calculated as a sum of added salt plus the solvent contribution ($c_s' = c_s + c_{s,0}$; where $c_{s,0}$ is the solvent contribution to the ionic strength). In section 5.7 a detailed account for such assumption of

the solvent contribution is given and the same value of $c_{s,0}$ is also used for fitting the apparent molar mass data.

According to coupled mode theory¹²⁵, the fluctuating electric field from the polyion and the small ions reversibly influence the dynamics of both. At 0 scattering angle limit with a 1-1 electrolyte which has the same counterion as the polymer, the diffusion coefficient of the polymer is given by,

$$D(q = 0) = \frac{1}{2} [D_p(1 - \Omega) + D_s(1 + \Omega)]$$
 Equation 5.12

where,

$$\Omega = \frac{D_{p}\alpha N - D_{s}\left[1 + \left(\frac{2c_{s}}{\alpha c_{p}}\right)\right]}{D_{p}\alpha N + D_{s}\left[1 + \left(\frac{2c_{s}}{\alpha c_{p}}\right)\right]}$$
Equation 5.13

where, D_p and D_s are the diffusion coefficients of the polyion and small ions at infinite dilution (no interaction). αN is the charge on polyion where N is the degree of polymerization and α is the fraction of ionized monomers. Inserting the expression for Ω , Equation 5.13 is converted to,

$$D(q = 0) = \frac{D_p D_s \left[1 + \frac{2c_s}{\alpha c_p} + \alpha N \right]}{D_p \alpha N + D_s \left[1 + \frac{2c_s}{\alpha c_p} \right]}$$
Equation 5.14

Fitting the measured data with Equation 5.14 for the big molar mass polymer (plot A, plot B Figure 5.16) is straight forward. A value of ~ $4*10^{-6}$ cm²s⁻¹ is used for the diffusion coefficient of the salt (D_s), which was experimentally measured with a 0.5 M solution of TBAB in 1-propanol (see appendix Figure A2). At very high added salt concentrations (c_s' /c_p>1) the conformational transition of the polyion chain due to screening of intramolecular interactions becomes important and the coupling mode theory will not be applicable in these conditions. So, D_p values are taken to be the minimum measured value of the diffusion coefficient at c_s/c_p ~1. The degree of polymerization N is same as the neutral polymer chain. The data points are fitted with α as the only parameter. The results of these fits are given in Table 5.6.



Figure 5.16. Fast diffusion coefficient (D_f) for all added salt and salt free measurements for (A) QPVP_850KD_4%, (B) QPVP_850KD_20% and (C) QPVP_65KD_20%. The solid lines represents fits of the data points according to coupled mode theory. c_p is the monomolar concentration of polymer and c_s' is the total salt concentration of the solution which includes added salt + a contribution from the solvent ($c_{s,0}$). (See text)

For the small molar mass polymer the fit could not be performed in a straight forward way like with the bigger molar mass. In this case, different theoretical plots are drawn for different values of α for a given set of values for D_s, D_p and N. No fit could be performed with a single unambiguous α ; as data at higher c_s'/c_p can be fitted well with a higher value of α , whereas a lower value of α seems to fit good for the data points at extreme low limits of c_s'/c_p (see plot C, Figure 5.16). A third theoretical plot is also shown (green curve) in the same graph using the α value as the average of the two extreme values.

Table 5.6 Fitting results for the fast diffusion coefficient data according to coupled mode theory

Polymer	$D_p / cm^2 s^{-1}$	$R_h(pol.) / nm$	$D_{s} / cm^{2}s^{-1}$	Ν	α
QPVP_850KD_4%	1.9*10 ⁻⁸	51	$4*10^{-6}$	8300	0.003
QPVP_850KD_20%	2*10 ⁻⁸	49	$4*10^{-6}$	8300	0.004
QPVP_65KD_20%	1.2*10 ⁻⁷	8.1	$4*10^{-6}$	711	0.003-0.01

5.5.2.2 Slow mode I: Salt free high polymer concentration

At few low added salt concentration solutions and also all salt free polymer solutions measured show the presence of a slow decaying part in the electric field autocorrelation function at longer correlation times which cannot be attributed to the single chain diffusion process (see Figure 5.17). At smaller correlation times a faster decay of the correlation function can be assigned to single polymer chains (coupled with small ions; R_f). This characteristic behaviour is found for almost all polyelectrolyte systems studied in literature¹²⁶¹²⁷¹²⁸¹²⁹ where the added salt concentration is much lower than the equivalent polymer concentration. The reason for appearance of such slow diffusing component commonly known as "slow mode" is still a matter of debate within the polyelectrolyte community and is still not well understood. But for dilute polymer solutions where different polymer chains do not overlap, a multichain aggregate or domains¹³⁰ produced by an effective interaction between same charged chains through the counterion charge fluctuation¹³¹ is believed¹³² to be the reason for the appearance of the "slow mode". Few examples of the electric field correlation functions from salt free solution of high polymer concentration of all three polymers are shown in Figure 5.17.



Figure 5.17 Normalized electric field correlation functions (g_1) for salt free solution of QPVP_850KD_4% (A), QPVP_850KD_20% (B) and QPVP_65KD_20% (C) (scattering angle is 20 degree). The inset in each plot shows the relative amplitude of the fast diffusive mode as a function of polymer concentration

The fitting for g_1 for the quaternized sample is also carried out with a bi-exponential function similar to the uncharged polymers. But for the cases where the existence of slow mode is seen, each exponential refers to individual components in the solution and the contribution of each of them to the scattered intensity is obtained from the amplitudes of the corresponding decays (see DLS data evaluation in section 4.10.2). Averaging of the two diffusion coefficient as done for the neutral polymer or for the charged polymers at high added salt concentration is physically not meaningful for these measurements and the dynamics of this system is characterized by at least two diffusion modes – fast(D_f, R_f) and slow (D_s,R_s) and respective amplitudes A_f and A_s. The relative values of the fast mode amplitude as function of polymer concentration are shown in the inset of each graph in Figure 5.17.

. Few points are to be noted from these graphs,

1) Radius of the slow mode increases with polymer concentration, which should increase the contribution slow mode to the scattering intensity. Certainly this is not the case here as it is seen from plot A and plot B in figure 5.17. The graphs clearly show that the fast mode contribution increases with polymer concentration.

2) For the same molar mass, an increasing degree of quaternization decreases the slow mode amplitude (compare plot A with plot B in Figure 5.17), which is probably because a higher nominal charge on the chain makes it more difficult to form aggregate with other chains due to electrostatic repulsion.

3) At least when the polymer concentration is very low, the slow mode amplitude does not depend upon the molar mass of the polymer when the nominal charge density is same (compare plot B and plot C in Figure 5.17). A similar comparison at higher polymer concentration is not possible due to too much scattering of the data for the smaller molar mass polymer.

4) The big molar mass polymer showed a systematic increase of the slow mode amplitude until polymer concentration ≤ 1 g/L. Two higher polymer concentrations of 2 g/L and 5 g/L with 20% quaternization falls out of this trend, which is probably because this two solutions are too concentrated (compare with the overlap concentration in Table 5.4) and probably contains big aggregates in the solution (these two solutions also gave a positive slope in static light scattering measurement).

5.5.2.3 Slow mode II: Disappearance with increasing added salt

As is seen, for example in Figure 5.12, fast diffusion mode for a very low polymer concentration of 10 mg/L starts to appear when $c_s < \sim 10^{-4}$ M and it is "visible" all the way to salt free solutions of high polymer concentrations and the slow mode appears somewhere in between when both C_p and c_s have very small values. For high polymer concentrations limit the two diffusional modes are well separated and the slow mode can be seen clearly in the electric field correlation function with "naked eye". But for the salt concentration dependent measurements with very low polymer concentration of 10 mg/L, detecting the slow mode, is by comparing the electric field correlation function functions functions of the quaternized polymers at few of the low ionic strength solutions to that of the unquaternized precursor polymer, for which no slow mode diffusion exits. In Figure 5.18 some examples are shown how the presence of the slow mode was detremined at this vanishing polymer concentration limits. What is done here is that the electric field correlation functions measured at very small scattering angle for the uncharged 2-PVP polymer along with with the two charged polymers are overlapped and the difference between them is noted at different correlation time.

As seen in Figure 5.18, the slow mode disappears when the salt concentration is increased keeping a fix polymer concentration. For the 10 mg/L polymer concentration measured here, in salt free solution (plot A) the correlation functions of the quaternized polymers are much broader than the neutral polymer. In fact the former starts decaying faster at small times and crosses the later and goes to the baseline at longer times. There is no reason that the quaternization process should impart more polydispersity to the charged polymers compared to the neutral ones whe the chains remain intact. The only possibility is the contribution of a slow diffusion mode in the solution with the charged polymers.



Figure 5.18 The electric field autocorrelation functions for the uncharged PVP_850KD (**•**), QPVP_850KD_4% (**•**) and QPVP_850KD_20% (**•**). Concentration for the uncharged polymer is 100 mg/L and concentration for the quaternized polymers is 10 mg/L with added TBAB concentrations of 0 M (A), 10^{-6} M (B) and $5*10^{-6}$ M (C) and 10^{-5} M (D)

When c_s is increased to 10^{-5} M (Figure 5.18 plot D) the "stretch" of the correlation functions for the charged polymers are almost similar to that of the uncharged polymer, and the slow mode can be assumed to have disappeared in the QPVP solutions at added salt concentration of 10^{-5} M. Given the experimental uncertainties, it's very difficult to judge the slow mode for the salt concentrations in between this limits (Figure 5.18, plot B and C) especially for the 20% quaternized polymer which has lower amplitude of the slow mode. In the present work, the lowest limit of the added salt concentration where only the initial decay of the correlation function is used (D_{avg} .) are 5*10⁻⁶ M for the 4.3% quaternized chain and 10⁻⁶ M for the 20% quaternized chain (see Table 5.7 for detailed description for the values or limits for both of polymer and salt concentrations where the slow mode contribution is taken into account for data evaluation).

The disappearance of the slow mode with increasing amount of salt is also found with the smaller molar mass polymer when the polymer concentration was kept fixed and the salt concentration is varied. Two series were done with polymer concentrations of 100 mg/L and 75 mg/L. With increasing polymer concentration, the amount of salt needed to make the slow mode disappear also increases. For, measurements with a 100 mg/L polymer solution, the slow mode could still be seen when added salt concentration is as high as ~ $8*10^{-5}$ M. whereas measurements with the 75 mg/L polymer, even a 10^{-5} M salt concentration was high enough to remove the slow mode. Which is surprising because if the appearance of the slow mode solely depends on the ratio c_p/c_s , then a 25% decrease (100 mg/L -75 mg/L) of both should not change the solution properties with respect to the presence of slow mode; that is if a $8*10^{-5}$ M salt solution with 100 mg/L polymer (cs/c_p=0.1) shows a slow mode, then for the 75 mg/L polymer solution the minimum amount of salt needed to remove the slow mode should be ~ $6*10^{-5}$ M.(c_s/c_p = 0.1) and lower concentration of salts should show a slow mode. From Figure 5.19 it is clear that the two concentrations of the charged polymers used do not follow simple c_s/c_p dependent property as long as the presence of slow mode is concerned, the absolute value of c_p gives different scattering properties even if c_s/c_p is same.



Figure 5.19 Normalized electric field correlation functions for QPVP_65KD_20% polymer in 1-propanol at polymer concentration of (**A**) 75 mg/L and (**B**) 100 mg/L compared with the neutral precursor polymer 2-PVP_65KD. Added salt concentrations are (A) (\blacksquare) $c_s = 10^{-5}$ M, (\square) $5*10^{-5}$ M, (\square) $2.5*10^{-4}$ M, (\blacksquare) $5*10^{-4}$ M, and (B) (\blacksquare) $c_s = 10^{-5}$ M, (\square) $7.5*10^{-5}$ M, (\square) $2.5*10^{-4}$ M, (\blacksquare) $5*10^{-4}$ M, and (B) (\blacksquare) $c_s = 10^{-5}$ M, (\square) $7.5*10^{-5}$ M, (\square) $2.5*10^{-4}$ M, (\blacksquare) $5*10^{-4}$ M, (\blacksquare) 5*1

These measurements also refutes the possibility of the origin of the slow mode because of the presence of some "foreign particles" introduced to the solid polymer sample which are not filtered out of the solution when using a bigger size filter. It was proposed¹³³ that when the scattering intensity from the polymer solution is very high, these foreign particles remains nascent in the solution and it is only "seen" in the electric field correlation function when the intensity of the polymer solutions drops. If that would be true then one would expect to see this so called nascent particle scattering at lower polymer concentrations but as discussed above, the slow mode appears when the polymer concentration is increased from 75 mg/L to 100 mg/L. Also using a filter of smaller pore sizes did not remove or change the amplitude of the slow mode (see appendix, Figure A3). These observations again support the source of the slow mode as some polymer aggregates which are formed only when dissolved in a solvent.

Due to more measured data points, the effect of added salt on slow mode could be studied with the smaller molar mass polymer when the polymer concentration is kept fixed at 100 mg/L and added salt concentration is changed. Figure 5.20 shows that the amplitude of the fast mode apparently increases with increasing added salt concentration because the slow mode gradually "dissolves" when more salt is added to the solution which indicates the reason for formation of the slow mode may be driven by electrostatic interactions, which are screened with increasing salt concentrations.



Figure 5.20 Relative amplitudes of the fast mode for QPVP_65KD_20% polymer as function of added salt concentration. Polymer concentration is fixed at 100 mg/L

The appearance (or disappearance) of slow diffusion mode depends on the ratio of the equivalent concentration of charged monomer and added salt (λ^*). In general, at very high values of λ^* , a polyelectrolyte solution shows only one diffusional mode characteristics to single polymer chains. The value of λ^* for which the first appearance of the slow mode is observed varies between 1 and 5^{106} . To show the nature of the transition from bi-modal to mono-modal system with the polymers measured here, all the diffusion coefficient values are plotted in Figure 5.21 as a function of the ratio of polymer to salt concentration. The polymer concentrations are expressed as the concentration of charged monomeric units (c_{n.e}). The effective degree of ionization (α) rather than the actual degree of quaternization is used to calculate $c_{p,e}$. The fitted values of α obtained from the fast diffusion mode are used as the effective degree of ionization (Table 5.6). The salt concentration cs' includes both the added salt and a constant amount of $1.5*10^{-6}$ M as the contribution from the solvent (c_{s.0}). As seen in Figure 5.21, the first appearance of the slow mode for all three polymers falls in the region where $0.1 < \lambda^* < 1$. This value of λ^* is seemingly lower compared to the literature values. A possible reason for this discrepancy may be due to the difference in calculating the value of the equivalent concentration for the polymer. Use of the actual degree of quaternization (assuming full dissociation) will shift the transition λ^* to higher values. The value of D_s at its appearance is almost same for all three polymers irrespective of their molar mass or nominal charge. Only at higher λ^* , each polymers behave differently in terms of the magnitude of D_s. The D_s values for the polymers with the bigger molar mass decreases sharply with increasing λ^* , whereas the small molar mass polymer shows almost no variation with the change in λ^* . Another interesting feature observed with the small molar mass polymer is the difference between the measurements using two different polymer concentrations as already discussed in before. For lower polymer concentration (shown as empty squares in plot C of Figure 5.21) no slow diffusion mode was observed within the aforementioned range of λ^* .



Figure 5.21 Fast(**n**) and slow (**n**) diffusion coefficients for (**A**)QPVP_850KD_4.3%, (**B**) QPVP_850KD_20% and (**C**)QPVP_65KD_20% in 1-propanol. $c_{p,e}$ is the molar concentration of the charged monomers and c_s' is the added salt plus $1.5*10^{-6}$ M salt from the solvent. The data points include both the added salt and salt free measurements for all three polymers

5.5.2.4 Effect of structure factor on the fast and slow diffusion mode

Both fast and slow diffusion co-efficient depends on the scattering angle as shown Figure 5.22 for the 4.3% quaternized polymer in salt free solution. The slow diffusion coefficient increases almost linearly with q^2 resembling the diffusion of a polydisperse big molecular object (which is most probably some aggregate). But the fast diffusion coefficient resembles to the q^2 dependence of the inverse scattering intensity measured in static light scattering and gives a minimum around the same q value(compare with Figure 5.6, plot A).



Figure 5.22 Fast (**■**) and slow (**•**) diffusion coefficient as a function of scattering angle for QPVP_850KD_4% polymer in pure 1-propanol for a polymer concentration of 10 mg/L

This behaviour of the fast diffusion mode as a function of the scattering angle is well known in literature and explained on the basis of Brownian movement of an ensemble of interacting particles where the diffusion coefficient is related to the static structure factor as,^{134,135}

$$D = D_0 \left(\frac{H(q)}{P(q)S(q)} \right)$$
 Equation 5.15

Where, D_0 is the interaction free diffusion coefficient and the Function H(q) reflects hydrodynamic interactions. If H(q) is neglected (fully drained chain), a maximum of the product P(q)S(q) at certain value of q gives a minimum in D. The appearance of the slow mode increases the scattering intensity and results in a higher calculated molar mass. To get the molar mass of only the individual polymer chains necessary correction has to be made in the measured scattered intensity, which will be discussed later in great detail when the measured molar mass will be compared with the Prins- Hermans theory (section 5.7.1). For now, only the general dynamic behaviour of all three polymers as measured by DLS at low c_s is summarized in the table below.

Polymer	Polymer concentration (mg/L	Salt concentration (M)	DLS measurement
	$10 \le C_p \le 10^3$	0	Fast + slow mode
QPVP_850 KD_4%	10	10 ⁻⁶	Fast + slow mode
	10	$6*10^{-6} \le c_s \le 10^{-4}$	Fast mode
QPVP_850KD_20%	$10 \le C_p \le 5*10^3$	0	Fast + slow mode
	$75 \le C_p < 5*10^3$	0	Fast + slow mode
QPVP_65KD_20%	100	$10^{-5} \le c_s \le 8*10^{-5}$	Fast + slow mode
	100	$8*10^{-5} < c_s \le 2.5*10^{-4}$	Fast mode

 Table 5.7 Appearance of fast and/or slow diffusion mode at various polymer and salt concentration measured

5.6 Molar mass

The molar mass values are obtained by extrapolating the KC/R vs. q^2 plots to 0 q using linear or polynomial fits depending upon the nature or extent of intermolecular interactions. As seen in Figure 5.23 to Figure 5.25, at high added salt concentration limit, the molar mass for all 3 polymers are almost similar to that of the calculated molar mass (shown as black horizontal line in the plot) from the precursor neutral polymer. Reducing the salt concentrations produces big difference between the expected and measured molar mass. The deviation of the measured molar mass from its expected value is correlated with effective charge on the polymer chains. The fluctuation theory of light scattering from multicomponent systems can be useful to obtain this effective charge from the measured molar mass.



Figure 5.23 Molar mass for QPVP_850KD_4% polymer in 1-propanol; (A) constant polymer concentration (\blacksquare) 10 mg/L, (\triangle) 20 mg/L and (\circ) 40 mg/L with added TBAB concentration varying from 0-10⁻³ M. (B) salt free solutions with polymer concentration ranging from 10–10³ mg/L. Red points indicate values that contains contribution from slow mode. The straight line in plot A shows the expected molar mass



Figure 5.24 Molar mass for QPVP_850KD_20% polymer in 1-propanol; (A) constant polymer concentration of 10 mg/L with added TBAB concentration varying from $0-10^{-3}$ M. (B) salt free solutions with polymer concentration ranging from $10 -5*10^{3}$ mg/L. Red points indicate values that contains contribution from slow mode. The straight line in plot A shows the expected molar mass



Figure 5.25 Molar mass for QPVP_65KD_20% polymer in 1-propanol; (A) constant polymer concentration of 75 (\Box) and 100 (**•**) mg/L with added TBAB concentration varying from 0-10⁻² M. (**B**) salt free solutions with polymer concentration ranging from 10–5*10³ mg/L. Red points indicate values that contains contribution from slow mode. The straight line in plot A shows the expected molar mass

5.7 Effective degree of ionization (α) from the molar mass measured by static light scattering

According to the Prins-Hermans theory, the apparent molar mass measured in salt free conditions should be independent of polymer concentration given the degree of ionization (α) of the polymer is constant (see Equation 3.9). This is surely not the case at least for the higher molar mass polymers as seen for example in Figure 5.23 and Figure 5.24 where the molar mass asymptotically reaches a constant value at high polymer concentration. The second problem with the experiments is the appearance of slow mode in all salt free and also few low added salt concentration measurements irrespective of the polymers used. The slow mode would invariably increase the scattering intensity and results in a higher calculated molar mass. What is interesting for this work is the molar mass (apparent or true) of single polymer chains and not the slow mode which is probably some multichain aggregates or domains of polymers with hydrodynamic radius at least 3 times larger than single polymer chain at the lowest polymer concentration of 10 mg/L. The necessary correction for the slow mode is discussed in the next section where the 4% and 20% quaternized 2-PVP with big molar mass are used as examples.

5.7.1 Slow mode correction

Polyelectrolyte solutions with slow modes can be treated as a multimodal system for which the total scattered intensity is a result of superposition of contributions from each individual component of the solution. The respective contributions can be quantified from the amplitudes of the relaxation processes (only diffusive) of each mode in the electric field correlation function which is given as:

$$g_1(q, t) = \sum_i A_i(q, 0) \exp(-t/\tau)$$
 Equation 5.16

where, $A_i(q, 0)$ is the amplitude of the i'th component and is given as,

$$A_i(q, 0) = KC_iM_iP_i(q)$$
 Equation 5.17

where, K is the optical contrast C_i , M_i and P_i (q) are the mass concentration, molar mass and form factor of the i'th component. The A_i (q, 0) values are obtained from the respective amplitudes (A_1 , A_2) from the bi-exponential fit of the correlation function .So,

$$A_1(q) = A_f(q) = KC_1 M_1 P_1(q)$$

Equation 5.18

And,

$$A_2(q) = A_s(q) = KC_2M_2P_2(q)$$

where the subscript 1 suggest non aggregated polymer chains (fast mode) and subscript 2 is for the polymer aggregates (slow mode). So, the relative contribution to the scattering intensity from the non-aggregated polymer chains is given by,

$$A_{f,rel.}(q) = \frac{A_f(q)}{A_f(q) + A_s(q)} = \frac{C_1 M_1 P_1(q)}{C_1 M_1 P_1(q) + C_2 M_2 P_2(q)}$$
 Equation 5.19

. $A_{f,rel}(q)$ depends on the scattering angle because of the form factors. The angular dependency is shown in Figure 5.26 for a high and low polymer concentrations of the bigger molar mass polymer in salt free solution. $q^2 = 0$ extrapolated values give the scatterer size independent values $A_{f,rel}$.

The absolute scattered intensity by the non-aggregated polymer is obtained from the total scattered intensity and $A_{f,rel}$ as,

$$I_{polymer} = I_{total} * A_{f,rel.}$$
 Equation 5.20

And accordingly the molar masses have to be corrected using:

$$M_{app,corr.} = M_{app} * A_{f,rel.}$$
 Equation 5.21



Figure 5.26 Angular dependence of relative amplitude of fast (**n**) and slow (**•**) mode for (**A**) QPVP_850KD_4% and (**B**) QPVP_850KD_20% in salt free 1-propanol. The polymer concentrations are shown in the respective graphs

In correcting the scattering intensity due to the presence of slow mode, the change in the concentration of the singly dispersed polymer chains is neglected. Some polymer chains will be 'removed' from dispersed state to form the aggregates (slow mode). So, the concentration of the individual chains in the solution will be smaller. It can be shown that neglecting this effect of the concentration change may give a maximum error of only $\sim 13\%$ (see appendix page 125). To compare with the Prins-Hermans equation, the apparent degrees

of polymerization are calculated from the apparent molar masses and the average monomer molar mass for respective polymers (see section 4.11). In Figure 5.27 the inverse apparent degree of polymerization for the 20% quaternizaed polymer of the bigger molar mass is plotted as a function of the polymer concentration in salt free solution. The theoretical plots for the Prins-Hermans equation are compared with the measured data for different values of α and an assumed ionic strength of $c_{s,0}$ from the solvent. The best fit is obtained for α =0.0085 and a solvent ionic strength of $1.5*10^{-6}$ M which is reasonable given the finite conductivity of the solvent measured (see section 4.5). Though very low, the solvent ionic strength has a substantial effect on the scattering properties of charged polymers, especially when polymer concentration is also very low.



Figure 5.27 Comparison of the experimentally determined $1/N_{app}$ values with the Prins-Hermans equation; Where (\Box) shows the measured values for QPVP_850 KD_20% polymer in 1-propanol without added salt and (•) shows slow mode corrected values (explained in the text). The solid lines are drawn using Prins-Hermans equation with $\alpha = 0.0085$ and different background or solvent ionic strengths of $c_{s0} = 6 \ 10^{-7}$ M (black), $c_{s0} = 1.5 \ 10^{-6}$ M (red) and $c_{s0} = 6 \ 10^{-6}$ M (blue). The dotted and dashed curves show the theoretical curves for the same set of c_{s0} but different degrees of ionization $\alpha = 0.012$ (dotted curves) and $\alpha = 0.005$ (dashed curves)

With the knowledge of a definite solvent contribution to the ionic strength, both the added salt and salt free measurements can be plotted in the same graph as shown in Figure 5.28. The measurement results for all three polymers are collapsed in the plot by evaluating the $(1/N_{app} - 1/N_{true})$ values for each data point. Only slow mode corrected values are shown for the measurements that showed a slow mode in D.L.S (which include all salt free measurements and few low added salt measurements). To fit the experimental data, the Prins- Hermans equation is rearranged as,

$$\frac{1}{N_{app}} - \frac{1}{N_{true}} = \frac{\alpha}{1 + \frac{2c_s}{\alpha c_p}}$$
 Equation 5.22

The solid lines in Figure 5.28 are obtained from the above equation by taking different values for the parameter α to match the experimental data. For Both quaternization degrees of the bigger molar mass polymer, satisfactory fits of the theoretical curves with the measured values can be achieved with single values of α . The highest polymer concentrations measured (2 g/L and 5 g/L) with the 20% quaternized polymer in salt free conditions are shown as red triangles in the plot. Certainly these two values fall outside the trend followed by the rest of the data points. The reason for extremely high values for these two measurements can be traced back to the very high polymer concentration of the polymer above the overlap concentration. These two data points are not included in the fit for this polymer.

For the small molar mass polymer, two theoretical plots are shown that individually fits the low and high c_s'/c_p data points. That gives two α values for this polymer. The similar behaviour was also found when the fast diffusion coefficients for this polymer were fitted with the coupled mode theory.

Two more theoretical plots with $\alpha = 0.04$ (which corresponds to complete dissociation of the 4.3% quaternized polymer) and $\alpha = 0.09$ (which is the expected value for the 20% quaternized polymers according to Manning's theory) are also shown in the graph for comparison of between the trends of measured data points and that of the prediction by Manning's theory.



Figure 5.28 Comparison of the experimentally determined $1/N_{app}$ values with the Prins-Hermans equation: (**■**) QPVP_850 KD_4%, (**▲**) QPVP_850 KD_20%, and (**●**) QPVP_65 KD_20%. The measured values include added salt and salt free measurements in 1-propanol for all three polymers. Only the slow mode corrected values are shown. The lines are drawn using Prins-Hermans equation with $\alpha = 0.0055(-)$, 0.0065(-), 0.0085(-), 0.0014, 0.04(-) and 0.09(-). $c_{s0} = 1.5 \ 10^{-6}$ M is used to calculate the total salt concentration c_s' .

The values of α for the closest fits for the data points for all three polymers are shown in Table 5.8. The α values obtained from these fits are systematically higher than that given from the coupled diffusion coefficients as shown in table 5.6. although the trend of the α values are quite similar for different polymers from the two fits and are in the same order of magnitudes. The quantitative differences of α values from the two methods can be attributed to many approximations involved in the derivation of the coupled mode diffusion equation (see appendix).

Table.5.8. α values obtained apparent molar masses using Prins-Hermans equation

polymer	α
QPVP_850KD_4%	0.0055
QPVP_850KD_20%	0.0085
QPVP_65KD_20%	0.0065-0.014

5.8 Symbols and constants used in this chapter

α	degree of ionization (of charged monomers / total # of monomers)
ξΜ	Manning charge density parameter
ξ _g	radius of the exclusion zone around a charged polymer
А	distance between two charges along the polymer contour
$l_{\rm B}$	Bjerrum length.
Ср	mass concentration of polymer
c _p	monomolar concentration of polymer
c _{p,e}	equivalent concentration of charged monomers
C _s	molar concentration of added salt (if any)
$c_{s,0}$	residual salt concentration in pure solvents
D	average diffusion coefficient of polymers
\mathbf{D}_{f}	coefficient for fast / coupled diffusion
\mathbf{D}_{f}	coefficient for slow diffusion
g(r)	radial distribution function
N _A	Avogadro's number
N_{app}/N_{true}	apparent/ true degree of polymerization
$M_{app}\!/\;M_{true}$	(weight average) apparent/ true molar mass
R(0)	excess Rayleigh ratio at 0 scattering angle
R (q)	excess Rayleigh ratio at scattering angle > 0
R _g	(z-averaged) radius of gyration
R _h	(z-averaged) hydrodynamic radius

6 Result and discussion (II): Effect of the solvent quality on the degree of dissociation of a polyelectrolyte

In the previous chapter, the light scattering properties of a polyion in solution is discussed as a function of its nominal charge density and molar mass. It is shown that even in a good solvent for the uncharged polymeric backbone the effective degree of ionization (α) of a polyion chain is very small even after taking account for the counterion condensation phenomenon. It is probably the low polarity of the solvent (1-propanol) which is responsible for such unusually small effective charges. It is then necessary to investigate the effect of the solvent by measuring the light scattering properties on the same polymeric molecule when it is dissolved in a solvent with high polarity like water.

In contrast to 1-propanol, water is a poor solvent for the polymers having a backbone comprised of hydrophobic poly(2-vinylpyridine). It was shown only recently both by theory ^{136,137} and simulation ¹³⁸ that the conformation of the polymers in a poor solvent depends on very short ranged solvent mediated interactions and when the charge on the polymer is not very high the chain contour may consist of charged strings interconnected by collapsed globules (pearls). This phenomenological picture of Pearl-Necklace (PN) like conformation of hydrophobic polyelectrolytes initiated a number of experimental studies although only indirect evidence of such pearl structures is found¹³⁹. Due to such collapsed hydrophobic patches along the counter length of the polymer chain, the theory predicts that in aqueous solutions the effective charge on such hydrophobic polyelectrolyte should be smaller than polymers with a hydrophilic backbone. The reason for that is very low local dielectric constant in the collapsed pearls which is also found by light scattering experiments.¹⁴⁰

Osmotic coefficient measurements in aqueous solution by Essafi et al.¹⁴¹ showed a distinct difference between polymers with hydrophilic and hydrophobic backbone with respect to the effective charge. They found out that for a nominal charge fraction range between 0.4-1 the polymer with the hydrophobic backbone (PSS) has less effective charge when compared to the other polymer (AMAMPS). They argued that their results actually support the pearl necklace model for the hydrophobic polymers. So, their study mainly focused on the effect of the solvent quality by using the same solvent (water) and changing the hydrophobicity of the backbone of the polymer.

An investigation, where different solvents are used with a same polymeric backbone is done in this thesis which may provide complementary information about the effect of the solvent quality on the effective charge on the backbone. The polymeric backbone used here is same as the big molar mass 2-PVP polymer discussed in section 5.1. A high charge density (35%) 2-QPVP is prepared for the present work which is soluble both in water and 1-propanol. The characteristic properties of the charged polymer in the two solvents are given in below.

Solvent	Bjerrum length (l _B) (nm)	Degree of polymerisation ^{‡‡}	Distance between two charges along the polymer contour length (A) / nm	Manning's charge density parameter $\xi_M = l_B/A$
1-propanol	2.84	3230	0.71	~4
water	0.7			~1

Table 6.1 Polymer and solvents used for the solvent quality dependent measurements

When the quaternized 2-PVP polymer is dissolved in water, two mutually opposing processes ensue. From electrostatic ground, the charged groups on the polymer will tend to dissociate more than in 1-propanol simply because of high dielectric constant of water. On the other hand, strong repulsive hydrophobic interactions of the polymer backbone with water (bad solvent for the 2-PVP backbone) will favor a more compact conformation of the polymer chain and hence a lower charge density. The competition between the electrostatic and hydrophobic interaction has been studied before by Monte Carlo simulation¹⁴². It shows that at low amount of charges the hydrophobic interactions dominates and the chain remains in a collapsed conformation, but with increasing charge the electrostatic interactions become too strong which expands the polyion chain.

^{‡‡} The neutral polymer with a degree of polymerization of ~ 8300 is probably degraded during quaternization process. The molar mass and degree of polymerization used for the quaternized polymer is obtained by SLS in presence of high added salt concentration (see section 4.11.2).

6.1 Light scattering measurements of the 35% quaternized polymer

6.1.1 Static light scattering – molar mass and radius of gyration

Different characteristic features for both static and dynamic light scattering measurements for the quaternized 2-PVP polymers at different added salt or polymer concentrations are already discussed in detail in the previous chapter (section 5.4 and section 5.5). Also examples of the extrapolation methods of the inverse scattered intensity to zero scattering angle for solutions with different c_s/c_p ratio has been shown. The salt and polymer concentration dependent measurements are similar to what have been done with the lower quaternized polymers of the same backbone with a molar mass of 850 KD. Qualitatively the behavior of the 35% quaternized polymer, both in 1-propanol and water, is same as that of the other lower quaternized polymers with respect to static structure, slow mode etc. which is summarized in Table 6.3 and Table 6.4 at the end of this section. Few apparent differences are found when the results are compared between measurements in two different solvents which will be discussed in short before actually trying to fit the measurement result with the theory in section 6.2.

In Figure 6.1 the apparent molar masses of the quaternized polymer are plotted as a function of salt concentration both in 1-propanol and water. The apparent molar mass in 1-propanol gives the actual value at high added salt concentration, but in water the measured value is much lower even at an added salt concentration of 0.005 M which has been found to be high enough to nullify all intermolecular interactions and give the true molar mass. The discrepancy due to use of a non equilibrium value of dn/dc can be ruled out because (i) the value of dn/dc does not change when measured in a salt free solution or in a high added TBAB concentration solution (see Table 4.6) and (ii) use of a different salt (NaBr) in water gives almost the same M_{app} values as with TBAB.


Figure 6.1 Apparent molar mass as a function of added salt concentration for QPVP_850KD_35% polymer in (**n**) 1-propanol+TBAB, (Δ) water + TBAB and (o) water + NaBr solution. The polymer concentration is ~ 10 mg/L for measurements in both solvents. The solid horizontal line shows the expected molar mass

Association or aggregation of the polyelectrolyte in 1-propanol is also not a possible reason for the difference in molar masses in the two solvents. As seen in Figure 6.2 and Figure 6.3, both the radius of gyration and the hydrodynamic radius of the polymer is bigger in aqueous solution compared to in 1-propanol in the whole salt concentration range studied. The only possible explanation is that the intermolecular interactions are much stronger in aqueous solution and a 0.005 M salt concentration is not high enough to screen the intermolecular interactions completely to produce the actual molecular weight. A higher added salt concentration of both TBAB and NaBr in water resulted in formation of big aggregates probably due to "salting out" effect.



Figure 6.2 Apparent radius of gyration of QPVP_850KD_35% polymer in (A) 1-propanol and (B) water. Polymer concentration is fixed at ~ 10 mg/L and the ionic strength of the solution is varied by adding (A) TBAB and (B) TBAB (\blacksquare) and NaBr (\Box)

6.1.2 Dynamic light scattering

Fast mode and the effective charge

In dynamic light scattering measurements, the added salt concentration where the coupling of the polyion and small ion takes place is different for different solvents. The onset of this coupling can be seen in as the position of maximum measured hydrodynamic radius. In aqueous solution this peak position is shifted almost a decade of higher added salt concentration compared to in 1-propanol, which is already an indication of higher effective charge on the polyion and hence an increased requirement of added salt to suppress this coupling effect.



Figure 6.3 Apparent hydrodynamic radius of QPVP_850KD_35% polymer in (A) 1-propanol and (B) water. Polymer concentration is fixed at ~ 10 mg/L and the ionic strength of the solution is varied by adding (A) TBAB and (B) TBAB (\blacksquare) and NaBr (\Box)

The coupled mode diffusion equation (Equation 5.14) is used to describe the observed variation of the fast diffusion coefficient for all added salt and salt free measurements as shown in Figure 5.32. Total salt concentration (cs') is calculated assuming a contribution of $1.5*10^{-6}$ M and $2*10^{-5}$ M (this value is in the same order that has been also used before to describe the osmotic pressure results in aqueous solution¹⁴³) contribution from the solvents 1-propanol and water respectively. The fitting procedure is already explained in section 5.5.2.1. For the diffusion coefficient of salt (D_s), in water, a value of $8*10^{-6}$ is used, which is calculated from the value in 1-propanol after correcting for the viscosity difference between the two solvents. The fitted α values are shown in Table 6.2 for both in 1-propanol and water.



Figure 6.4 Comparison of D_f curves calculated from Equation 5.14 with the experimental values for QPVP_850KD_35% polymer in 1-propanol (A) and water (B). The background ionic strength from the solvent is assumed $1.5*10^{-6}$ M for 1-propanol and $2*10^{-5}$ M for water

The fit quality is not very good for the measurements in aqueous solutions where $0.1 < c_s/c_p < 10$. The measured points in this region lie below the theoretical prediction. The coupled motion of the polyions in this region may be affected by high local viscosity of the solvents due to much extended conformation of the chains in water compare to in 1-proapnol for which all measured data points fall on the theoretical curve (except few points at $c_s/c_p > 1$, where conformation of the polyion chain may perturbs the nature and extent of the coupling phenomena).

 Table 6.2 Fit results for the fast diffusion coefficient for QPVP_850KD_35%

solvent	Dp/cm^2s^{-1}	R_h (pol.) / nm	$Ds / cm^2 s^{-1}$	Ν	α
1-propanol	3.4*10 ⁻⁸	29	4*10 ⁻⁶	3230	0.006
water	5.8*10 ⁻⁸	37	8*10-6	3230	0.062

The variation of the diffusion coefficients and appearance of different diffusion modes as a function of the characteristic ratio $\lambda^* = c_{p,e}/c_s$ are shown in Figure 6.5 where $c_{p,e} =$ $c_{p}*\alpha$ is the concentration of the charged monomers. The values of α obtained from the fitting of the fast diffusion mode are used here. In both solvents, the slow mode appears when $\lambda^* \sim$ 0.1 which is also found with the low charged polymers in 1-propanol. With increasing λ^* , the slow diffusion coefficient decreases much faster in water than in 1-propanol which is probably due to the attractive interactions between chain segments from different chains in poor solvent conditions which facilitates the formation of interchain aggregates in the solution. Moreover, for $C_p \ge 50$ mg/L in salt free aqueous solution ($\lambda^* > 1$), the slow decay mode in the electric field autocorrelation functions becomes too broad to be approximated by a single exponential decay. The complete correlation function for this concentration limits are best fitted by a tri-exponential function giving a well separated third diffusion mode intermediate between the fast and slow modes (Figure 6.5). An Intermediate diffusion mode is also reported before ¹⁴⁴ for the same polymer at different charge densities on the chain in aqueous solutions. For the aim of this thesis, only the contribution of the fast mode to the scattering intensity is important, and both the intermediate and slow diffusion mode is treated together as a combined disturbance which has to be eliminated from the raw light scattering intensities. The fractions of the fast mode amplitudes are shown in the inset of Figure 6.5 as a function of polymer concentration in salt free conditions. Lower amplitude of the fast mode in water suggests a higher contribution of the slow mode to the scattering intensity.



Figure 6.5 Fast (**n**), slow (**n**) and intermediate (**n**) diffusion modes for QPVP_850KD_35% polymer in 1-propanol (A) and water (B). The background ionic strength from the solvent is assumed $1.5*10^{-6}$ M for 1-propanol and $2*10^{-5}$ M for water

solvent	Polymer concentration (mg/L)	Salt concentration (M)	Nature of the KC/R plotted against q ²
	10	$10^{-6} - 5*10^{-6}$	Structure peak
1-propanol	10	$10^{-5} \le c_s \le 10^{-3}$	+ve slope
	$10 \le C_p \le 30$	0	Structure peak
	$50 \le C_p \le 10^3$	0	-ve slope
	9	$10^{-5} - 5*10^{-5}$	Structure peak
	9	$8*10^{-5} \le c_s \le 5*10^{-3}$	+ve slope
water	5≤C _p ≤21	0	Structure peak
	$50 \le C_p \le 500$	0	-ve slope
	750	0	+ve slope

Table 6.3 Qualitative features of static light scattering properties of QPVP_850KD_35%

 polymer in 1-propanol and water

solvent	Polymer concentration	Salt concentration	DLS measurement
	(mg/L	(M)	
	-		
1-propanol	$10 \le C_p \le 10^3$	0	Fast + slow mode
	10	10-6-5*10-6	Fast + slow mode
	10	$7*10^{-6} \le c_s \le 10^{-4}$	Fast mode
QPVP_850KD_20%	$10 \le C_p \le 5*10^3$	0	Fast + slow mode
water	$4 \le C_p < 750$	0	Fast + slow mode
	9	$10^{-5} \le c_s \le 5*10^{-5}$	Fast + slow mode
	9	$8*10^{-5} < c_s \le 8*10^{-4}$	Fast mode

Table 6.4 Appearance of fast and/or slow diffusion mode with QPVP_850KD_35% polymer

 both in 1-propanol and water

6.2 Effective degree of ionization of QPVP_850KD_35% polymer in 1-propanol and water from the molar mass measured by static light scattering

 N_{app} values are calculated from the measured apparent molar masses both in 1propanol and in water using an average molar mass of 143.2 g/mol for the monomers for a quaternization degree of 35%. Comparison of the experimentally obtained values of $1/N_{app}$ with the theoretical prediction according to Prins-Hermans formula is shown in Figure 6.6 For small values of c_s'/c_p , the slow mode corrected values of $1/N_{app}$ is used which are shown in the graph as red symbols. The theoretical plots are drawn with given values of N_{true} and the effective degrees of ionizations (α) are obtained by optimising the plots to resemble the measured data points. The resulting values of α are given in Table 6.5.

The polymer in 1-propanol has a very similar value of α obtained in the last chapter with the 4% and 20% quaternization chains. In water α is almost 10 times higher than in 1-propanol for the same degree of quaternization. A similar value of α for highly quaternized 2-PVP polymers in aqueous solution is reported ¹⁴⁵before. A higher α in water suggests the

domination of strong electrostatic interactions over repulsive hydrophobic interactions between the polymer backbone and the solvent and also explains the higher R_g and R_h values of the polyion chain compared to in 1-propanol.

The results of a high purity 100% quaternized NaPSS polymer is also shown in the same graph along with the QPVP polymers to verify the validity of the Prins-Hermans equation in determining the effective charge of a polyelectrolyte by light scattering measurements. The purpose of such exercise is that the NaPSS polymer in aqueous solution is the most studied polyelectrolyte in literature¹⁴⁶. There is a huge amount of reports determining the effective charge of this polymer in water through various experimental methods. A value of α between 0.2-0.3 is frequently measured which is independent of the molar mass of the polymer. The particular polymer used in the present work has a molar mass of ~ 50,000 g /mol or a degree of polymerisation of 258 (see appendix Figure A4) Mainly salt free aqueous solutions with high polymer concentrations are studied in this work to reach to a plateau of $1/N_{app}$ for $c_s '/c_p \ll 1$, only 1 measurement at high concentration of added NaBr is done ($c_s'/c_p \sim 20$) to compare with the theoretical baseline for very high c_s'/c_p values (see Figure 6.6). The value of α obtained for this polymer is 0.26 by comparing the measurements with the Prins-Hermans equation. The value is very similar to the literature values hence the validity of the Prins-Hermans theory in determining the effective charge of a polyelectrolyte by light scattering experiments is ascertained.



Figure 6.6 Comparison of the Prins-Hermans theory with the measured $1/N_{app}$ values for QPVP_850KD_35% polymer in 1-propanol (\Box) and in water (Δ). Measurement results for a standard 100% neutralized NaPSS polymer in aqueous solution are also shown (\circ). The red symbols show the slow mode corrected values where it is necessary. The salt concentration (c_s') is the sum of added salt (c_s) and the solvent contribution ($c_{s,0}$), where $c_{s,0}$ is taken as $1.5*10^{-6}$ M and $2*10^{-5}$ M in 1-propanol and water respectively. N_{true} values for the QPVP and NaPSS are 3230 and 258 respectively. Theoretical curves (solid lines) are plotted for α = 0.007 ($_$), 0.013 ($_$), 0.11 ($_$), and 0.26 ($_$)

Polymer	Solvent	N _{true}	α
QPVP_850KD_35%	1-propanol	3230	0.007-0.013
QPVP_850KD_35%	water	3230	0.11
100% neutralized NaPSS	water	258	0.26

 Table 6.5 The effective charge of QPVP and NaPSS polymers obtained according to the Prins-Hermans equation

7 Summary

A systemic study of the solution properties of partially quaternized poly(2-vinyl pyridine) (QPVP) polymers at different polymer (c_p) and/or added salt (c_s) concentrations is conducted using static and dynamic light scattering techniques. The polymers are synthesized by quaternizing well characterized, low polydispersity 2-PVP polymers to different degrees (4.3%, 20% and 35%) of quaternization. Two different solvents namely 1-propanol and water were used to prepare the QPVP solutions. From the measured molar masses and the diffusion coefficients, the effective degrees of ionization α (fraction of ionized / dissociated monomers) for the charged polymers are obtained. The determination of α is done by SLS in terms of the apparent molar masses and by DLS in terms of the "coupled mode" diffusion coefficients. The α values obtained from these two different techniques and the corresponding theories are in the same order of magnitude and shows same trend for all the polymers used. Many ad hoc approximations involved in arriving to the analytical expression of the coupled mode theory might be responsible for the quantitative difference of α values obtained from SLS and DLS.

For experiments at low c_s/c_p ratio all QPVP solutions showed the fast/slow mode dynamics characteristic for polyelectrolyte solutions in general. The fast mode is attributed to the coupled diffusion of the charged polymers and the corresponding diffusion coefficient is used to obtain α using the analytical expression given by coupled mode theory. The relative scattering amplitude of the fast mode is used to calculate the contribution of the individual polymer chains (excluding the slow mode or aggregates) to the total scattering intensity. This procedure prevents the possibility of obtaining a wrong molar mass from static light scattering measurements due to the presence of the slow mode. After this necessary correction for the slow mode, the measured degree of polymerization is compared to the Prins-Hermans equation to obtain the value of α . For a better agreement of the experimental values of diffusion coefficient and molar mass with the corresponding theories, the concentration of the added salt was rescaled by a constant amount which corresponds to the presence of some residual salts in the respective solvents. A value of $1.5* 10^{-6}$ M. in 1-propanol and $2*10^{-5}$ M for the residual salts were found to be appropriate for this work.

In 1-propanol, the calculated α values for all QPVP polymers were found to be very low compared to the actual degree of quaternizations. The so called Manning condensation parameter (ξ_M) seemingly does not play any role in determining the ionization/dissociation characteristics in these cases. Irrespective of the molar mass of the polymer or the degree of

quaternization (with ξ_M values both smaller and greater than 1) the values of the calculated α was found to be in the range from 0.003 to 0.01 (which implies only 0.3%-1% monomers being ionized).

The 35% quaternized polymer was soluble in both 1-propanol and water, which enabled me to study the effect of the solvent polarity on α . Almost 10 times increase (from both the DLS and SLS data) in α was found in water when compared to the value obtained for the same polymer in 1-propanol. The value of α in water was found to be ~ 0.1 which is still small when compared to the prediction (0.35) of Manning's theory. The applicability of the Prins- Hermans theory for a consistent prediction of α was checked by measuring the molar masses of a NaPSS polymer in salt free aqueous solution at varying polymer concentrations. The reason behind choosing this particular polymer was the availability of a huge amount of literature data on the effective degree of dissociation of this polymer in water. From the measurements done in the thesis, the NaPSS polymer in water gave value of α = 0.26 which is in good agreement with literature values.

The reason for low values of α in 1-propanol may indicate to a different kind of counterion condensation mechanism rather than from solely electrostatic origin as pictured by Manning. Specific interactions between the charged monomer and the counterions leading to formation of ion pairs might be a possible explanation for such low values of α . If this is the case, then the extent of counterion condensation and hence the value of α will change depending upon the experimental conditions ¹⁴⁷ like the polymer or added salt concentration. A conductivity measurement test was performed aiming to study the dissociation behavior of the quaternary pyridinium groups in 1-propanol. A simple salt N-ethyl 2-ethyl pyridinium bromide (which is equivalent to a charged monomer of the QPVP polymers) showed characteristic conductivity behaviour of a strong electrolyte which dissociates completely irrespective of the concentration. On the other hand with the QPVP polymers, sharp decrease of the equivalent conductivity with increasing concentration was seen which is similar to the behaviour of weak electrolytes (see appendix Figure. A5).

This extremely low effective α may be explained by a novel theory of counterion adsorption by Muthukumar¹⁴⁸ which postulates an equilibrium between the condensed (adsorbed) and free counterions. In addition to the different interaction energies, a contribution of this equilibrium to the free energy of the system is assumed through the equilibrium constant k. Depending on this equilibrium constant k, the effective dissociation

may adopt very small values. Unfortunately a quantitative comparison with experimental values of this work was not possible within the time frame of this thesis.

8 References

¹Philipp, B.; Dautzenberg, H.; Linow, K.; Kötz, J.; Dawydoff, W. *Prog-Polym. Sci.* **1989**, *14*, 91

²Netz, R. R.; Andelman, D. Phys. Rep. 2003, 380, 1

³Schonhoff, M. Curr Opin Colloid Interface Sci **2003**, *8*, 86

⁴Fuoss, R. M. *J. Polym. Sci.* **1948**, *3*, 603

⁵Lundberg, R.D.; Makowski, H.S. *J Polym Sci Polym Phys Ed* **1980,** 18, 1821

⁶Agarwal, P. K.; Garner, R. T.; Graessley, W.W.; *J Polym Sci Polym PhysEd* **1987**, *25*, 2095

⁷Hara, M.; Wu, J.; Lee, A.H.; *Macromolecules* **1988**, *21*, 2214

⁸ Schmitz, K. S. in *Macro-ion Characterization*. American Chemical Society, Washington, **1994**

⁹Mandel, M. *Eur. Polym. J.* **1983**,19, 911

¹⁰Chepelianskii, A.; Mohammad-Rafiee, F.; Trizac, E.; Raphël, E. J. Phys. Chem. B

2009, *113*, 3743

¹¹Barrat, J. L.; Joanny, J. F. AdV. Chem. Phys. **1996**, *94*, 1

¹²Lyons, J. W.; Kotin, L. J. Am. Chem. Soc. **1965**, 87, 1670

¹³Rice, S.A.; Nagasawa, M. "Polyelectrolyte Solutions" Academic Press Inc., New York, N. Y. **1961**

¹⁴Nyquist, R. M.; Ha, B. Y.; Liu, A. J. *Macromolecules* **1999**, *32*, 3481

¹⁵Joanny, J.F.; Pincus, P. Polymer **1980**, *21*, 274

¹⁶Kumar, R.; Kundagrami, A.; Muthukumar, M. *Macromolecules* **2009**, *42*, 1370

¹⁷Barbosa, M. C.; Deserno, M.; Holm, C. *Europhys. Lett.* **2000**, *52*, 80

¹⁸Schiessel, H. *Macromolecules* **1999**, *32*, 6673

¹⁹Popov, A.; Hoagland, D. A. J. Polym. Sci. Part B Polym. Phys. **2004**, 42, 3616

²⁰Dobrynin, A. V. *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 376

²¹Fuoss, R.M.; Katchalsky, A.; Lifson, S. Proc. Natl. Acad. Sci. USA 1951, 37, 579

²³Rivas, B. L.; Pereira, E. D.; Horta, A.; Renamayor, C. S. Eur. Polym. J. **2004**, 40, 203

²⁴Meyer, E. M.; Vasconcellos, S. R. *ACS Symp.Ser.* **1993**, *548*, 131

²⁵Oman, S. *Makromolekul Chem*. **1974,** *175,* 2133

²⁶Reddy, M.; Marinsky, J.A. J. Phys. Chem. **1970**, 74, 3884

²⁷Kakehashi, R.; Yamazoe, H.; Maeda, H. Colloid Polym. Sci. 1998, 276, 28

²⁸Oosawa, F. *Polyelectrolytes*. Marcel Dekker, New York, NY, **1971**

²⁹Doi, M.; Edwards, S. F. *The theory of polymer dynamics*. Oxford: Clarendon Press;

1989

³⁰Katchalsky, A. Pure Appl. Chem. **1971**, 26, 327

³¹Huizenga, J.W.; Grieger, P.F.; Wall, F.T. J.Am.Chem.Soc. **1950** 72, 2636

³²Debye, P. J. *The collected Papers of Peter J. W. Debye*. Interscience Publishers Inc.

New York, NY, **1954**

³³Odijik, T. *Macromolecules* **1979**, *12*, 688

³⁴Skolnick, J.; Fixman, M. *Macromolecules* **1977**, 10, 944

³⁵Odijik, T.; Mandel, M. *Physica A* **1978**, *93*, 298

³⁶Imai, N.; Ohinshi, T. J. chem. Phys. **1959**, 30, 1115

³⁷Manning, G. S. J. Chem. Phys. **1969**, 51, 924,3249

³⁸Manning, G. S. *Biophys*.Chem. **1977**, 7, 95

³⁹Manning, G. S. J. Phys. Chem **1981**, 85, 1506

⁴⁰Manning, G. S.; Ray, J. *Langmuir*. **1994**, *10*, 962

⁴¹Dautzenberg, H.; Jaeger, W.; Kötz, J.; Philipp, B.; Seidel, C.; Stscherbina, D.

Polyelctrolytes. Formation, Characterization and Application Hanser Publishers 1994

⁴²Panafiel, L. M.; Litovitz, T. A. J. Chem. Phys. **1992**, 96, 3033

⁴³Manning, G. S. J. Chem. Phys. **1988**, 89, 3772

⁴⁴Mandel, M. Physical Properties of Polyelectrolyte Solutions. **1999**

⁴⁵Manning, G. S. *Physica A*. **1996**, *231*, 236

²²Antypov, D.; Holm, C. *Macromolecules*. **2007**, *40*, 731

⁴⁶Dobrynin, A.; Rubinstein, M. *Macromolecules* **2001**, *34*, 1964

⁴⁷Gonzalez-Mozuelos, P.; Olvera de la Cruz, M. J. Chem. Phys. **1995**, 103, 3145

⁴⁸Deshkvski, A.; Obukhov, S. P.; Rubinstein, M. *Phys. Rev. Lett.* **2001**, *86*, 2341

⁴⁹Stevens, M. J.; Kremer, K. *Phys. Rev. Lett.* **1993**, *71*, 2228

⁵⁰Schmitz, K. S. *Biopolymers* **1977**, *16*, 2635

⁵¹Manning, G. S. Acc. Chem. Res. **1979**, 12, 443

⁵²Muthukumar, M. J. Chem. Phys. **2004**, 120, 9343

⁵³Oosawa, F. J. Polym. Sci. **1957**, 23, 421

⁵⁴Manning, G. S. Annu. rev. Phys. Chem. **1972**, 23, 117

⁵⁵Kratky, O.; Porod, G.; *Rec. Trav. Chim*. Pays-Bas **1949**, *68*, 1106

⁵⁶Odijik, T. J. Polym. Sci. Polym. Phys. **1977,** 15, 477

⁵⁷Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944

⁵⁸Benoit, H.; Doty, P.M. *J. Phys. Chem*. **1953**, *57*, 958

⁵⁹Teraoka, I. Polymer Solutions. *An Introduction to Physical Properties*. John Wiley & Sons, **2002**

⁶⁰de Gennes, P. G. *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca **1979**

⁶¹de Gennes, P.G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Paris)* **1976**, *37*, 1461

⁶²Pfeuty, P. J. Phys. Collog. **1978**, 39, C2-149

⁶³Alexandrowicz, Z. J. Polymer Sci. **1959**, 40, 91

⁶⁴Katchalsky, A. *Biophys. J.* 1964, 4(1), 9

⁶⁵Blaul, J.; Wittemann, M.; Ballauff, M. J. Phys. Chem. B **2000**, 104, 7077

⁶⁶Donnan, F.; Guggenheim, E.M. Z. Phys. Chem. **1934**,162,364

⁶⁷Hill, T. J Phys. Chem. **1957**, 61, 548

⁶⁸Inagaki, H.; Hirami, M.; Z. Elektrochem. **1959**, 63, 419

⁶⁹Tanford, C. *Physical Chemistry of Macromolecules*. Wiley, NY, **1961**

⁷⁰Schneider, N. S.; Doty, P. *J. Phys. Chem.* **1954**, *58*, 762

⁷¹Yamakawa, H. *Modern Theory of Polymer Solutions* **1971**

⁷²Landau, L.; Lifshitz, E. Statistical Physics.Oxford University Press, London **1938**

⁷³Smoluchowski, M. Ann. D. Physik. **1908**,25,205

⁷⁴Smoluchowski, M. Phil. Mag. **1912**, 23, 165

⁷⁵Einstein, A. Ann. D. Physik. **1910**,33,1275

⁷⁶Casassa, E. F.; Eisenberg, H. Adv Protein Chem. 1964, 287, 19

⁷⁷Stejskal, J.; Kratochvíl, P.; Pouchly, J. Polym. Sci. Pol. Phys **1974**, *12*, 891

⁷⁸Edsall, T. J.; Edelhoch, H.; Lontie, R.; Morrison, P. R. *J. Am. Chem. Soc.* **1950**, *72*, 4641

⁷⁹Zernike, F. **1918** Thesis, University of Amsterdam

⁸⁰Brinkman, H. C.; Hermans, J. J. J. Chem. Phys. **1949**, 17, 574

⁸¹Kirkwood, J. G.; Goldberg, J. J. Chem. Phys. **1950**, 18, 54

⁸²Stockmayer, W. H. J. Chem. Phys. **1950**, 18, 58

⁸³Prins, W.; Hermans, J. J.; J. Phys. Chem. **1955**, 59(6), 576

⁸⁴Vrij, A.; Overbeek, J. Th. G. *J. Coll. Sci.* **1962**, *17*, 570

⁸⁵Strauss, U. P.; Wineman, P. L. J Am. Chem. Soc. **1958**, 80, 2366

⁸⁶Eisenberg H. Biological macromolecules and Polyelectrolytes in Solution, Oxford

University, London, 1976, Chap.4

⁸⁷Mysels, K. J. J. Phys. Chem. **1954**, 58(4), 303

⁸⁸Mie, G. Ann physik. **1908**, 25, 377

⁸⁹Debye, P. Ann Physik. **1909**, 30, 59

⁹⁰Teraoka, I. Polymer Solutions. An Introduction to Physical Properties. John Wiley & Sons, **2002**

⁹¹Zernicke, F.; Prins, J. A. *Z. Physik* **1927**, *41*, 184

⁹²Schärtl, W. Light Scattering from Polymer solutions and Nanoparticle Dispersions. Springer **2007**

⁹³Gröhn, F.; Antonietti, M. *Macromolecules* **2000**, *33*, 5938

⁹⁴Berne, B. J; Pecora, R. Dynamic Light Scattering: With Application to Chemistry,

- Biology and Physics. Dover Publications, third edition, 2000
- ⁹⁵Tanahatoe, J.J.; Kuil M. E. *J.Phys.Chem. B* **1997**,*101*,9233
- ⁹⁶Fennel Evans, D.; Gardam, P. J. Phys. Chem. **1968**, 72(9), 3281
- ⁹⁷Goffredi, M.; Shedlovsky, T. J Phys. Chem. **1967**, 71(7), 2176

⁹⁸Baylaucq, A.; Watson, G.; Zéberg-Mikkelsen, C.; Bazile, J. P.; Boned, C. J. Chem. Eng. Data 2009, 54, 2715

⁹⁹Becker, A.; Köhler, W.; Müller, *B. Ber.Bunsen-Gas.* **1995**, *99*, 600.

¹⁰⁰Loh, P. PhD thesis; Johannes Gutenberg University Mainz, **2008**

- ¹⁰¹Borochov, N.; Eisenberg, H. *Macromolecules* **1994**, *27*, 1440
- ¹⁰²Stepanek, P.; Tuzar, Z.; Kadlec, P.; Kriz, J. *Macromolecules* **2007**, 40, 2165

¹⁰³Ricker, M.; Schmidt, M. *Makromol.Chem*. **1991**, *192*, 693

¹⁰⁴Zimm, B. H. J. Chem. Phys. **1948**, 16, 1093

¹⁰⁵Förster, S.; Schmidt, M.; Antonietti, M. J. Phys. Chem. **1992**, *96*, 4008

- ¹⁰⁶Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, 120, 53
- ¹⁰⁷Beer, M.; Schmidt, M.; Muthukumar, M. *Macromolecules* **1997**, *30*, 8375
- ¹⁰⁸Lee, N.; Thirumalai, D. Macromolecules **2001**, 34, 3446
- ¹⁰⁹Debye, P. J. Phys. Colloid. Chem. **1947**, 51, 18
- ¹¹⁰Bodycomb, J.; Hara, M. *Macromolecules* **1994**, 27, 7369

¹¹¹ Maier, E. E.; Krause, R.; Deggelmann, M.; Hagenbüchle, M.; Weber, R. *Macromolecules* **1992**, *25*, 1125

- ¹¹²Nierlich, M.; Boue, F.; Lapp, A.; Oberthür, R. *Colloid Polym. Sci.* **1985**, *263*, 955
- ¹¹³Kaji, K.; Urakawa, H.; Kanaya, T.; Kitamaru, R. *Macromolecules* **1984**, *17*, 1835
- ¹¹⁴Drifford, M.; Dalbiez, J. P. J. Phys. Chem. **1984**, 88, 5368
- ¹¹⁵Förster, S.; Schmidt, M.; Antonietti, M. *Polymer* **1990**, *31*, 781

¹¹⁶Schulz, S. F.; Maier, E. E.; Weber, R. J. Chem. Phys. **1989**, 90, 7

¹¹⁷Hayter, J.; Jannink, G.; Brochard-Wyart, F.; de Gennes, P. G. J. Phys.(Paris), Lett. **1980**, 41, L-451

¹¹⁸Physical Chemistry of Polyelectrolytes, edited by Tsetska Radeva **2001**

¹¹⁹Wang, L.; Bloomfield, V. A. *Macromolecules* **1991**, *24*, 5791

¹²⁰Li, X.; Reed, W. F. J. Chem. Phys. **1991**, 96, 4568

¹²¹de Gennes, P. G.; Pincus, P.; Velaso, R. M.; Brochard, F. *J. Phys.(Paris)* **1976**, *37*, 1461

¹²²Borsali, R.; Rinaudo, M.; Noirez, L. *Macromolecules* **1995**, *28*, 1085

¹²³Krause, R.; Maier, E. E.; Deggelmann, M.; Hagenbüchle, M.; Weber, R. *Physica A* **1989**, *160*, 135

¹²⁴Lifson, S.; Katchalsky, A. J. Polym. Sci. **1954**, 13, 43

¹²⁵Tivant, P.; Turq, P.; Drifford, M.; Magdelenant H.; Menez, R. *Biopolymers* **1983**, *22*,
643

¹²⁶Koene, R.S.; Mandel, *M. Macromolecules* **1983**, *16*, 973

¹²⁷Lin, S.C.; Lee, W.; Schurr, J.M. *Biopolymers* **1978**, 17, 1041

¹²⁸Drifford, M.; Dalbiez, J.P. *Biopolymers* **1985**, *24*, 1501

¹²⁹Sedlák, M.; Koňák, C.; Štěpánek, P.; Jakeš, J. Polymer **1987**, 28, 873

¹³⁰Schmitz, K. S.; Lu, M.; Gauntt, J. J. Chem. Phys. **1983**, 78, 5059

¹³¹Sogami, I.; Ise, N. J. Chem. Phys. **1984**, 481, 6320

¹³²Schmitz, K. S.; Ramsay, D. J. *Biopolymers* **1985**, *24*, 1247

¹³³Ghosh, S.; Li, X.; Reed, C. E.; Reed, W. F. *Biopolymers* **1991**, *30*, 1101

¹³⁴Pussey, P. N.; J. Phys A: Math Gen. **1975**, 8, 1433

¹³⁵Ackerson, B. J. J. Chem. Phys. **1976**, 64, 242

¹³⁶Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1996**, 29, 2974

¹³⁷Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **1999**, *32*, 915

¹³⁸Micka, U.; Holm, C.; Kremer, K. *Langmuir* **1999**, *15*, 4033

¹³⁹Essafi, W.; Lafuma, F.; Williams, C. E. Eur. Phys. J. B. **1999**, 9, 261

¹⁴⁰Carbajal-Tinoco, M. D.; Williams, C.E. *Europhysics Letters* **2000**, *52*, 284

¹⁴¹Essafi, W.; Lafuma, F.; Baigl, D.; Williams, C.E. **2005**, *71*, 938

¹⁴²Hooper, H. H.; Beltram, S.; Sassi, A. P.; Blaras, H. Prausnitz, J. M. J. Chem. Phys. **1990**, 93, 2715

¹⁴³Dobyrinin, A. V.; Colby, R.H.; Rubinstein, M. *Macromolecules* **1995**, *28*, 1859

¹⁴⁴Topp, A.; Belkoura, L.; Woermann, D. **1996**, *29*, 5392

¹⁴⁵Beer, M. Dissertation, Bayreuth, **1995**

- ¹⁴⁶ Takahashi, A.; Kato, N.; Nagasawa, M. J. Phys. Chem. **1970**, 74, 944
- ¹⁴⁷ Raspaud, E.; de la Cruz, M. O.; Sikorav, J. L.; Livolant, F. *Biophys. J.* **1998**, 74, 381
 ¹⁴⁸ Muthukumar, M. *J. Chem. Phys.* **2012**, *137*(3), 034902

9 Appendix

G.P.C measurements results with the 2-PVP polymers (charged and uncharged) in water + acetonitrile mixture



Figure A1 Molar mass distribution for the neutral and quaternized 2-PVP polymers: (A) 65 KD backbone and (B) 850 KD backbone. The G.P.C measurements are done in water + acetonitrile mixture (vol. ratio 0.8:0.2) in presence of 0.5M Na_2SO_4 +CH₃COOH buffer. The experiments are performed with: VWR 7614 degasser; Hitachi L-2130 pump; TosoHaas TSK-PWXLgel column; Waters 486 UV-Detector: flow rate: 0.7- 1 mL/min in room temperature. The results are shown in the table below:

Polymer	M _w / g/mol	M _n / g/mol	P.D.I=M _W /M _n
2-PVP_850KD	$1.16^{*}10^{6}$	3*10 ⁴	39
QPVP_850KD_2%	9.54*10 ⁵	5.13*10 ⁴	19
QPVP_850KD_20%	7.84*10 ⁵	4.87*10 ³	161
QPVP_850KD_35%%	2.98*10 ⁵	1.95*10 ³	152
2-PVP_65KD	$7.17*10^4$	6.1*10 ⁴	1.17
QPVP_65KD_20%	$6.22*10^4$	5.11*10 ⁴	1.21
QPVP_65KD_35%	4.99*10 ⁴	4.24*10 ⁴	1.18

Table A1 summary of the GPC results for 2-PVP polymers

Concentration loss for different polymers by filtration through membrane filters

The concentrations of the stock solutions of different polymers are measured before and after filtration through the membrane filters (which are used to make the solution dust free) to check for any loss due to adsorption in the filter. The results are shown in the table below:

Polymer (concentration of the solution filtered)	Solvent	Filter material (pore size(µm))	% of concentration recovered after filtration
QPVP_850KD_4.3% (1 g/L)	1-PrOH	polytetrafluoroethylene(P.T.F.E) (0.22)	100
QPVP_850KD_4.3% (0.2 g/L)	1-PrOH	polytetrafluoroethylene(P.T.F.E) (0.22)	96
QPVP_850KD_20% (1 g/L)	1-PrOH	polytetrafluoroethylene(P.T.F.E) (0.22)	97
QPVP_850KD_35% (0.5 g/L)	1-PrOH	polytetrafluoroethylene(P.T.F.E) (0.22)	100
QPVP_850KD_35% (0.5 g/L)	Water	polyvinylidine fluoride(P.V.D.F) (0.22)	96
Na-PSS_65KD (5 g/L)	Water	Polyvinylidine fluoride(P.V.D.F) (0.22)	95

Table A2 Check for concentration loss of the polyelectrolytes measured



Figure A2 Correlation function measured at a scattering angle of 30 degree for a high concentration solution of TBAB in 1-propanol. The concentration of the salt is 0.5 M. A single exponential fit of the correlation function gives diffusion coefficient of the salt as $4*10^{-6}$ cm²S⁻¹. This value is used to fit the fast diffusion coefficient of the QPVP polymers in 1-propanol using the coupled mode theory.

Reason of lower α values obtained from coupled mode theory compared to that obtained from Prins-Hermans fitting

The coupled mode equation, at the limit of very low added salt concentration ($c_s \approx 0$ M) is given as following,

$$D(q = 0) = \frac{D_p D_s [1 + \alpha N]}{D_p \alpha N + D_s}$$
(1)

This can be rearranged to give the expression for α as,

$$\alpha = \frac{\left[1 - \frac{D(q = 0)}{D_{p}}\right]}{N\left[\frac{D(q = 0)}{D_{s}} - 1\right]}$$
(2)

At finite added salt concentration, the diffusion coefficient (D(q=0)) of a single flexible polymer will increase with increasing salt concentration (smaller polymer size at higher salt concentration). The coupled mode theory ignores this change in diffusion coefficient due to conformational change. In other words, the experimental $D(q=0)/D_p$ ratio will be always higher for a flexible chain in comparison to a rigid molecule at any finite added salt concentration. A higher value of this ratio invariably results in a lower α value as seen in equation (2) above. This fact is seen in the comparison of α values for the smaller and bigger molar mass polymers. For the high molar mass sample the α values from the Prins –Hermans fits are almost double than that obtained from coupled mode theory whereas for the smaller molar mass polymer the α values are very close at high added salt (compare table 5.6 and table 5.8). Which could be due to the fact that the smaller molar mass polymer does not undergo very large conformational transition with the ionic strength. Although, only the conformational change effect is not sufficient to explain a factor of 2 difference in α values from the Prins-Hermans fit and from coupled mode theory for the bigger molar mass polymer. Other effects like the hydrodynamics of the solution and the finite size of the polymer chain (in coupled mode theory, the polymer molecules are assumed be point like) may also be the reason of the difference of the α values.

Test for the effect of the filter pore size on the slow diffusion mode



Figure A3. Normalized electric field correlation function at scattering angle 20° for QPVP_65KD_20% polymer in pure 1-propannol at a polymer concentration of 75 mg/L. The solution is filtered with two different pore size filters of same material (PTFE) having pore size (\Box) 0.22 µm and (\blacksquare) 0.1 µm.

Calculation of the error in polyion concentration due to slow mode correction of the scattering intensity

Let a fraction f of the polymer chains be aggregated to produce the slow modes. Assuming the intermolecular structure factor at 0 angle as S(0), $A_{f,rel}$ at 0 scattering angle is given by,

$$A_{f,rel.} = \frac{(1-f)M_1}{(1-f)M_1 + fM_{agg.}}$$
 Equation A.1

Where, M_{agg} is the molar mass of the aggregate and M_1 is the molar mass of a single chain. The fitted $A_{f,rel}$ values are found to vary from 0.74 to 0.9 for the 20% quaternized sample of the big molar mass 2-PVP depending upon the polymer concentration. So, using Equation A.1, we can write,

$$0.74 \le \frac{(1-f)M_1}{(1-f)M_1 + fM_{agg.}} \le 0.9$$
 Equation A.2

or,

$$\frac{1}{0.74} \ge 1 + \frac{f}{1 - f} \frac{M_{agg.}}{M_1} \ge \frac{1}{0.9}$$
 Equation A.3

The average hydrodynamic radius for the aggregates is found to be~ 110 nm whereas that of a single polymer is ~ 40 nm. Assuming a $R_h \sim M^{0.5}$ scaling for Gaussian coils, M_{agg}/M_1 is ~8. After some simple algebraic calculation we get from Equation A.3:

$$0.01 \le f \le 0.04$$

Similarly for the 4% sample (A_{f,rel} varies from 0.45 to 0.65) it can be shown that :

$$0.06 \le f \le 0.13$$

Molar mass of the sodium poly (styrene sulfonate) polymer used in this thesis



Figure A4 Zimm plot with NaPSS sample in water in presence of 0.1 M NaBr. The nominal molar mass of the sample is 64,000 g/mol according to the manufacturer. From the light scattering measurement, the value obtained for the molar mass is 53,000 g/mol which correspond to a degree of polymerization of 258. A literature value of 0.198 is used for dn/dc for this polymer in water

Qualitative comparison of the dissociation of quaternary pyridinium groups on the QPVP polymers with that of a simple salt

A conductivity test was performed to account for very low degree of dissociations (α) obtained for the QPVP polymers in 1-propanol. The conductivity of two QPVP polymers in pure 1-propanol is compared to that of a simple salt N-ethyl 2-ethyl pyridinium bromide (which is chemically equivalent to the charged monomers of QPVP). From the measured equivalent conductivities a notable difference, regarding the dissociation of the quaternary pyridinium group, could be seen between the monomeric salt and the charged polymers. Almost linear decrease of the molar conductivity with the square root of concentration for the monomeric salt suggests a complete dissociation of the salt. in 1-proapanol. At the same conditions, the molar conductivity of the QPVP polymers are at least 5 times lower than that of the monomer and also the molar conductivity decreases much faster with increasing concentration which may indicate ion pair formation between the charges on the polymer chain and free bromide ions.



Figure A5 Comparison of the equivalent conductivity between N-ethyl 2-ethyl pyridinium bromide salt (**n**) and QPVP polymers with 20% (**n**) and 35% (Δ) degree of quaternization. The polymer concentrations are varied from ~ 10 mg/L to ~ 500 mg/L. c_e gives the concentration of charged monomers from the polymers. The measurement is done in 1-propanol at 20 °C. The solid lines drawn for the QPVP polymers are polynomial fits of the measured data points and does not correspond to any particular theory





Figure A6 QPVP_850KD_4%: Angular variation of the reduced inverse scattering intensity as a function of added salt (TBAB) concentration at a fixed polymer concentration in 1-propanol: The polymer and added salt concentrations are shown next to the graph



Figure A7 QPVP_850KD_20%: Angular variation of the reduced inverse scattering intensity as a function of added salt (TBAB) concentration at a fixed polymer concentration in 1-propanol: The polymer and added salt concentrations are shown next to the graph



Figure A8 QPVP_65KD_20%: Angular variation of the reduced inverse scattering intensity as a function of added salt (TBAB) concentration at a fixed polymer concentration in 1-propanol: The polymer and added salt concentrations are shown next to the graph



Figure A9 QPVP_850KD_35%: Angular variation of the reduced inverse scattering intensity as a function of added salt (TBAB) concentration at a fixed polymer concentration in 1-propanol: The polymer and added salt concentrations are shown next to the graph



Figure A10 QPVP_850KD_35%: Angular variation of the reduced inverse scattering intensity as a function of added salt (TBAB) concentration at a fixed polymer concentration in water: The polymer and added salt concentrations are shown next to the graph

All light scattering results in tabular form

$C_p(mg/L)$	c _s (M)	$M_{app} * 10^{-5}$	R _{g,app}	R _{fast}	R _{slow}	R _h (nm)	ρ-
		(g/mol)	(nm)	(nm)	(nm)		ratio
		Adde	ed salt measu	rements			
10	10 ⁻⁶	1.98	N.A	11.54	100.2		
10	6*10 ⁻⁶	3.15	66.2			32.1	2.06
10	10 ⁻⁵	4.08	72.77			35.5	2.05
10	2*10 ⁻⁵	4.24	88.1				
10	2.6*10 ⁻⁵	4.75	91.15			40.05	2.28
10	5*10 ⁻⁵	5.84	97.77			42.3	2.31
10	7*10 ⁻⁵	6.17	99.85			45.03	2.22
10	10 ⁻⁴	7.09	97.6			47.59	2.05
10	1.01*10 ⁻⁴	6.96	92			46.2	1.99
10	1.3*10 ⁻⁴	7.39	96.2			50.31	1.91
10	1.5*10 ⁻⁴	7.89	96.6			50.38	1.92
10	2*10 ⁻⁴	8.75	97.7			45.03	2.17
10	3*10 ⁻⁴	7.11	83.3			41.1	2.03
10	5*10 ⁻⁴	8.99	82.5			40.2	2.05
10	8*10 ⁻⁴	8.51	77.9			37.85	2.06
10	10-3	9.42	78.9			38.88	2.03
10	0.1	8.62	52.7			35.3	1.49
20	10-5	1.83		11.44	104.24		
20	5*10 ⁻⁵	4.87	84.96			39.55	2.148
20	7*10 ⁻⁵	5.46	90.35			44.14	2.047
20	10 ⁻⁴	6.23	90.5			43.2	2.095
20	5*10 ⁻⁴	8.23	79.2			39.23	2.018
20	9*10 ⁻⁴	8.32	75.35			38.43	1.961
40	10-5	1.29		9.44	100.3		
40	5*10 ⁻⁵	3.86	67.6			33.7	2
40	10-4	5.89	78.2			37.26	2.099
40	5*10 ⁻⁴	8.38	78.3			39.6	1.975
40	8*10 ⁻⁴	7.82	73.2			37.74	1.94
40	8.2*10 ⁻⁴	8.92	80			-	1

Table A3 QPVP_850KD_4% in 1-propanol

..Continued

Cp	c _s (M)	M_{app} $*10^{-5}$	R _{g,app}	R _{fast}	R _{slow}	R _h (nm)	ρ-	
(mg/L)		(g/mol)	(nm)	(nm)	(nm)		ratio	
	Salt free measurements							
10	0	1.44		6.99	123.02			
15	0	1.62		10.35	117.9			
20	0	1.27		8.13	140.1			
25	0	1.13		6.11	111			
30	0	0.87		5.51	117.1			
50	0	0.76		4.77	148.7			
100	0	0.59		4.69	135			
150	0	0.54		3.99	113.3			
200	0	0.5		3.3	202.6			
300	0	0.46		3.15	197.7			
500	0	0.4		2.84	259.5			
750	0	0.37		2.73	174.9			
1000	0	0.36		2.79	258.8			

- P	$C_{S}(\mathbf{WI})$	IVI _{app} *IU	$\mathbf{K}_{\mathrm{g,app}}$	R _{fast}	R _{slow}	$\mathbf{R}_{\mathbf{h}}(\mathbf{nm})$	ρ-
(mg/L)		(g/mol)	(nm)	(nm)	(nm)		ratio
		Add	ed salt measu	irements			
10	1e-6	1.21		8.99	60.3	12.4	
10	5e-6	2.41		13.25	51	26.6	
10	7.5e-6	3.83	69.5			37.7	1.84
10	1.1e-5	4.53	67			39.1	1.71
10	2.6e-5	5.64	77.42			43.1	1.8
10	3.7e-5	6.38	80.72			-	-
10	5.11e-5	6.82	85.75			47.9	1.79
10	5e-5	7.07	91.03			47.8	1.9
10	7.5e-5	8.64	89.03			45.67	1.95
10	9.6e-5	8.35	87.8			48.38	1.81
10	2.51e-4	9.49	87.43			43.8	1.99
10	5e-4	9.84	79.86			40.83	1.96
10	7.5e-4	9.84	74.33			38.15	1.95
10	9.52e-4	9.65	70.4			37.49	1.88
		Sal	t free measur	ements	1	I	
10	0	0.96		8.73	57.9		
14	0	1.16		11.3	82.3		
20	0	0.46		4.63	39.7		
27	0	0.38		3.16	47.6		
50	0	0.42		3.83	102.5		
100	0	0.28		2.93	84.8		
140	0	0.26		2.47	59.7		
200	0	0.2		2.16	129.4		
400	0	0.2		2.19	93.9		
500	0	0.17		2.01	217		
1000	0	0.16		1.95	368		
2000	0	0.16	43.7	1.79	369		
5000	0	0.16	44	1.9	371		

Table A4 QPVP_850KD_20% in 1-propanol

C _p (mg/L)	c _s (M)	M _{app} *10 ⁻⁴ (g/mol)	R _{g,app} (nm)	R _{fast} (nm)	R _{slow} (nm)	R _h (nm)	ρ- ratio
		Wit	h salt measu	rements			
100	10-5	3.19		3.3	85.21		
100	2.5*10 ⁻⁵	4.44		4.03	97.25		
100	5*10 ⁻⁵	5.32		5.12	86.24		
100	7.5*10 ⁻⁵	6.07		6.03	98.8		
100	10-4	6.07				7.36	
100	2.5*10 ⁻⁴	7.79	13.09			8.48	1.54
100	5*10-4	9.13	13.89			8.56	1.62
100	7.5*10 ⁻⁴	9.08	11.56			8.17	1.41
100	1.1*10 ⁻³	9.20	14.09			8.76	1.61
100	2.5*10 ⁻³	9.68	13.72			7.95	1.73
100	5*10 ⁻³	9.28	15.15			7.61	1.99
100	7.5*10-3	9.11	15.39			7.46	2.06
100	10-2	10.06	12.13			8.46	1.43
75	10-5	2.45				3.37	
75	2.5*10 ⁻⁵	3.14				6.34	
75	5*10 ⁻⁵	4.24				5.95	
75	10-4	5.44				7.21	
75	2.5*10 ⁻⁴	7.64				8.21	
75	5*10 ⁻⁴	8.43				7.42	
75	1*10 ⁻³	8.60	10.9			8.12	1.34
75	$2.5*10^{-3}$	9.24				-	
75	5*10-3	9.58	14.65			8.2	1.79
75	10 ⁻²	9.52	7.7			-	
		Sal	t free measur	ements			·
75	0	2.48		2.59	80.8		
100	0	2.26		2.62	125.4		
200	0	2.53		2.89	93.2		
300	0	2.61		2.8	98.4		1
400	0	3.03		2.76	99.9		1
500	0	2.48		2.99	79.37		1
767	0	1.93		2.76	115.7		
1033	0	2.77	33.2	2.8	150.1		1

Table A5 QPVP_65KD_20% in 1-propanol
..Continued

Cp	c _s (M)	M_{app} *10 ⁻⁵	R _{g,app}	R _{fast}	R _{slow}	R _h (nm)	ρ-	
(mg/L)		(g/mol)	(nm)	(nm)	(nm)		ratio	
Salt free measurements								
1510	0	4.03	62.6	2.89	170.6			
2000	0	1.55	13.6	2.67	102.2			
2670	0	2.36	11.6	2.9	129			
3000	0	2.15	19.7	-	-			
5000	0	3.34	38.55	2.81	97.4			
5370	0	3.12	46.55	2.93	182			

c _s (M)	M _{app} *10 ⁻⁵ (g/mol)	R _{g,app} (nm)	R _{fast} (nm)	R _{slow} (nm)	R _h (nm)	ρ- ratio			
With salt measurements									
10-6	1.11		8.99	52.4					
3*10 ⁻⁶	1.64		9.68	46.3					
5*10 ⁻⁶	1.80		9.87	46.6					
7*10 ⁻⁶	2.02				20.6				
9.9*10 ⁻⁶	2.52	37.1			22.75	1.63			
5*10 ⁻⁵	3.66	53.7			27.5	1.96			
9.5*10 ⁻⁵	3. 98	62			28.5	2.17			
5*10 ⁻⁴	4.76	51			25.5	2.0			
9.8*10 ⁻⁴	4.68	45.9			23.9	1.92			
9.8*10 ⁻⁴	4.36	44.4			23.92	1.86			
5*10 ⁻³	4.90	30.8			21.33	1.44			
10 ⁻²	4.65	28.47			20.65	1.38			
Salt free measurements									
0	0.66		6.39	62.1					
0	0.73		4.71	45.4					
0	0.66		4.63	66.33					
0	0.45		3.83	58.92					
0	0.35		2.68	53.83					
0	0.38		2.87	103					
0	0.36		2.53	128					
0	0.31		2.42	131.3					
0	0.33		2.51	114.1					
0	0.37		2.441	189.9					
0	0.34		2.508	180					
	$c_{s}(M)$ 10^{-6} $3*10^{-6}$ $5*10^{-6}$ $9.9*10^{-6}$ $9.9*10^{-6}$ $9.5*10^{-5}$ $5*10^{-4}$ $9.8*10^{-4}$ $9.8*10^{-4}$ $5*10^{-3}$ 10^{-2} 0 0 0 0 0 0 0 0	$c_s(M)$ $M_{app}*10^{-5}$ (g/mol) 10^{-6} 1.11 10^{-6} 1.11 3^*10^{-6} 1.64 5^*10^{-6} 1.80 7^*10^{-6} 2.02 $9.9*10^{-6}$ 2.52 5^*10^{-5} 3.66 9.5^*10^{-5} 3.98 5^*10^{-4} 4.68 $9.8*10^{-4}$ 4.68 $9.8*10^{-4}$ 4.68 $9.8*10^{-4}$ 4.65 10^{-2} 4.65 0 0.73 0 0.35 0 0.35 0 0.35 0 0.31 0 0.31 0 0.37 0 0.37 0 0.34	$c_s(M)$ $M_{app}*10^5$ (g/mol) $R_{g,app}$ (m)Wit salt measure 10^6 1.11 $3*10^6$ 1.64 $5*10^6$ 1.80 $7*10^6$ 2.02 $9.9*10^6$ 2.52 37.1 $5*10^5$ 3.66 53.7 $9.5*10^5$ 3.98 62 $5*10^4$ 4.76 51 $9.8*10^4$ 4.68 45.9 $9.8*10^4$ 4.65 28.47 $5*10^3$ 4.90 30.8 10^2 4.65 28.47 C 0 0.66 0 0.73 0 0.35 0 0.38 0 0.36 0 0.31 0 0.33 0 0.37 0 0.34	cs(M)Mapp*10°5 (g/mol)Rg,app (m)Rfast (m)With salt measurements10°1.118.993*10°1.649.685*10°1.809.877*10°2.029.879.9*10°2.5237.15*10°3.6653.79.5*10°3.98625*1044.6845.99.8*1044.6845.99.8*1044.6344.45*1034.9030.810°24.6528.4710°30.666.3900.664.6300.664.6300.352.6800.352.6800.352.6800.362.5300.312.4200.332.5100.372.44100.342.508	c.(M)Mapp*10*5 (g/mol)R. app (m)R. fast (m)R. slow (m)Wit=sat measurents10°1.118.9952.43*10°1.649.6846.35*10°1.809.8746.67*10°2.029.8746.67*10°2.0237.119.9*10°2.5237.115*10°3.6653.7115*10°3.6653.7115*10°3.9862119.8*10°4.7651119.8*10°4.7651119.8*10°4.6344.41110°4.6528.471110°0.664.6366.3300.664.6366.3300.663.8358.9200.352.6853.8300.362.5312800.362.5312800.312.42131.300.372.41189.900.342.508180	cs(M)Mapp*10° (g/mol)Rgapp (nm)Rfaat (nm)Rslow (nm)Rh (nm)WIFFERENEE10°1.118.9952.43*10°1.649.6846.35*10°1.809.8746.67*10°2.0220.69.9*10°2.5237.122.755*10°3.6653.725.59.5*10°3.986223.925*10°3.98629.5*10°3.98629.5*10°3.98629.5*10°3.98629.5*10°3.98629.8*10°4.6845.99.8*10°4.6364.400.662.8.4700.664.6366.3300.663.8358.9200.352.683.8300.36			

Table A6 QPVP_850KD_35% in 1-propanol

Table A7 QPVP_850KD_35% in water

Cp	c _s	$M_{app}^*10^{-4}$	R _{g,app}	R _{fast}	R _{slow}	R _h	ρ-		
(mg/L)	(M)	(g/mol)	(nm)	(nm)	(nm)	(nm)	ratio		
With salt measurements									
9	9.4*10 ⁻⁶	3.76		4.75	59.27				
9	2.4*10 ⁻⁵	3.09		6.02	57.66				
9	4.8*10 ⁻⁵	5.82		12.83	61.27				
9	8*10 ⁻⁵	10.20	53.88			25.9	2.08		
9	9.2*10 ⁻⁵	8.08	52.06			26.15	1.99		
9	1.8*10 ⁻⁴	12.5	67.93			30.07	2.26		
9	3*10 ⁻⁴	15.60	82			33.15	2.47		
9	4.8*10 ⁻⁴	15.50	88.68			37.15	2.38		
9	7.4*10 ⁻⁴	21.30	88.27			35.27	2.5		
9	7.6*10 ⁻⁴	20.90	91.35			35.88	2.55		
9	8.7*10 ⁻⁴	21.80	96.8			37.52	2.58		
9	1.9*10 ⁻³	25.30	83.59			35.51	2.35		
9	2.9*10 ⁻³	24.50	78.65			34.44	2.28		
9	5*10 ⁻³	26.90	71.01			31.8	2.23		
	1	Sal	t free measur	rements					
4.5		6.30		7.58		82.82			
10.4		3.70		11.53		120.39			
16.6		1.53		4.66		85.2			
21.2		0.78		3.12		100.6			
50		0.93		1.08	31.96	282.6			
81.5		0.72		0.938	42	352.8			
120		0.58		0.855	44.39	317.33			
160		0.53		-	-	-			
200		0.54		0.6	42.5	592.5			
350		0.51		0.49	36.5	610			
500		0.49		0.49	33.93	627.8			
750		1.05	18.3	0.55	46.9	797			