

FOAM FILMS CONTAINING POLYELECTROLYTES OF DIFFERENT MOLECULAR ARCHITECTURES

vorgelegt von

Diplom - Chemiker

Branko Kolaric

aus Belgrad

Von der Fakultät II –Mathematik und Naturwissenschaften

der Technischen Universität Berlin

zur Erlangung des akademischen Grades

Doktor der Naturwissenschaften

(Dr.rer.nat.)

genehmigte Dissertation

Promotionsausschuss:

Vorsitzender: Prof. Dr. R. Schomäcker

Berichter : Prof. Dr. G. Findenegg

Berichter: Prof . Dr. W. Jäger

Tag der wissenschaftlichen Aussprache: 8.11.2002

**Berlin 2003
D83**

CONTENTS

ACKNOWLEDGMENTS	III
ABSTRACT	IV
APENDIX	V
1.FOAM FILMS	1
1.BASIC CONCEPTS	1-2
1.1 PREVIOUS RESERCH	3-5
1.2 INTERMOLECULAR FORCES BETWEEN FILM SURFACES	6-12
2. POLYELECTROLYTES	13
2.1 CLASSIFICATION OF POLYELECTROLYTES	13-14
2.2 POLYELECTROLYTE CONFORMATION	15-18
2.3 SEMI DILUTE REGION AND SCALING CONCEPTS OF LINEAR POLYELECTROLYTES	19-21
2.4 SCALING THEORY OF BRANCHED POLYELECTROLYTES	22-23
2.5 POLYELECTROLYTES WITHIN FOAM FILMS	24-25
3. EXPERIMENTAL PART	
3.1 CHEMICAL STRUCTURES OF POLYELECTROLYTES	26
3.2 CHEMICAL STRUCTURES OF SURFACTANTS	27
3.3 MATERIALS	28-30
3.4 METHODS	
THIN FILM BALANCE METHOD	31-34
VISCOSIMETRY	35
4. RESULTS –LINEAR POLYELECTROLYTES	36
4.1 INFLUENCE OF CONCENTRATION	37-44
4.2 INFLUENCE OF MOLECULAR WEIGHT	45-50
4.3 INFLUENCE OF CHARGE DENSITY	51-55
4.4 INFLUNCE OF SALT	56-57
5. RESULTS –BRANCHED POLYELECTROLYTES	58
5.1 LINEAR PEI	59-60
5.2 BRANCHED PEI	61-62
5.3 INFLUENCE OF MOLECULAR WEIGHT	63-67
5.4 INFLUENCE OF ELECTROSTATICS	68-70
5.5 BRANCHED PEI – SURFACTANT INTERACTION	71-73

6. RESULTS –AMPHIPHILIC POLYELECTROLYTE	74
6.1 INFLUENCE OF PSSH-PEE CONCENTRATION	75-79
6.2 INFLUENCE OF IONIC STRENGTH	80-82
7. SUMMARY	83-85
8. OUTLOOK	86-78
REFERENCES	88-93
BIOGRAPHY	94-95

ACKNOWLEDGMENTS

Those persons who have inspired me, helped me, corrected me and encouraged me during my Ph.D. thesis in the course of time are too numerous to be named. Because of that I will mention here only few people. First I would like to thank my doctor “vater” Regine v. Klitzing for her support and advises during my work.

I am also very grateful to my referees Prof. Findenegg and Prof. Jäger for careful reading of my thesis and fruitful discussion.

Last but not least I would like to thank my wife Ivana and daughter Sandra, for their patience and support during the time I spent to understand and write this manuscript.

ABSTRACT

Polyelectrolytes play an important role in colloid science and are often exploited for their ability to act as colloidal stabilizers as well as flocculants. Since in many applications polyelectrolytes are confined between two surfaces, thus there is a strong impetus for systematic studies of properties of polyelectrolytes and interactions with other molecules in confined space.

The structuring of polyelectrolytes of different molecular architectures in a confined space was investigated and these results are described in this thesis. The confined space was achieved by the incorporation of polyelectrolytes within the foam film core, between two surfactant layers. The basic motivation for this research was to estimate the influence of confinement on the structuring of polyelectrolytes. The investigation of structuring of polyelectrolytes within foam film was performed by thin film pressure balance method (TFPB). From disjoining pressure measurements it was possible to estimate influence of various factors such as molecular weight, molecular architecture, counterions concentration and ionic strength on the structuring of polyelectrolytes within the foam films. Since the foam films were prepared from different surfactants solutions the influence of surfactants on the properties of polyelectrolyte foam films are also estimated. Experimental results have shown that structuring of polyelectrolytes in the confined space is the same as in the bulk and caused by electrostatic interactions between and among chains. The stability of the foam films are determined by interactions between surfactant and polyelectrolytes.

Since proteins and DNA are polyelectrolytes it must be noticed that the understanding a properties of polyelectrolytes in a confined environment is also crucial for understanding a properties of biological systems such as adsorption of proteins, confinement in lamellar phases etc.

APENDIX - ABBREVIATIONS

The most often used abbreviations in this thesis:

CBF - *Common black film*

l_b - *Bjerrum length*

κ^{-1} - *Debye length*

NBF- *Newton black film*

Π - *Disjoining pressure*

PDADMAC-*Poly(diallylmethyl-ammonium chloride)*

PEI 5000 - *Poly(ethylenimine) with molecular weight of 5000*

PEI 25000 - *Poly(ethylenimine) with molecular weight of 25000*

PSSH –b- PEE – *Poly(styrene sulfonic acid-ethylethylene)*

1. FOAM FILMS-BASIC CONCEPT

Foams and foam films are very old subjects in colloid science⁷ which are still a very promising field of research^{7,10,11,28,29,30,40,43,71,76,85,86} because of their importance for many industrial applications. Modern industry use certain properties of the foam in a wide range of applications but a limiting factor for many applications is the stability of the foam films⁸. However in concentrated emulsions the thin films separating the oil droplets are very similar to the foam films¹⁰ which is an additional impetus for the study of the foam film structure. Knowledge about foams is also important for understanding the properties of human and animal lungs on a molecular level.s⁹

A foam is a two phase system in which gas cells are enclosed by a liquids. Foam films present a interface which separates the gas cells^{7,11,12,13} Fig.1.1

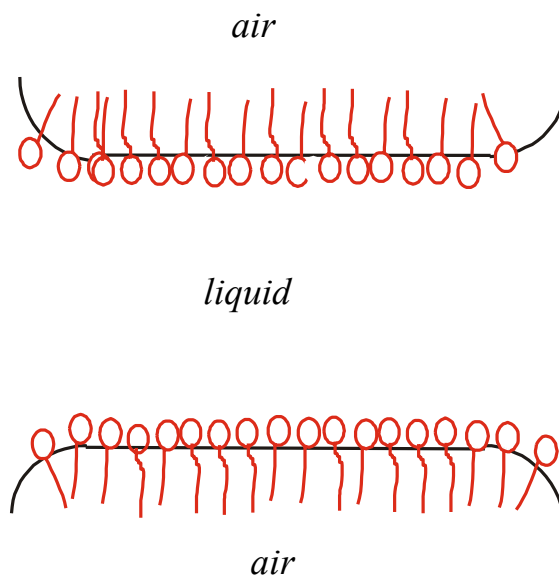


Figure1.1 The schematic model of foam film

The surface of a foam film is covered by surface active molecules known as surfactants^{1,3,4,13} and the film core consists of a liquid. Since the film is in thermodynamical equilibrium with the bulk phase the chemical potential (μ) of the components in the bulk phase and film are equal¹⁴.

The stability¹³ of the pure surfactant film depends on the adsorption of surfactant at the interface. The changes in surfactant adsorption affect drastically the stability of the film but if the film core contains polymers, the stability of the film is additionally controlled by molecular interactions between the polymers and surfactant. Two different equilibrium states of the foam films exist, common black films (CBF), and Newton black films (NBF)^{7,10,11,15}.

The CBF^{7,10,15}, consists of two surfactant monolayers with a water core between them. The CBF is stabilized by electrical double layer forces and the thickness of the film depends on the concentration of electrolyte. The screening of electrical charges by salt induces a decrease in thickness^{7,15}. The thickness of the CBF is approximately between 10-100 nm.

The NBF^{7,10,11,15,16,17} consists of two amphiphilic monolayers which are in contact to each other. Hydration and steric forces are responsible for stabilization of NBFs and the thickness of these films is not sensitive to the electrolyte concentration. The hydration forces become very large when an NBF appears, so that De Fejter and Vries¹⁸ proposed a liquid crystal like structure for NBF. NBFs have been very well investigated^{7,10,11,16,33} but the knowledge about the NBF is still rather poor³³. The thickness of the NBF is between 5-10 nm.

1.1 PREVIOUS RESEARCH

Since the chemistry of foam films is not the major topic of this thesis, only a short overview of the most important discoveries in this field of colloid science is presented in this section.

The formation of foam films is very simple and because of that, they are one of the oldest and most studied systems in colloid science. From the 17th century, up to present day scientists have investigated the properties of foam and foam films^{7,15,19,22,24,28,29,30,66,73,74}. The first recorded study of foam films was given by Hook and Newton^{7,19,26}. Hook and Newton used foam films for the investigation of reflections, refractions, and the colors of light. They were the first who described transitions in the film thickness, from CBF to the NBF. Two hundred years later Reinold and Rucker^{20,26} studied foam films to determine “the radius of molecular action”. They recorded the existence of additional forces between the two layers which appear and become detectable at distances of approximately 50-100 nm. Today in colloid science these forces are known as surface forces.

At the beginning of the 20th century, Johannott and Perin observed and described the phenomenon of stepwise thinning of foam films^{21,22,26} which is called stratification^{22,24}. Until today, many other groups observed and studied stratification in different systems such as surfactant²⁶, emulsion¹², diblock^{27,74} and polyelectrolyte films^{28,29,30,66,71,73,74,86,8599}.

The first attempt to explain the stratification of films was based on the idea about formation of liquid crystal like structure^{24,25} within the foam film.

Since stratification was also observed in films formed from polystyrene latex suspension²³ which has a high surface charge density and suppresses the formation of liquid crystal structures as well as in surfactant solution above the cmc²⁶, it is clear that stepwise thinning is related to the layer by layer destruction of the colloidal structure formed within the film core. In the case of polyelectrolyte films stepwise thinning is related to the structuring of polyelectrolytes^{30,74,86} (Chapter 2).

After Derjaguin developed the first quantitative theory of surface forces today known as DLVO theory which explains the stability of colloids by intermolecular forces (dispersion and double layer forces) which operate between them (section 1.2)³⁵, the interest for foam films increases because foam films present the most simple system for the investigation of colloidal stability^{35,36}. During the seventies many investigations on foam films have been performed by various methods such as, conductivity, thin film balance, ellipsometry and radiochemical methods^{7,31,32}. The thin film balance method was improved by Shedulko^{7,38} and Exerova^{7,11,37} who developed a method for the direct measurement of the film thickness and disjoining pressure (TFPB method).

From ellipsometry and conductance measurements^{7,31,32} a different structure of the film core of the NBF and CBF was observed. The refractive index of the film core and film surfaces were estimated from ellipsometric measurements^{31,32}. However the electrostatic origin of the stability of a CBF was confirmed by many experiments in which the thickness of the films were measured in the presence of different inorganic ions^{7,11,17,30}. The film thickness decreases due to the electrostatic screening of ions at the interface. The origin of the repulsive electrostatic potential between the surfaces of the non ionic surfactant⁷ foam film was explained by Exerova. According to Exerova the repulsive potential is related to the adsorption of the hydroxy ions at the film interface^{7,39}. This explanation is supported by different authors^{7,11,39}.

Today foam films are much more investigated as model systems to study interactions between biologically relevant molecule like DNA, protein and lipids⁵, since they present the most simple bilayer system. The second important application of the foam films is the possibility to investigate the structuring and properties of molecules in confined space, entrapped between two surfactant layers^{26,28,29,30,71}. The stability and properties of these composite systems become important in many technological applications as well as in fundamental research.

The thin film balance method is an unreplacable method in thin film research but today some modern spectroscopic techniques such as Raman microscope spectroscopy^{41,42}, fluorescence microscopy⁴³ and permeability coefficient measurements¹⁵ are used to extract more structural information about molecules within the film core and the film itself.

In the next section the basics of the DLVO theory are shortly described.

1.2. INTERMOLECULAR FORCES BETWEEN FILM SURFACES

The DLVO theory was developed in the forties in order to explain the stability of hydrophobic colloids^{3,4,34}. It assumes that the stability of the system arises from the competition between the repulsive electrostatic interaction between identical charges and attractive van der Waals forces.

Derjaguin was the first who recognized that changes in the interlayer thickness of the thin film between colloidal particles generate a pressure which is different from the bulk value³⁴. This pressure is called the disjoining pressure and the difference is caused by the interactions between interfaces. Derjaguin and Landau linked the disjoining pressure (Π) to intermolecular forces. Theoretical descriptions of intermolecular interactions have been derived from statistical physics. Verwey and Overbeek^{3,4,34,91} presented a similar physical understanding of colloidal stability.

According to the ideas of Derjaguin the disjoining pressure is related to the sum of electrostatic and van der Waals interaction:

$$\Pi_{(h)} = \Pi_{(EL)} + \Pi_{(VW)} \quad (1.1)$$

The electrostatic contribution of the disjoining pressure is generated by charges at the interface. The DLVO theory uses the Poisson-Boltzmann equation³ and the Debye – Hückel theory^{3,4} to describe quantitatively the electrostatic component of the disjoining pressure:.

$$\Pi_{el} = 64n^0kT\gamma^2 \exp(-\kappa h) \quad (1.2)$$

n^0 , κ , h , refer to the bulk concentration of ions the inverse Debye length and the film thickness, respectively

where γ is given by following expression

$$\gamma = \left(\frac{\exp(Z/2) - 1}{\exp(Z/2) + 1} \right) \quad Z = \frac{e\Psi_0}{kT}$$

e is the elementary charge and Ψ_0 is the electric potential at the interface

The van der Waals force is the collective name given to a set of forces characterized by the same power law dependence. In contrast to other forces, the dispersion forces always involve in interactions between molecules or particles. The forces arise from the correlation of charges between particles.

The major parameters which describe the van der Waals interactions are the dipole moment and atomic and molecular polarizabilities. The dipole moment is related to unsymmetrical charge distribution within molecules and the polarizability presents a tendency of the charge distribution to change under the influence of an electrical field. The van der Waals component of the disjoining pressure was calculated by the Hamaker approach^{3,4}. The Hamaker approach is based on pairwise summation of the individual dispersion interactions between molecules. The van der Waals component of the disjoining pressure between two plane parallel surfaces [e.g. two continuous] separated by a vacuum gap of thickness h is given by eq.1.3

$$\Pi_{vdw} = -\frac{A_{12}}{6\pi h^3} \quad (1.3)$$

A_{12} is the Hamaker constant and it is defined by equation 1.4

$$A_{12} = \pi^2 C \rho_1 \rho_2 \quad (1.4)$$

where ρ is the number density of molecules in both continuous phases, C is the interaction constant.

The last equation was improved by Derjaguin. He corrected the van der Waals part of disjoining pressure for the retardation effect^{3,4,34} and the correction of the disjoining pressure is described by eq 1.5

$$\Pi_{vdw} = -\frac{B}{h^4} \quad (1.5)$$

where B is the Hamaker constant corrected for the retardation effect

The origin of the retardation effect is related to the finite velocity of the propagation of electromagnetic interactions. The attraction occurs because the first dipole induces a dipole in the second atom which is oriented in *exactly the same direction as itself*. If in the meantime, the first atom has changed the orientation of its dipole significantly, the correlation between two dipoles will be affected. Since in colloid system the attraction operates over such a large distance, that the finite time taken for the signal to be propagated from one atom to another is significant, that the correction for the retardation effect becomes important.

The shortcoming of the microscopic approach is related to the fact that pairwise additivity of molecular interactions is assumed. This problem is overcome in the macroscopic theory developed by Lifshitz^{3,4,7}, considering the macroscopic bodies as a continuous medium.

Many scientist but especially Langmuir⁴⁴ showed strong disagreement with the pairwise approach, especially because there were a lot of observations that long range attractive interactions could not be explained in terms of DLVO theory.

However the classical DLVO theory explained the stability of liophobic colloids and simple foam films without stratification but the classical approach cannot explain stepwise thinning as well as the stability⁴⁰ of the NBF and the properties of films which contain organic molecules⁴⁰ because the stability of these films is a result of the interplay of double layer forces, dispersion forces and short range molecular interactions (i.e. hydration forces).

NON DLVO APPROACH

The classical DLVO theory considers only dispersion and electrostatic forces. The non DLVO approach takes into account other forces as steric and *structural forces (hydration and supramolecular)* which involve an interactions between molecules^{45,46}.

The total interaction potential between colloids in non classical DLVO theory is described by:

$$\Pi_{tot} = \Pi_{el} + \Pi_{vdw} + \Pi_{nonDLVO} \quad (1.6)$$

The non-DLVO part of the interaction potential is usually related to steric, hydration and supramolecular interactions.

$$\Pi_{nonDLVO} = \Pi_s + \Pi_{hyd} + \Pi_{stru} \quad (1.7)$$

STERIC and ENTROPIC FORCES^{34,44,46}

Steric interactions appear at small separations where electron shells of both molecules overlap Derjaguin was first who described the stabilization of the NBF by steric interaction. He described steric interactions as an “adsorption component of the disjoining pressure“. Recently, the origin of these forces has been explained more precisely⁴⁶.

The steric forces between surfaces include four types of interactions:

Undulation- forces created by undulations of the interface. These forces are inversely proportional to the bending modulus.

Peristaltic- forces generated by peristaltic fluctuations as the two interfaces approach. They are inversely proportional to the compressibility modulus

Head group overlap-stabilization forces between system containing large nonionic head groups. This interaction is very important for films which contain a brush like polymer.

Protrusion-interactions which are related to the molecular scale protrusion of surfactant molecules at the interface.

SOLVATION or HYDRATION FORCES

The molecular ordering of solvent molecules near the interface generate solvation forces. The solvation forces were originally proposed by Langmuir⁴⁷. Simple electrostatic approach could not explain solvation forces because they also occur between uncharged molecules and layers. The solvation forces are partially explained by polarization of solvent molecules near the interface^{45,46,48}.

SUPRAMOLECULAR FORCES^{45,46}

The supramolecular forces are a relatively new class of forces. These forces are related to the structuring (e.g. supramolecular ordering) of molecules within the film core^{26,30,45,98}.

The two most common supramolecular structures which exist within surfactant foam films are bilayers and micelles⁴⁵. The presence of micelles (layering of micelles) within the film core causes oscillations in the force curve. The period of oscillation (ξ) corresponds to the size of micelles (plus screening length)³⁰ and scales with concentration by scaling law $\xi \sim c^{-1/3}$. The exponent -1/3 indicates dense packing of spherical micelles within film core.

Recently DFT theory^{*45} was used to calculate a micellar contribution of supramolecular forces to the disjoining pressure. The simulation confirmed the oscillatory nature of supramolecular forces and showed some possible orientation of micelles within the foam film in spite of the fact that the shape of the simulated curve is far away from experimental observation.

The structuring of polyelectrolytes within foam film also causes oscillation in the force curve and it is described in the Chapter 2.4.

- - density functional theory

POLYELECTROLYTES

2.1 CLASSIFICATION OF POLYELECTROLYTES

During the last forty years, polyelectrolytes have been investigated intensively but still knowledge about their conformations, structuring and interactions with other molecules is rather poor in comparison with neutral analogues^{50,58}. In spite of a relatively poor understanding of polyelectrolytes, industrial applications is enormous and cover almost all segments of human life, e.g. from food to material and pharmaceutical technology^{50,52,56}. Recently, a special design hybrid of polyelectrolytes and inorganic particles promises to yield new materials for molecular electronics, drug delivery and nano technology⁵². In biotechnology polyelectrolyte structures are used for the immobilization of enzymes and everyday the number of possible applications of polyelectrolytes increases^{50,52,83,87}.

The macromolecules which carry covalently bound charged groups^{50,58} (cationic or anionic) and low molecular counterions are called polyelectrolytes. However, every neutral polymer can be transformed into a polyelectrolyte by covalently attaching an appropriate number of ionic groups. A special class of polyelectrolytes are called “polyampholytes”, macromolecules which carry both anionic and cationic groups covalently bound to the polymer chain. Polyelectrolytes are mostly produced by free radical, ionic, stepwise polymerization methods^{50,56,69} as well as by chemical modification of neutral polymers

In analogy to the low molecular electrolytes one distinguishes between weak and strong polyelectrolytes. The distinguish is based on the charge distribution along the polymer chain^{50,58}.

On the basis of molecular architecture polyelectrolytes are divided into⁵⁴:

Linear polyelectrolytes belong to the class of polyelectrolytes where a large number of atoms are connected together in order to make a chain called the backbone. The backbone is linear in a topological sense, but the actual shape of the polymers in solution is quite different. Due to their simple architecture they are used as model molecules in many investigations^{54,58}.

Branched polyelectrolytes are chains which are not linear in a topological sense. However, the physics of branched molecules is less known in comparison with linear analogues^{50,56,63,64,88,89}. Various branched structures are known such as comb, stars, (regular and unregular), H-shaped, super H-shaped polymers and dendrimers^{51,55,56,80,83,84,87}. The dendrimers^{51,56} are macromolecules consisting of a polyfunctional central core covalently linked to layers of repeating units (generations) and a number of terminal groups.

A Special class of polyelectrolytes is presented by *amphiphilic polyelectrolyte*^{56,68}. The conformation and structuring of these polymers is much more affected by the quality of the solvents since the different solubility of the monomer units generates the appearance of polyelectrolyte supramolecular structures in solution.

2.2 POLYELECTROLYTE CONFORMATION

In water^{4,50,58} the polyelectrolyte is dissociated into macroions (charged polymer) and small ions (counterions). The amount of macroions and counterions has to be equal in order to satisfy electrical neutrality of the solution. The charges along the chain generate long range electrostatic interactions along and between polymer chains. The electrostatic interaction depends on the effective charge density per chain which is given by the interplay of formal charge density and counterion density. Since the persistence length* of a polyelectrolyte chain is strongly influenced by long range electrostatic interaction, the polyelectrolyte chains are much more extended than their linear analogues^{50,54,58}. The persistence length* of a polymer chain is the parameter which determines the chain stiffness and it is used to describe the conformation of single polymer chains^{50,54}.

The charges density (formal charge density) of polyelectrolytes are partially screened by counterions. The difficulties in the description of counterions in the vicinity of a polyelectrolyte show that polyelectrolytes cannot be considered as simple combinations of the neutral macromolecules and electrolytes^{50,54}. The behavior of the counterions in the vicinity of polyelectrolytes chains cannot be described satisfactorily by the Debye Hückel theory^{3,4,70} because of the presence of strong electrostatic fields in the vicinity of the chains, even in dilute solution. Energetically, it is much more favorable that a fraction of the counterions is condensed at chains. This so called counterion condensation and has been explained by Manning^{50,57}. The physical background of the counterion condensation is related to the competition between the gain of energy in the electrostatic interaction and a loss of entropy in the free energy. More precisely when the distance between charges is smaller than the Bjerrum length [eq.2.2] for the strongly charged chain the Manning condensation must be taken into account. The Manning theory describes quantitatively and successfully the process of counterion condensation only for DNA and rod like polyelectrolytes^{50,57}. The counterion condensation are investigated with different experimental and

* persistence length – orientational correlation function which describes correlation between two segments of chain

theoretical methods but still many questions are open⁵⁰. Up to date the process of counterion condensation on flexible coils is not described properly on a quantitative level and direct application of the Manning theory should be considered a very cautiously.

The first theoretical model which describes conformation of polyelectrolyte was developed by Flory. The model of Flory describes conformation of a single polyelectrolyte chain.⁵⁸ He described a chain of charged and uncharged units in the dielectric continuum which replace the solvent. The model is not a very realistic one because polyelectrolytes are hydrated in water, and the structure of the hydration shell as well as the interaction between polyelectrolyte and solvent depends on the local solvent structure.

In Florys model the total hamiltonian of the polyelectrolyte isolated chain with N monomers is described as the energy of a neutral chain with corrections for electrostatic interaction eq.2.1

$$H = H_0 + \frac{1}{2} k_B T \sum_{i=1, N} \sum_{j \neq i} \frac{l_B z_i z_j}{|r_i - r_j|} \quad (2.1)$$

where H_0 is the Hamiltonian of the neutral polymer, z is charge, T is the absolute temperature and l_B is the Bjerrum length. The energy of the covalent bond and short range excluded volume interaction are included in the Hamiltonian of the neutral chain H_0 . The Bjerrum length l_B eq.2.2 represents the strength of the electrostatic interactions in the corresponding solvent.

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (2.2)$$

ϵ_0 , ϵ_r refers to the dielectric constant of vacuum and polymer respectively. In water at $T=300K$, l_B is approximately 0.7 nm.

The Flory's theory describes the conformation of one single polyelectrolyte chain. In practice it is difficult to measure the properties of one chain in solution since polyelectrolyte chains start to overlap^{50,59,60} at very low concentrations. The overlapping of chains and the electrostatic interactions between them cause the appearance of mesoscopic ordering (structuring) in solution. De Gennes proposed a model^{59,60} which describes the structuring of the polyelectrolyte in solution.

2.3. SEMI DILUTE REGION AND SCALING CONCEPT OF LINEAR POLYELECTROLYTES

The properties of polymers, charged and uncharged in the semi dilute region is explained by the scaling theory which was developed from Des Cloiseaux^{58,59,60} work. De Gennes extended his concept and developed a theory which describes the properties of polymers at finite concentration^{58,59,60}

The dilute solution is defined as the concentration region in which polymer chains are isolated and do not interact with other chains. In dilute solution, polyelectrolytes have a large overall size and rather stiff local conformation⁵⁸ but when salt is added or the concentration increases, they become more flexible. With increasing polymer concentration the chains start to overlap and the conformation of single chains is strongly modified. (Fig. 2.1). The concentration at which chains start to overlap is called the overlap concentration and is marked with c^* . The critical overlap concentration is very low for long and polyelectrolyte chains.

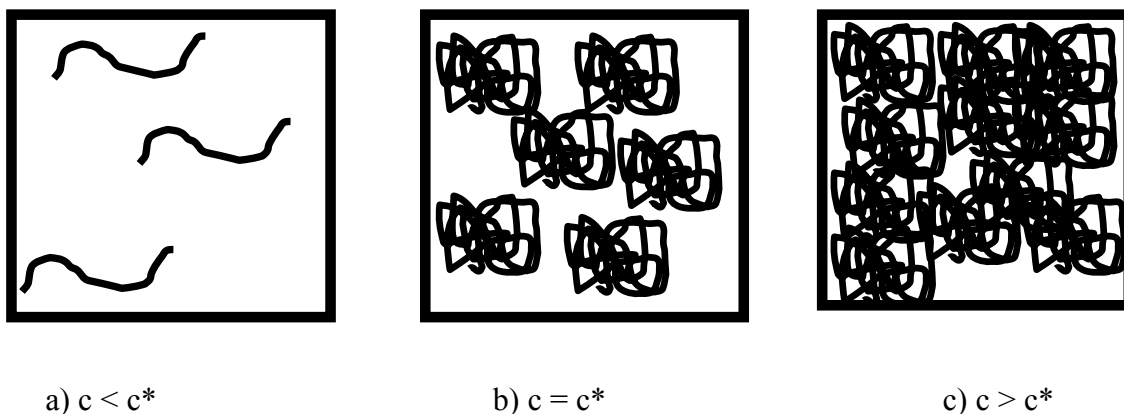


Figure 2.1. Concentration regions of polymer solutions, a) dilute, b) semi dilute and c) concentrated

The semi dilute region, the region which is doubtless more realistic to the experimental conditions presents the main interest of this thesis. In the semi dilute regime above the overlap concentration the structuring of chains begins and de Gennes proposed that at the overlap concentration the chains form an isotropic transient network like structure (Figure 2.2). One chain can be part of different meshes.

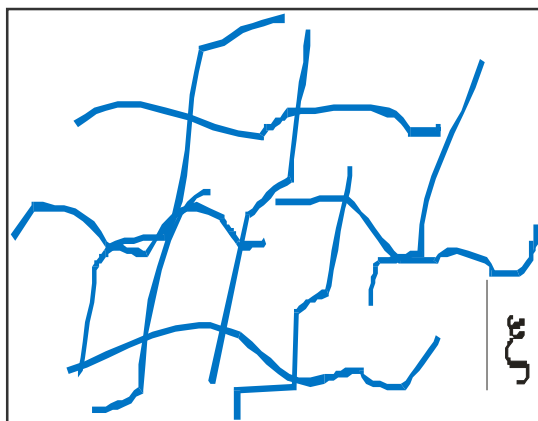


Figure 2.2. The schematic view of the structuring of chains in the semi dilute regime

The correlation length ξ corresponds to the mesh size.

The network of chains could be described as network of blobs^{50,54,58,59,60}. Inside one blobs, the part of the chain of n segments behaves as an isolated chains under excluded volume effect^{50,58}. Outside the blob the chain can be considered as an ideal chain of g ($g = N/n$) segments (g blobs where each blob contains n segments, N represents degree of polymerization)

The correlation length determine the properties of the network, it is related to the monomer concentration :

$$\xi = R_{(0)} \left(\frac{c^*}{c} \right)^{1/2} = \left(\frac{1}{ca} \right)^{1/2} \quad (2.6)$$

a -distance between charges

The correlation length must satisfy the following requirements:

At fixed c , ($c > c^*$), the correlation length must be independent of N (local properties)

Both c^* and R radius of single chain depend on N (degree of polymerization) but ξ itself must not.

This scaling concept was developed for polymer chains in good solvents. In poor solvents the situation is more complicated and attractive interaction can overcome repulsive forces and phase separation can occur^{50,54,59,60}. Result from many experimental investigations (mainly scattering measurement)^{50,58,60} support de Gennes idea of a transient network and the correlation length calculated from experimental results is in good agreement with the theory^{50,60}.

2.4 SCALING THEORY OF BRANCHED POLYELECTROLYTES

The scaling theory is also used to describe structuring of branched polyelectrolyte. In the pioneering work of Zimm and Stockmayer branched polyelectrolytes⁸⁸ were described ideally disregarding any interactions between monomer and taking into account only the branched topology of the macromolecules. A new approach takes into account intermolecular excluded volume interaction and polydispersity of the branched chains^{54,88,89,95}. The branched architecture influences strongly the distribution of counterions which becomes non uniform. Very often electrostatic swelling of branches is determined by the osmotic pressure of the trapped ions inside the branched core^{88,89}.

However scaling approaches for branched polyelectrolyte are more complex in comparison to its linear analogues and more system dependent^{54,88,89}. In our investigations we were interested in a special class of branched polyelectrolytes – irregular branched polyelectrolytes.

In the first approximation these branched polyelectrolytes in semi dilute solution are described as charged colloidal spherical particles^{83,84,87,88,89,95} and structuring of these particles in semi dilute solution is :

$$\xi \sim c^{-1/3} \quad (2.7)$$

The characteristic length is related to the diameter of spheres enlarged by the Debye screening length. The experimental results for irregular branched polyelectrolytes as well as for polydisperse dendrimers⁸⁴ of high generation confirm this model.

The same model describes the structuring of different spherical systems as micelles or particles^{26,30,85,89}.

However, structuring of the irregular branched polyelectrolytes is not investigated as linear analogous and many experiments and theoretical simulations are needed before the structuring of these polymers could be completely described.

2.4. POLYELECTROLYTES WITHIN FOAM FILMS

Since foam films which contain strong polyelectrolytes cannot be formed without surfactants, the interactions between them determine the stability and the final thickness of the foam films^{30,74,86}. The disjoining pressure isotherms of the polyelectrolyte foam films show discrete stepwise thinning commonly referred as film stratification^{27,28,29,30,71,72,73,74,75,76,85,86}. The number of steps increases with polyelectrolyte concentration while the step size and peak height decrease. The observed stepwise thinning of the polyelectrolyte foam film is explained by the oscillatory form of disjoining pressure $\Pi(h)$. At nearly the same time Milling⁶¹ observed oscillatory forces between hard silica surfaces in the presence of poly(styrene sulfonate) without surfactants using AFM. The force oscillation in confined geometry was also recorded by the surface force apparatus (SFA)^{29,30,102}.

The period of oscillations scales with the polyelectrolyte concentration by the same law as the bulk correlation length of polyelectrolytes in the semi dilute solution ($\xi \sim c^{-1/2}$). This exponent suggests that oscillatory forces are closely related to the macromolecular structuring in the bulk and the observed step size is proportional to the bulk correlation length ($\Delta h \sim \xi$). The stratification of the polyelectrolyte foam film is explained by reorganization of the polyelectrolyte transient network within the film core⁷⁴. During the thinning the polyelectrolyte concentration is reduced in comparison with the concentration in surrounding meniscus which induces (attractive) depletion forces between film surfaces.

The electrostatic nature of oscillatory forces was confirmed by different groups^{28,30,61,66,71,86}. The oscillation diminished and vanished with increasing ionic strength because counterions induce screening of charges per chain which destroy the structuring of the polyelectrolytes.

The oscillations in disjoining pressure have also been observed in concentrated micellar solution without polyelectrolyte. In this case the step size is

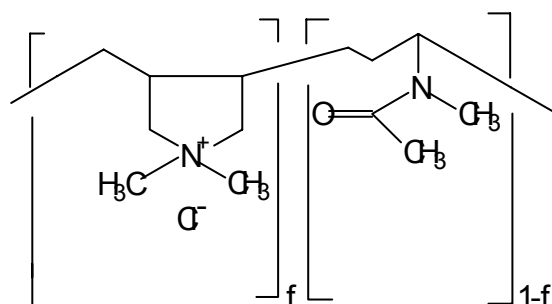
found to be equivalent to the diameter of micelles (plus twice the screening length) and follow the scaling law $f(\xi \sim c^{-1/3})^{26,30}$.

The theoretical investigation⁷⁹ of forces between non adsorbing hydrophobic surfaces immersed in polyelectrolyte solution predicts oscillatory forces with a period which scale with concentration as $c^{-1/3}$ and $c^{-1/2}$ in dilute and semi dilute solution respectively but more theoretical modeling and simulations are needed before the nature of oscillatory forces can be explained.

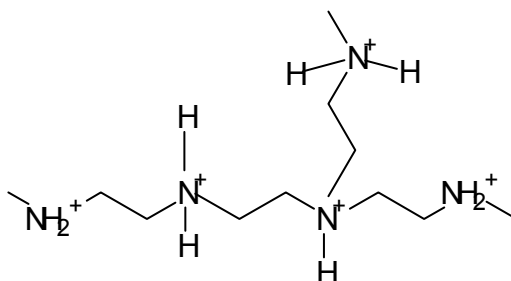
3. EXPERIMENTAL PART

3.1. CHEMICAL STRUCTURE OF POLYELECTROLYTES

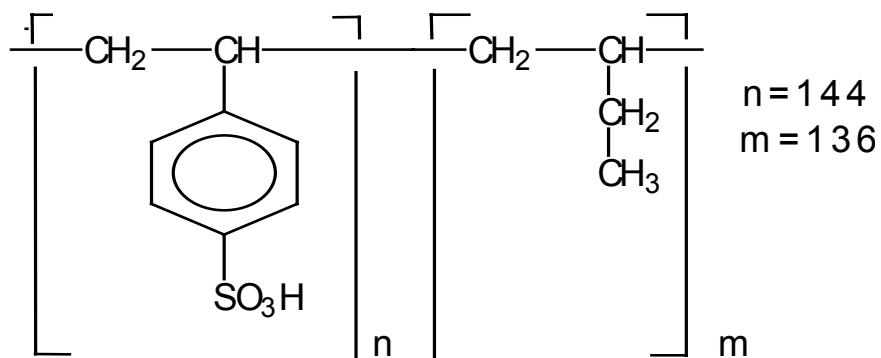
P(DADMAC-*stat*-NMVA)



PEI

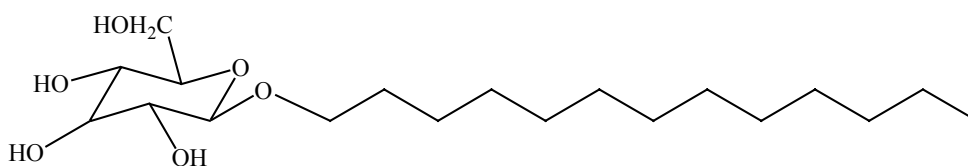


PSSH-*b*-PEE

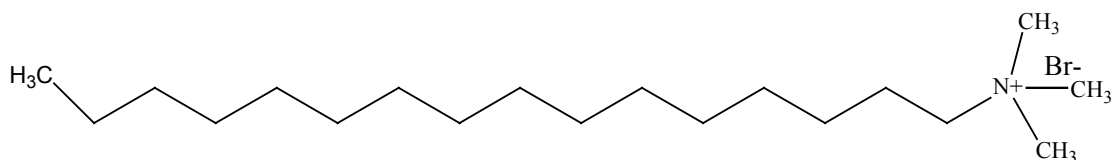


3.2 CHEMICAL STRUCTURE OF SURFACTANTS

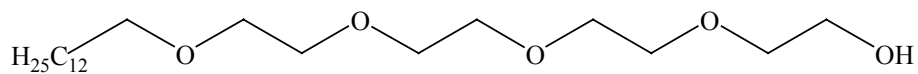
APG1200



C₁₆TAB



C₁₂E₅



3.3. MATERIALS

Polyelectrolytes

P(DADMAC-*stat*-NMVA)

PDADMAC, a strong cationic polyelectrolyte^{50,61,62} with a molecular weight available between 5000 to 709000, was a gift from Dr. W. Jäger (FHI-AP Golm). P(DADMAC-*stat*-NMVA) is a statistical copolymer with a random distribution of positively charged diallyldimethyl-ammonium chloride (*DADMAC*) monomers and neutral monomers of N-methyl-N-vinylacetamide (NMVA). Details about synthesis, purification and characterization of these polymers are published elsewhere^{50,61,62}.

PDADMAC is very often used as a model polyelectrolyte for various investigations in fundamental polymer and colloidal research. The industrial applications of PDADMAC are enormous – from the paper technology, oil recovery, flocculants, to the cosmetic industry^{50,69,87}.

PEI

Poly(ethylenimine) PEI, a weak cationic polybase is available with linear and branch molecular architecture⁶³. The percentage of secondary atoms in the polymer chain is used to describe the molecular architecture of PEI. The PEI was a gift from BASF. The basic character of PEI was determined by potentiometric titration^{63,64}.

The synthesis of the PEI and its various applications have been reviewed from 1969 until the present day^{63,64}. The paper industry and environmental technology are one of the most important consumers of PEI in modern industry. Environmental technology is a relatively new field of PEI application, and it is related with a strong affinity of PEI to anionic materials and heavy metal particles.

In our investigation PEI was used with two molecular weights (5000 and 25000) and two different percentages of secondary N atoms: 100%, and 38%. The PEI with 100 % of secondary atoms corresponds to the linear chain and 38% corresponds to a polyelectrolyte with branched architecture. The PEI was additionally purified in our lab.

PURIFICATION PROTOCOL FOR LINEAR PEI

4 g of linear PEI are dissolved in 80 ml of hot ethanol with vigorous stirring of the solution (15min). A small amount of active coal is added to the suspension during stirring. After 15 min of stirring, the suspension is filtrated by a G 4 glass filter. After filtration, the suspension is evaporated by a vacuum evaporator until 25 % of starting volume remains. The residual is rinsed, between 10-15 times by 150 ml of cold water. During rinsing the sample changes color from brown to white. After rinsing, the residual is dried.

PSSH-b-PEE

The amphiphilic diblock copolymer PSSH-b-PEE consist of a hydrophilic charged block of poly(styrene sulfonic acid and hydrophobick block of poly(ethylethylene). It was a gift from Prof. S. Förster, (Hamburg University). The synthesis and characterization are published elsewhere^{56,68}. The amphiphilic polyelectrolytes belong to the class of “polymeric surfactants” and these are relatively new compounds with a lot potential applications especially in the pharmaceutical industry as drug carriers (drug delivery agents).

Surfactants:

APG –C₁₂/C₁₄ –alkylpolyglycoside, is a sugar surfactant which belongs to the class of non ionic surfactants produced by Henkel Düsseldorf , Germany. This APG is a mixture of alkyl chains with 12 and 14 , atoms, with average critical micelle concentration of 1.7 glycoside units. In all experiments APG was used at a fixed concentration of 0.045g/l.

C₁₆TAB is a cationic surfactant with quarternary nitrogen. This surfactant was purchased from Merck. The critical micelle concentration (cmc) is $1 \cdot 10^{-3}$ mol/l. The C₁₆TAB fixed at $9.2 \cdot 10^{-5}$ mol/l in the presented experiments

C₁₂E₅ is a nonionic surfactant. This surfactant was purchased from Sigma Aldrich. The critical micellar concentration (cmc) is $6.5 \cdot 10^{-5}$ The concentration of surfactant which was used in experiments was fixed at $9 \cdot 10^{-6}$ mol/l.

-

3.4 METHODS:

THIN FILM PRESSURE BALANCE

Thin film pressure balance (TFPB) method is one of the many surface force methods which allow direct measurement of intermolecular interactions between interfaces⁶⁵. It should be noted that only mechanically stable points of the force curve can be measured by a TFPB. The physical principle of the TFPB method and the standard experimental setup are described elsewhere^{7,14,26,45,65}. In this section our experimental setup⁶⁶ is fully described with a short introduction to physics³⁴ and history of the TFPB method⁶⁵.

The TFPB method is used for measuring forces between “liquid” interfaces and this method allows investigations of single foam and emulsion films. A slight modification of the TFPB setup allows the investigation of the solid/fluid/fluid interface by TFPB method^{10, 65,72}.

The TFB method was developed by Mysels⁶⁷ and improved by Exerova^{7,65} for measuring the disjoining pressure within a foam film. The film is formed on the hole (diameter about 1.5 mm) of a porous glass plate. The glass plate is dipped into the film solution and it is connected with the reservoir of constant pressure (atmospheric pressure) by capillary tube. The film holder is placed in a closed metal cell which allows a constant pressure, to be applied using a syringe pump. The scheme of the TFPB is presented at Fig. 3.1

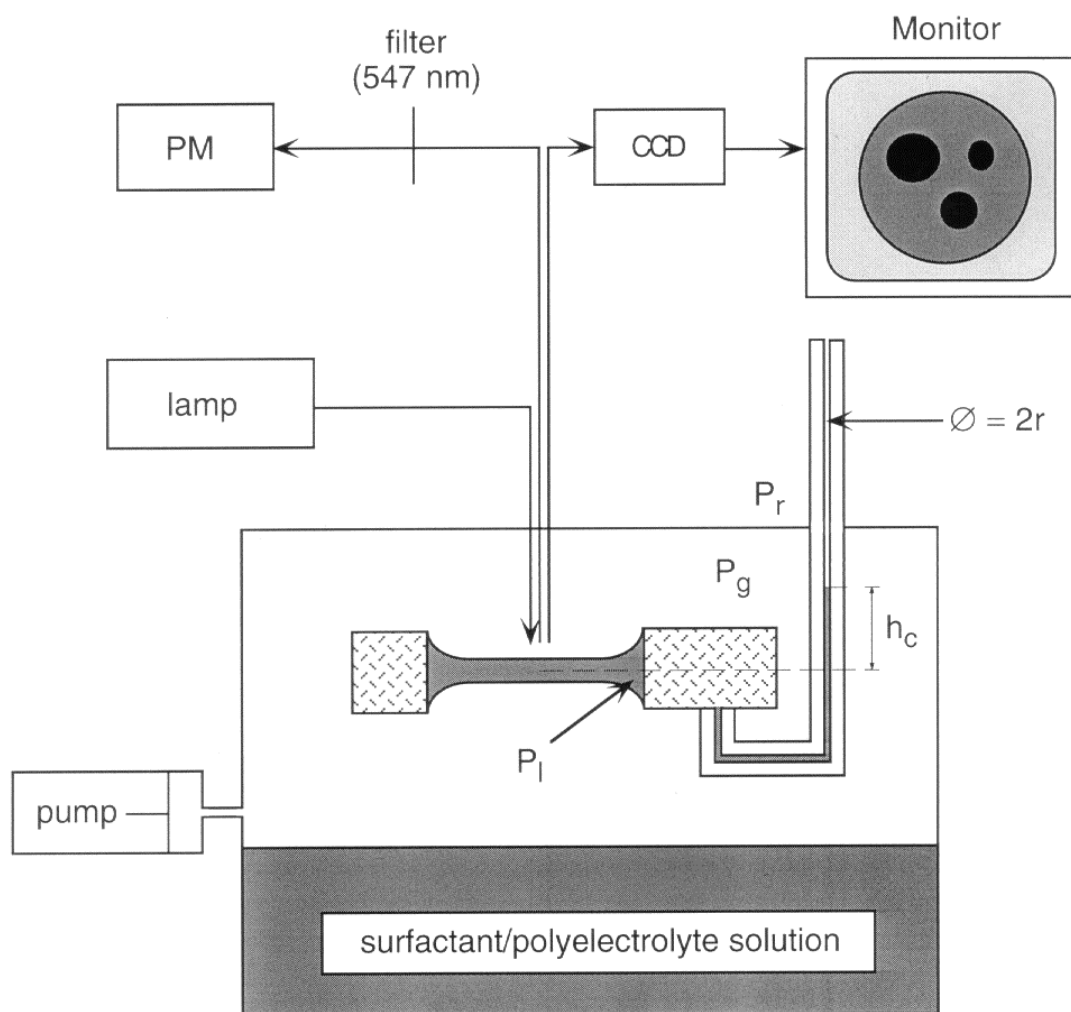


Figure 3.1 The scheme of the experimental set up of TFPB method

The capillary pressure P_c in the film depends on the gas pressure inside the cell P_g and it is changed. During the film drainage, the capillary pressure causes sucking of the film liquid into the Plateau borders³ until the disjoining pressure begins to affect the dynamics of the film. The capillary pressure and the disjoining pressure compensate each other under equilibrium conditions. The disjoining pressure Π is defined by :

$$\Pi = P + \frac{2\sigma}{r} - \rho gh \quad (3.1)$$

where P is defined as the difference between the gas pressure inside the cell and the external reference pressure.

$$P = P_g - P_r$$

σ is the equilibrium surface tension of the solution, r is the radius of the capillary (see the Figure 3.1), $\Delta\rho$ difference between density of the film solution and the surrounding gas, h_c is the height of the solution in the capillary tube above the film and g is the gravitational constant.

The first term in eq. 3.1 is measured by a differential pressure transducer, the second term is the capillary pressure and it is determined from the radius of the tube and the surface tension of the solution. The last term is the hydrostatic pressure, which is determined by the height h_c of liquid in the column. The hydrostatic and capillary correction of the disjoining pressure is very important for low pressures (< 400 Pa).

The film thickness is detected and measured by an interferometric method. The standard optical system consists of a special reflected-light microscope supplied with a Hg lamp which has a heat filter.

The light is focused perpendicularly on the film. After reflection from the film, light passes through a beam splitter, which transmits light to the digital camera and fiber optic probes located in the microscope ocular. At the same time, the light intensity reflected from the film is filtered by a unit consisting of an interference filter which transmits light of a wavelength of 550 nm, magnified and detected by a photomultiplier.

The light waves reflect from the top surface of the film, and interfere with reflected waves from the bottom of the film. The optical path difference between interfering waves generates a phase difference from which it is possible to calculate the film thickness. The Shedulko³⁸ method scales the light intensity reflected from the film with the interference maximum (I_{Max}) and minimum (I_{Min}) and in the case of a symmetric film the film thickness is calculated :

$$h = \left(\frac{\lambda}{2\pi n} \right) \arcsin \left\{ \frac{\Delta}{1 + \left(\frac{4R}{1-R^2} \right) (1-\Delta)} \right\} \quad (3.2)$$

where

$$\Delta = \frac{I - I_{min}}{I_{max} - I_{min}} \quad R = \frac{(n-1)^2}{(n+1)^2}$$

where n is refractive index of the film , and I and λ are the light intensity and the wave length of the light respectively.

In the first approximation the film is homogenous with a refractive index equal to 1.33 (i.e. water). The film is monitored by video camera.

VISCOSIMETRY

The basics of the theory of viscosity and experimental setup are fully described in almost every text book of physical, colloidal and polymer chemistry^{3,4,69,70}. The viscosity in our experiments, was measured using a MICROUBBELOHDE viscometer (Shott, Mainz, Germany) by the Ostwald capillary method. The viscosity is calculated by :

$$\eta = K(t - \theta) \quad (3.3)$$

where is K the capillary constant, and θ the time correction for specific capillary. Viscosity measurements were performed under the ambient condition ,T= 23° C.

4.RESULTS

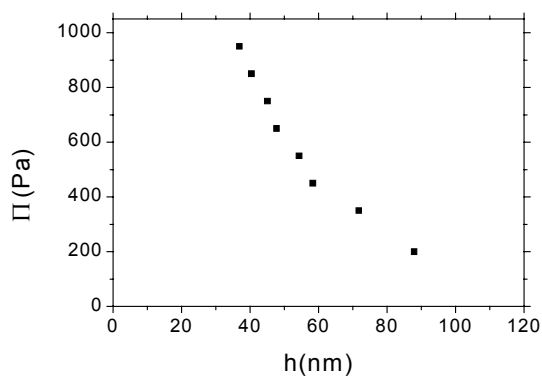
LINEAR POLYELECTROLYTES

Many strong linear polyelectrolytes are often used as model system for different investigations in colloid and polymer chemistry^{28,29,30,50,52,56,59, 61,62, 71,73,} because they have the most simple molecular architecture and all theories of polymer physics are well established for linear chains^{50,59,60}.

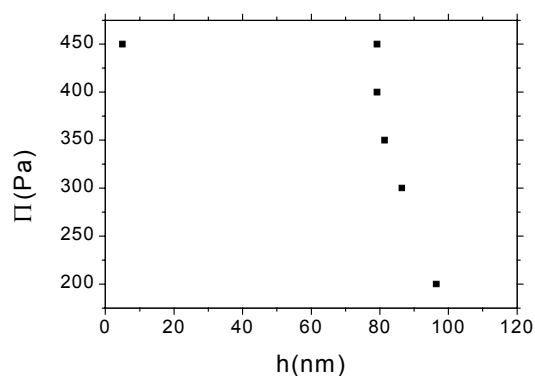
Since PDADMAC belongs to the class of strong linear polyelectrolytes⁵⁰ it was chosen to be the model molecule in our investigation. The structuring of PDADMAC within foam film^{66,73,74} and the possible theoretical models which are used to describe the structuring of linear polyelectrolytes are discussed in this chapter.

4.1. LINEAR POLYELECTROLYTES

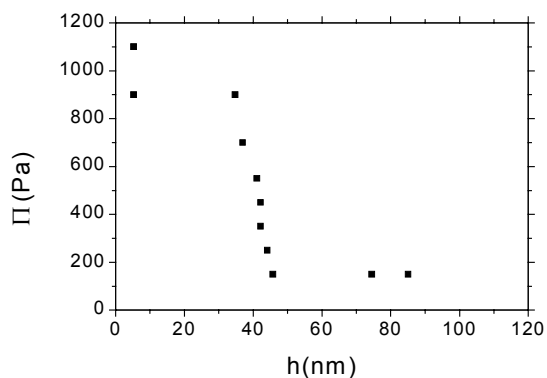
4.1.1. Influence of the PDADMAC concentration on film thickness:



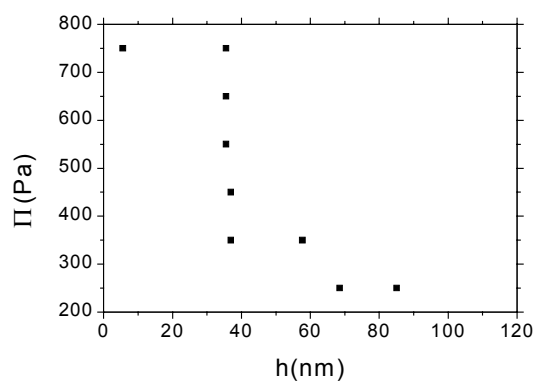
a) $c_p = 5.33 \times 10^{-7}$ mol/l



b) $c_p = 1.33 \times 10^{-3}$ mol/l



c) $c_p = 5.33 \times 10^{-3}$ mol/l



d) $c_p = 2.1$ mol/l

Figure 4.1.1. Disjoining pressure isotherms for a mixed system of PDADMAC and APG as a function of film thickness at different polyelectrolyte concentrations and at a fixed concentration of surfactant (APG) $c_s = 0.0045$ g/l.

Figure 4.1.1. shows the disjoining pressure as a function of the film thickness for the mixture of strong polyelectrolyte PDADMAC and APG. The measurements were done at a low surfactant concentration (ten times below cmc).

Below a certain polyelectrolyte concentration (1.33×10^{-3} mol/l) the isotherms are continuous and look similar to the isotherms of pure surfactant molecules at low concentration. Above a concentration of 1.33×10^{-3} mol/l, the film thins in a stepwise manner. The disjoining pressure isotherms are considered as part of oscillatory pressure curve^{26,30,66,71,74,79}. With increasing of polyelectrolyte concentration the number of steps (transitions) increases and the slope of the isotherms becomes steeper. The steps in film thickness are not reversible and the attenuation explains the irreversibility of the steps⁷⁴. The final thickness of the film corresponds to the NBF. Photos of the film transitions are presented in Figure 4.1.2

-

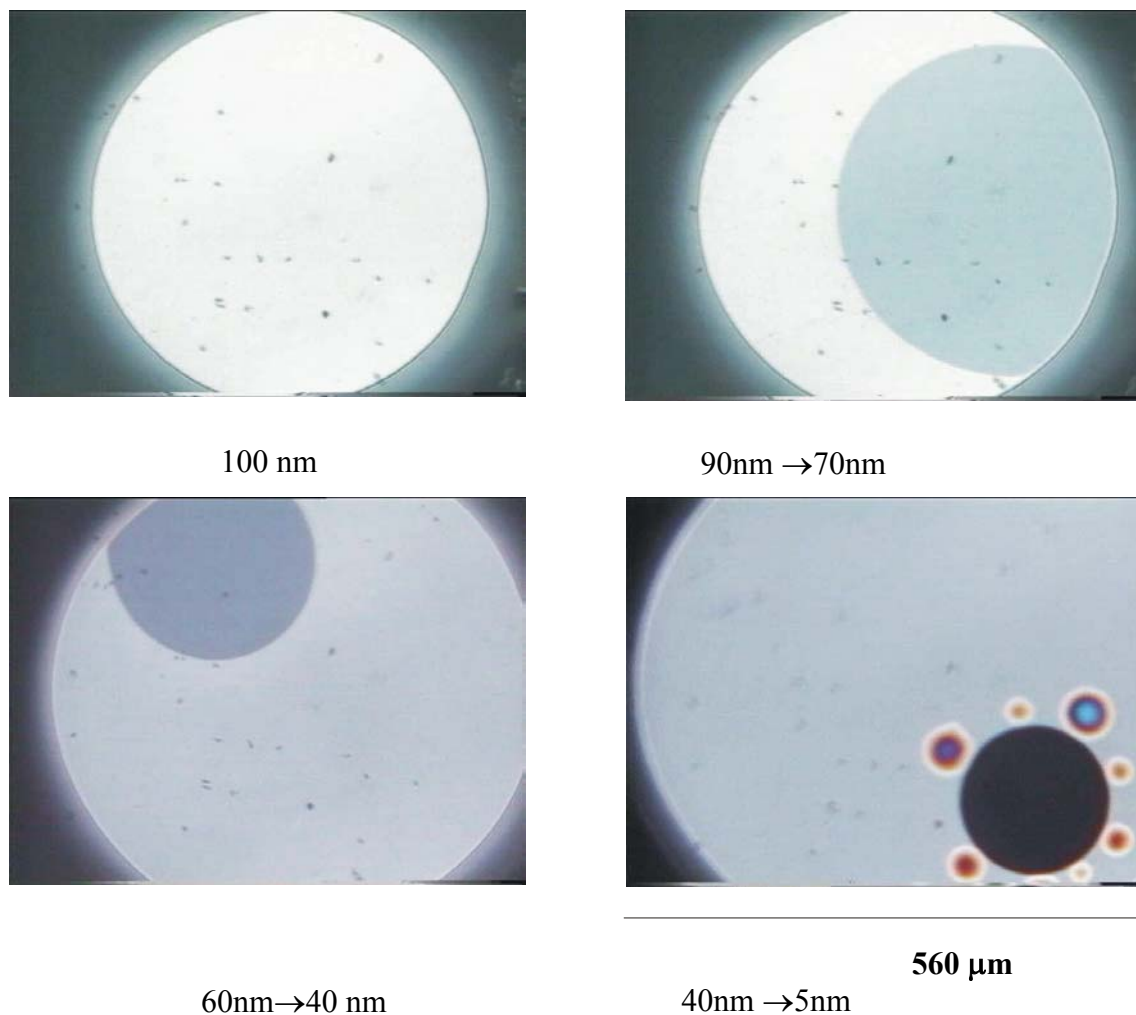


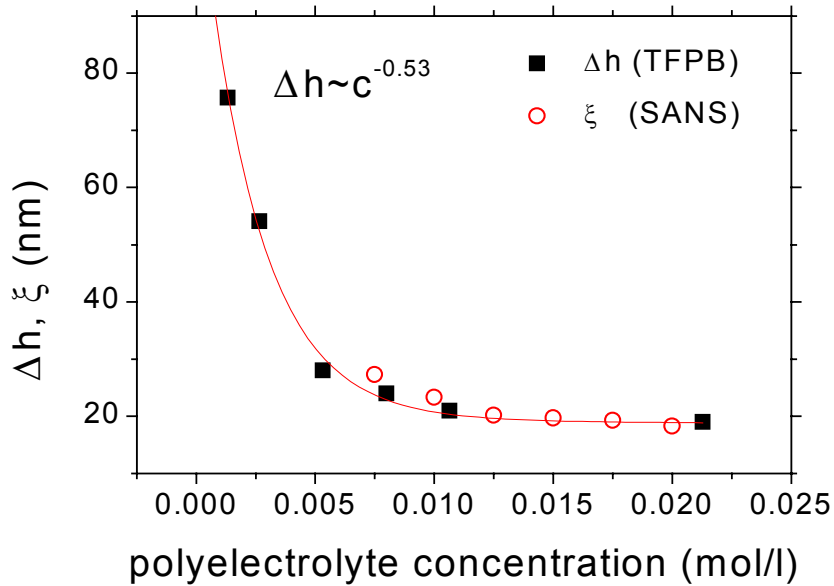
Figure 4.1.2 Snapshots of the film transitions at a polyelectrolyte concentration of $c_p = 2.1 \cdot 10^{-2} \text{ mol/l}$

Figure 4.1.2 shows that the intensity reflected from the film is homogenous and bright before the first jump. A transition starts as darker spot on the bright background and spreads over the whole film after few seconds. When the transition is finished, the whole film is thinner and therefore darker. The foam film can be considered as an interferometer the brighter part of the spots correspond to the thicker film.

Although the NBF is a very stable structure^{7,10,33} in the case of pure surfactant films but in the case of the PDADMAC/APG system, an appearance of the NBF causes the rupturing of the film. The rupturing of the film starts immediately after the last step from CBF to the NBF occurs.

The appearance of NBF indicates the presence of attractive interaction between the film surfaces and PDADMAC. The fact that the NBF appears at high pressure, suggests that at least one chain of polyelectrolyte is located within the film core. Recently, spectroscopic investigations⁴³ of a foam film which contain polyelectrolyte labeled with a fluorescent dye showed that polyelectrolyte is still inside the film core. Further investigation of the NBF for the PDADMAC/APG system was impossible because the film ruptured immediately after the occurrence of black spots.

The size of the steps in the film of PDADMAC/APG changes with the polyelectrolyte concentration which indicates that the steps in the film thickness are caused by structuring of polyelectrolyte chains within the film core^{28,29,30 66,74}. Recently, the stratification of films formed from semi dilute solution of different linear polyelectrolytes^{28,29,30,70,71,73,74,86,99} was detected. Since the step size scales in the same way and with the similar exponent -0.53 with concentration as the correlation length in the bulk (see Figure 4.1.3) it indicates that structuring of the PDADMAC chains within foam film is the same as in the bulk .



4.1.3. The jump size (Δh) and correlation length (ξ) of PDADMAC as a function of polyelectrolyte concentration

Figure 4.1.3 also shows that the correlation length in the solution is similar to the step size in the film which confirms that the structuring of the polyelectrolyte chains is the same in the confined and in the infinite space. The correlation length of PDADMAC in the bulk was measured by the scattering method (SANS) and calculated from the maximum value of structure factor⁷⁴ q_{\max} ($q_{\max} = 2\pi / \xi$).

The schematic presentation of polyelectrolyte structuring within foam films is shown at Fig.4.1.4

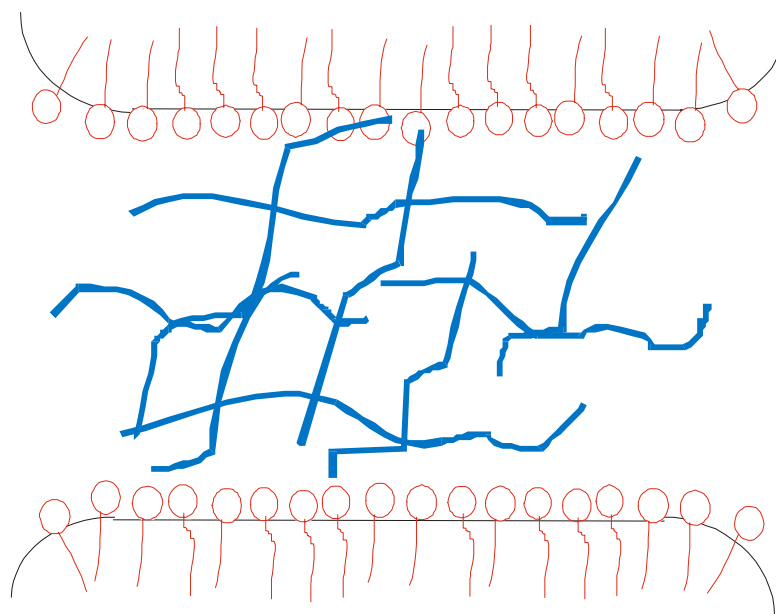


Figure 4.1.4. Scheme of the polyelectrolyte structuring within foam film

Figure 4.1.4. shows the transient network structure of strong linear polyelectrolytes within the film core. It has been noticed that, when polyelectrolytes are located within the film core the step size in the film thickness is not directly related to the molecular length (size) as in the case of colloids and small molecules. The stratification of films containing colloids or small molecules is explained by layer by layer expulsion of molecules or aggregates from the film bulk^{26,46}.

The structuring of polyelectrolytes within the foam film is related to the existence of the same transient network within the film core as in the bulk. The stratification of the film can be described as a process of destroying and rebuilding of transient network structures within the film core⁷⁴. Since the network is transient it breaks down and rebuilds and its reorganization rate is much higher than the resolution time of the TFPB. Up to a certain pressure the network reorganizes itself with n mesh sizes and the polyelectrolyte chains, which do not contribute to the network, are pressed out until the thickness of the film core fits to a $n-1$ mesh size.

Since the film is only a few times thicker than the correlation length in the bulk but this length does not change in the foam film in comparison to the solution it indicates that the film does not present a strong geometrical confinement for polyelectrolytes.

As was mentioned before recently, Milling^{61,74} observed oscillatory forces of a PSS solution entrapped between silica interfaces. The oscillations are related to the structuring of polyelectrolyte since the period of oscillation scales with the polyelectrolyte concentration by a power law with an exponent of -0.48 . This exponent is very similar to the exponent of -0.5 , but Milling explained the oscillation by an ordering of polyelectrolyte coils between silica surfaces. In his model, the jump size is related to the diameter of the coils. Fig .4.1.5

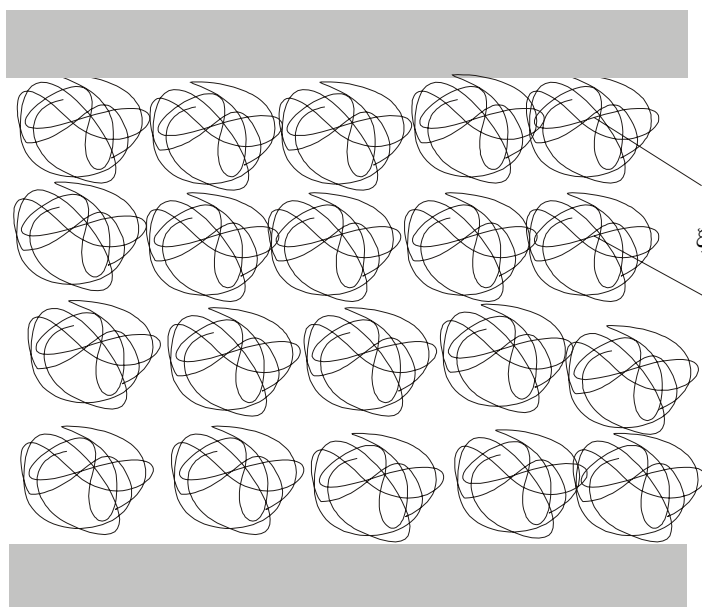


Figure 4.15. The Milling model of structuring of polyelectrolytes in confined space.

The Millings model is in conflict with the widely accepted de Gennes model^{59,60} of polyelectrolytes in semi dilute regions. In order to check the de Gennes model and the idea about the structuring of polyelectrolytes within the foam films, disjoining pressure isotherms of different molecular weights of PDADMAC were measured.

If the Milling assumption is correct, the TFPB method should detect an increase in the step size with an increase in the molecular weights of the single chain. The increase in the step size is a consequence that the radius of the coil (i.e. radius of gyration) depends on the degree of polymerization⁵⁰.

Since non ionic surfactant cannot not produce a stable film with the higher molecular weights of PDADMAC, the cationic surfactant C₁₆TAB was chosen. The repulsion between the surfactant adsorbed at the interface and the polyelectrolyte within the film core makes the physical condition in our experiments similar to Milling's .

As in the case of non ionic surfactant the concentration of C₁₆TAB was very low approximately ten times bellow the cmc. The aggregation of surfactant with polyelectrolyte was not detected by surface tension measurements and it was not expected since surfactant and polymers bear the same sign of charge. The experiments with cationic surfactant offer possibility to investigate the influence of surfactant on properties of the polyelectrolyte foam film

4.2.1. INFLUENCE OF MOLECULAR WEIGHTS

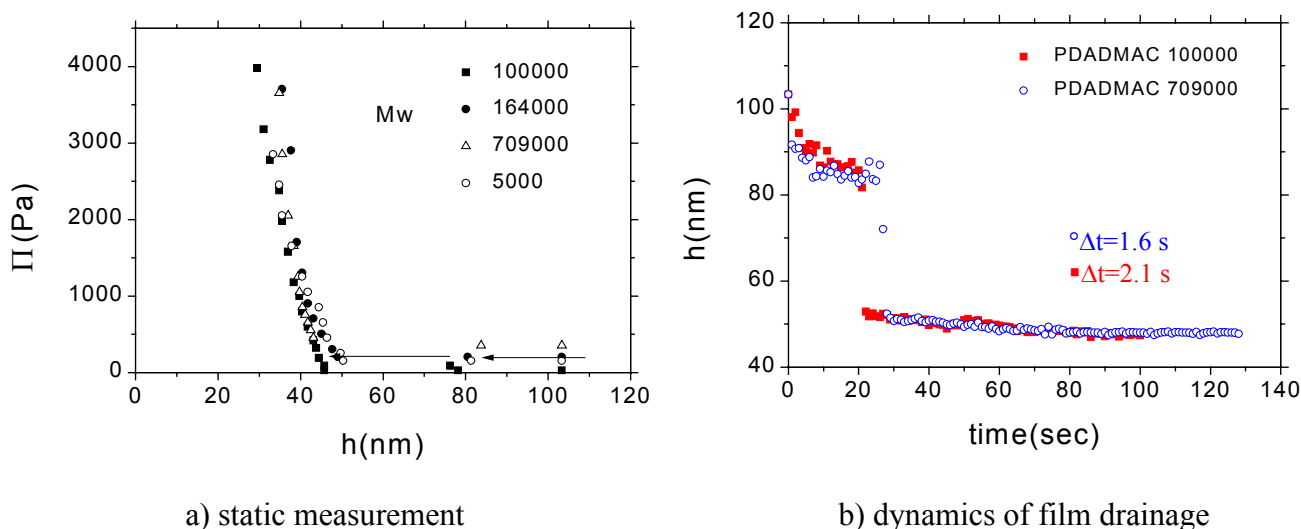


Figure 4.2.2 a) Disjoining pressure isotherms for different molecular weights at a fixed concentration of PDADMAC $c_p = 5.32 \times 10^{-3} \text{ mol/l}$, and at a fixed concentration of $C_{16}TAB$ $9.2 \times 10^{-5} \text{ mol/l}$, b) the drainage of the PDADMAC/ $C_{16}TAB$ foam film as a function of time, Δt -transition time.

The disjoining pressure isotherms for different molecular weights of PDADMAC show almost the same size of steps which indicates that the structuring of PDADMAC within foam films is not related to the molecular mass of single chains⁷⁴. The drainage curves show the same similarity in the thinning process which is again an indication that structures within a foam film are similar for different molecular weights.

An unexpected result is that the structuring of PDADMAC of molecular weight of 5000 has been observed since, the chains are shorter which reduce c^* .

The cause of this structuring is still under investigation and up to date an explanation for it does not exist⁷⁴.

SANS measurements also show that the structuring of PDADMAC in the bulk is independent of the molecular weight of a single chain (Fig.4.2.3).

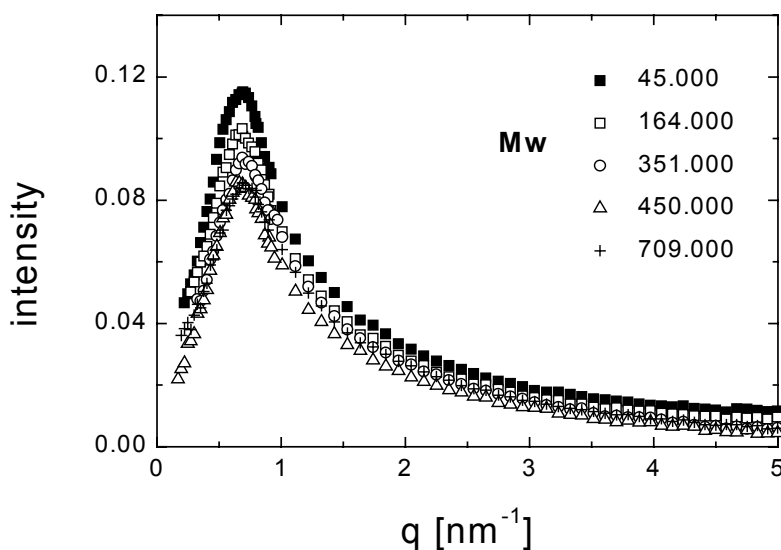


Figure 4.2.3 Influence of molecular weight on the structure peak of PDADMAC at concentration 0.1mol/l (Reprinted with permission of Dr. Regine v. Klitzing).

The SANS curves in Fig. 4.2.3. show a maximum of the structure peak at the same q value for all molecular weights. The polyelectrolyte concentrations are higher than in the TFPB experiments because at lower concentration a correlation peak occurs in the very low q regime where its position is difficult to determine. The peak position is not affected by molecular weight but the peak intensity slightly decreases with increasing molecular weight⁷⁴.

Since the jump size does not depend on molecular weight, it leads to the conclusion that the structuring is not induced by the layering of polyelectrolytes coils. Another model in which the correlation length is independent of molecular weight of a single chain is the de Gennes model of isotropic transient network^{59,60}. The de Gennes transient network model has been confirmed by other authors^{28-30,66,73,74} as the best model which describes the structuring of chains in bulk and film core.

Since disjoining pressure isotherms were measured with different surfactants [C₁₆TAB, APG] it is possible to see the influence of surfactant on the properties of the polyelectrolyte foam films. The disjoining pressure isotherms of PDADMAC with different surfactants are presented on Fig 4.2.4.

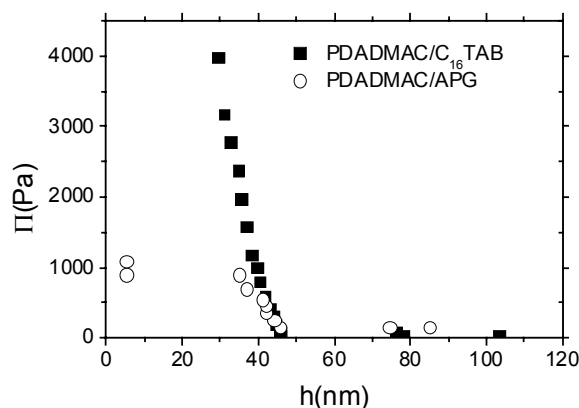


Figure 4.2.4. Disjoining pressure isotherms of PDADMAC with different surfactants, at fixed concentration of PDADMAC at $c_p = 5.32 \times 10^{-3} \text{ mol/l}$ and fixed relative concentration of surfactants ten times below that of cmc.

Figure 4.2.4 shows that the size of the jumps does not depend on the two surfactant APG and C₁₆TAB what confirms that the stratification in the film is only caused by the structuring of polyelectrolyte within the film core.

Differences in the final thickness are caused by different interfacial interactions between surfactant and polyelectrolyte since different surfactants bear charges of different sign on the head of the molecule^{7,74}. It is assumed that the interface of the foam films formed from non ionic surfactants^{7,40} is slightly negatively charged due to adsorption of hydroxy ions at the air/water interface^{7,40}. These ions induce attractive interactions with positively charged PDADMAC and cause the appearance of the NBF⁷⁴. In the case of positively charged surfactant C₁₆TAB, the interface is positively charged and electrostatic repulsion between cationic surfactant and cationic polyelectrolyte stabilize the film and the final thickness corresponds to a CBF. The stabilization of the film is so strong that rupturing of the film only occur at very high pressure (higher than 4000 Pa)⁷⁴.

The assumption that the CBF→ NBF transition is caused by electrostatic interactions between surfactants at the film surface's and polyelectrolytes within

film core was confirmed for different combinations of polyelectrolytes and surfactants (see Table 1).

Table 1. The film thickness as result of polyelectrolytes /surfactants interaction

POLYELECTROLYTES	SURFACTANTS	FILM THICKNESS
PDADMAC-cationic⁶⁶	APG-non ionic	NBF
PDADMAC⁷⁴	C₁₆TAB-cationic	CBF
PSS-anionic²⁹	APG	CBF
PSS³⁰	C₁₂E₅-non ionic	CBF
PAH-cationic⁴³	C₁₂E₅	NBF
PEI-cationic	C₁₂E₅	NBF
PSS^{29,30}	C₁₂TAB-cationic	CBF
PAAS^{29,30}-anionic	C₁₂TAB	CBF
PEI	C₁₂G₂-non ionic	NBF
PEI⁸⁶	C₁₆TAB	CBF

From Table 1 it is possible to see that when repulsion between the film surfaces exist the final thickness of the film corresponds to the CBF. It has been noticed that in the case of complexation of oppositely charged surfactants and polyelectrolytes at the interface such as PSS/DTAB and PAAS/DTAB, the process of charge reversal occurs at interfaces of the foam film. In the case of the DTAB foam films, the film surfaces are positively charged, but after the complexation with PSS due to the charge reversal process, the film surfaces become negatively charged. The electrostatic repulsion between “new” negatively charged surfaces and negatively charged PSS stabilizes the film and the final thickness of these films corresponds to a CBF²⁹. However the strong attractive interactions which appears between oppositely charged polyelectrolytes and surfactants, can also caused the appearance of crystal structures (aggregates) within the foam film^{29,30,76}.

The film thickness can also be changed with increasing the polyelectrolyte concentration. With increasing the polyelectrolyte concentration the counterion concentration also increases what induces the electrostatic screening of charges at the film surfaces. Due to the electrostatic screening the final thickness of the film changes from the CBF to the NBF. This is again proof of electrostatic origin of the CBF→NBF transition.

The final proof that the only electrostatic interactions between molecules at film surfaces and molecules within the film core are responsible for CBF→NBF transition was found in the experiments with the foam films formed from the corresponding surfactant solutions (APG, C₁₆TAB) which contain the monomer of PDADMAC (DADMAC) (see Figure 4.2.5).

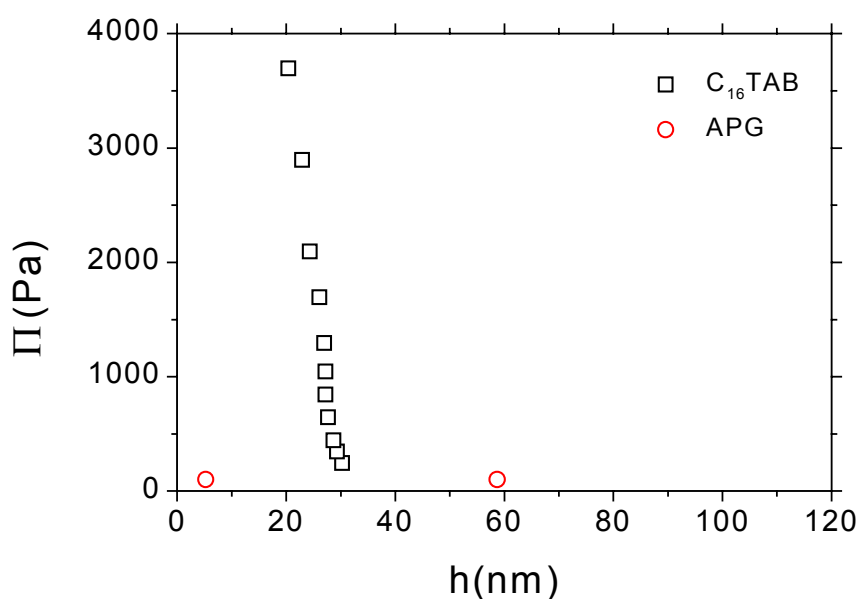


Figure 4.2.5. Disjoining pressure isotherms of DADMAC with different surfactants, at fixed concentration of DADMAC at $c_p = 5.32 \times 10^{-3} \text{ mol/l}$ and fixed relative concentration of surfactants ten times below the cmc.

In the case of mixed system DADMAC/C₁₆TAB the final thickness of the film corresponds to the CBF Figure 4.2.5 and for the system DADMAC/APG CBF → NBF transition is observed. Since the electrostatic interaction between surfactants and DADMAC is the same as between surfactants and PDADMAC, the final thickness of the foam film does not change. The experiment directly

shows that the macromolecular structure has not any influence on the CBF→ NBF transition. This experiment strongly confirms the electrostatic origin of the CBF→ NBF transition.

In order to investigate the influence of electrostatics on the structuring of linear polyelectrolytes within the foam film, the experiments with polyelectrolytes which have different charge density per chain were performed. In the next section the influence of electrostatics on the structuring of polyelectrolytes within the foam film is described.

4.3. INFLUENCE OF CHARGE DENSITY PER CHAIN

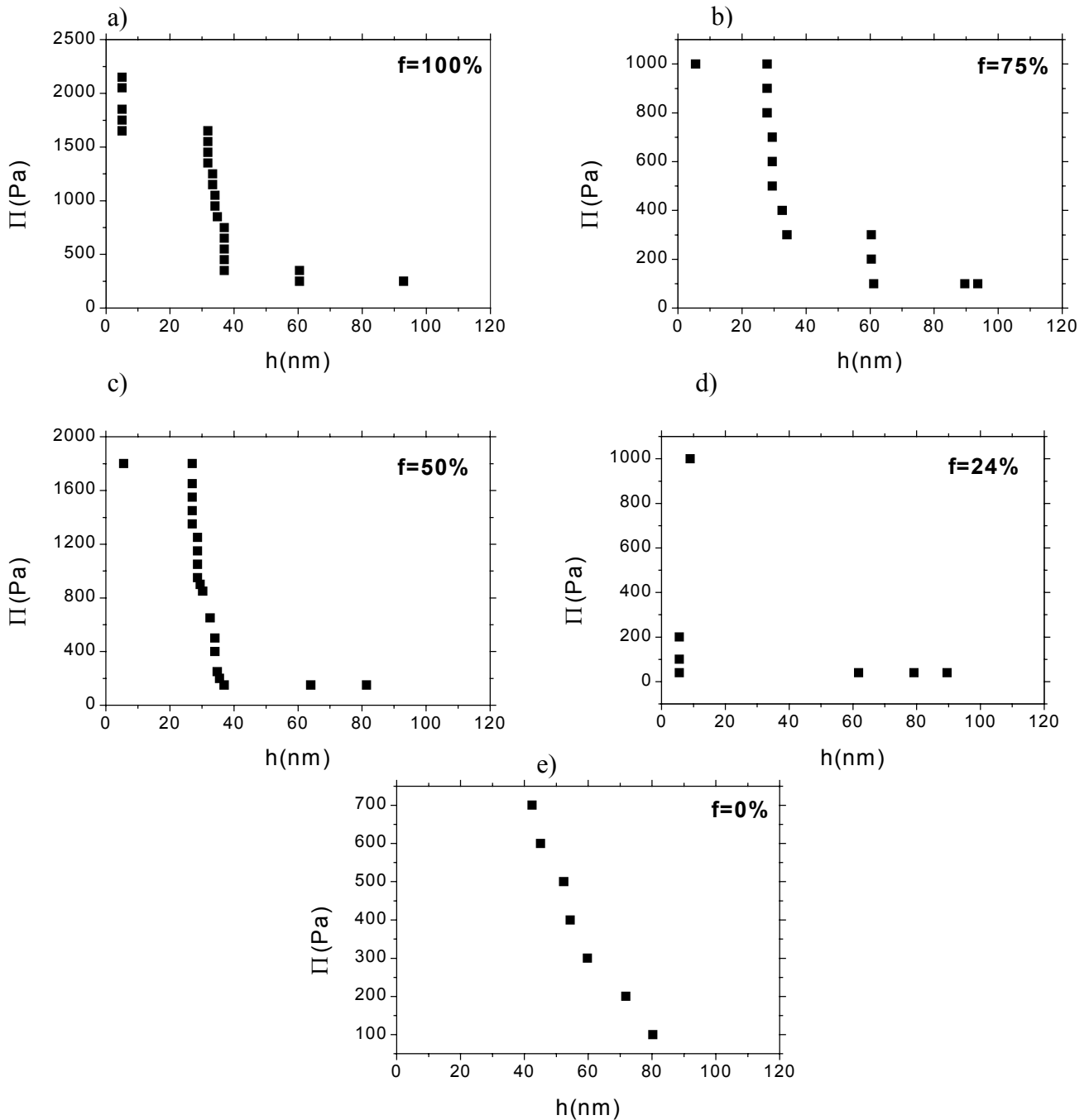


Figure 4.3.1. Disjoining pressure isotherms for the mixed systems of APG and polyelectrolyte at different charge densities f a) 100% b) 75%, c) 50%, d) 24%, e) 0%. The polyelectrolyte concentration is $c_p = 2 \times 10^{-2}$ mol/l, and the (APG) concentration is $c_s = 0.004$ g/l.

The isotherms in Fig 4.3.1 directly show how electrostatic interactions determine the structuring of PDADMAC within a foam film. Differences in stratification are caused by different charge densities at the polyelectrolyte backbone. Above 50% degree of charge disjoining pressure isotherms look relatively similar. At a degree of charge of 24%, jumps are induced at very low pressure and different thicknesses occur simultaneously, (Fig 4.3.2) and the film could not be stabilized before reaching the final thickness⁶⁶. The film containing neutral polymer does not show any jumps in film thickness and ruptures at relatively low pressure⁶⁶.

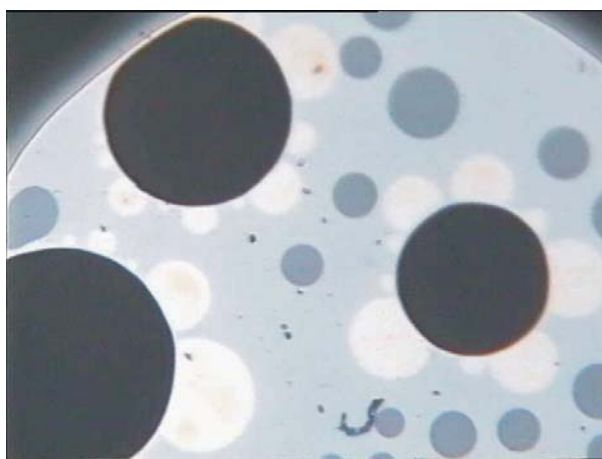


Figure 4.3.2. The Photo of the transitions for the mixed system PDADMAC-NMVA/APG , at a charge density of 24% per polymer chain

In order to check the influence of electrostatic interactions on the structuring of polyelectrolyte in bulk, the viscosity of the polyelectrolyte solution was measured by the Ostwald method (Fig 4.3.3).

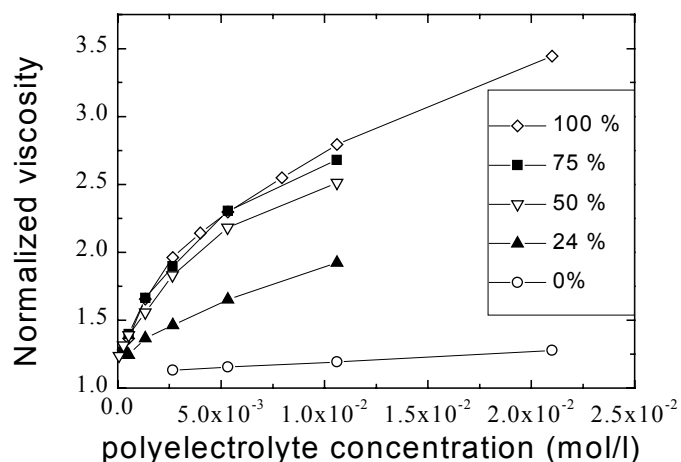


Figure 4.3.3. Normalized viscosity as function of polyelectrolyte concentration at different charge densities.

Figure 4.3.3 shows that the chains with higher charge density have higher viscosity due to more extended conformation as consequence of stronger electrostatic repulsion along and between the chains. The polyelectrolyte chains with a degree of charge between 100% and 50% have similar viscosity which indicates similar structure in the bulk. The viscosity strongly decreases for polyelectrolytes with a degree of charge 24% and for neutral polymer. Since electrostatic repulsion along and between chain decreases with decreasing of the charge density per chain, coiling of chains begins and the structuring of polyelectrolyte becomes less pronounced and diminish for neutral polymer. However, the structuring of polyelectrolyte in the bulk is affected by electrostatics in the same way as structuring in the foam film⁶⁶.

Disjoining pressure isotherms and viscosimetric curves show that electrostatic repulsion along and between chains is the decisive factor which determine the structuring of PDADMAC in confined and infinite space. The electrostatic origin of the polyelectrolyte structuring within the foam film is confirmed by different groups^{28,29,30,71}. In order to describe more quantitatively the influence on electrostatics, the distance between two charges per polyelectrolyte chain is calculated (Table 2).

Table 2. Nominal and effective charge density for PDADMAC

f_{nominal}	$A(\text{\AA})$	l_b/A	f_{eff}
1.00	3.8	1.87	0.53
0.75	5.1	1.39	0.53
0.5	7.6	0.93	0.5
0.24	15.2	0.47	0.24

The values presented in Table 2 show that the distance between two monomers of PDADMAC with a degree of charge of 100 % at room temperature is smaller than the Bjerrum^{50,58} length and in this region the condensation^{50,57,76} of counterions must be taken into account. Taking the Manning condensation into account, the effective charge per monomer (f_{eff}) becomes smaller than the nominal charge (f_{nominal}).

P(DADMAC-*stat*- NMVA) with a degree of charge between 50 – 100 % has a distance between the two charges smaller or similar to the Bjerrum length, which indicates that the effective charge on the chain and the amount of uncondensed counterions are almost constant in this region. The similarity between the effective charge and amount of uncondensed counterions leads to the formation of films which have similar thicknesses and step sizes. The viscosity measurements show that in this region P(DADMAC-*s*-NMVA) has also a similar viscosity. When the distance between neighboring charges is larger than the Bjerrum length, electrostatic interaction significantly decreases and the structuring of the polyelectrolyte becomes “softer” and disappears for neutral chains.

Scattering experiments^{74,77} in semi dilute polyelectrolyte solution confirm that a correlation length above the condensation threshold is independent of charge density.

Another possibility to change electrostatic interaction along and between polyelectrolyte chain is to screen them with salt. In the next section the influence of salt (NaCl) on the structuring of PDADMAC is described.

4.4. INFLUENCE OF SALT

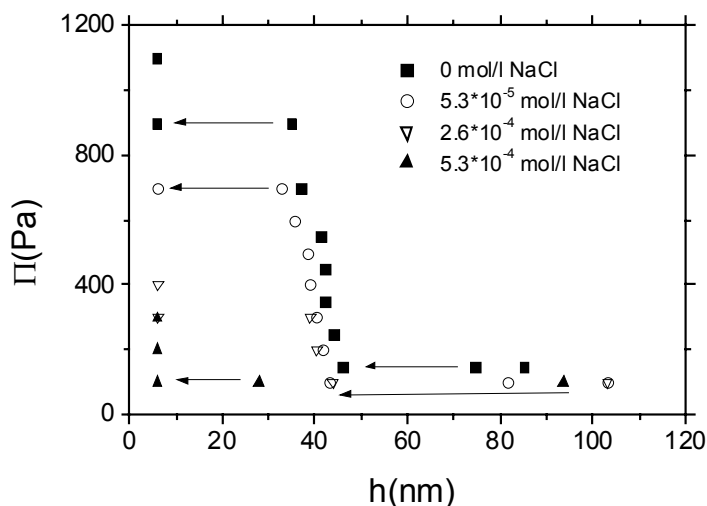


Figure 4.4.1. Disjoining pressure isotherms for mixed systems of PDADMAC/APG at different NaCl concentrations. The polyelectrolyte concentration is $c_p = 5.32 \cdot 10^{-3}$ mol/l, and the APG concentration is $c_s = 0.004$ g/l.

Figure 4.4.1 shows that the increase in salt concentration causes a decrease in the pressure needed to induce a transition in film thickness. At higher salt concentration ($5.32 \cdot 10^{-4}$ mol/l) the jumps are induced almost at the same time and on very low pressure. The film thickness at these concentrations can not be stabilized.

In order to check the influence of salt on the structuring of PDADMAC chains in the bulk the viscosity of aqueous PDADMAC solution is measured in the presence of different concentrations of salt (Fig 4.4.3.)

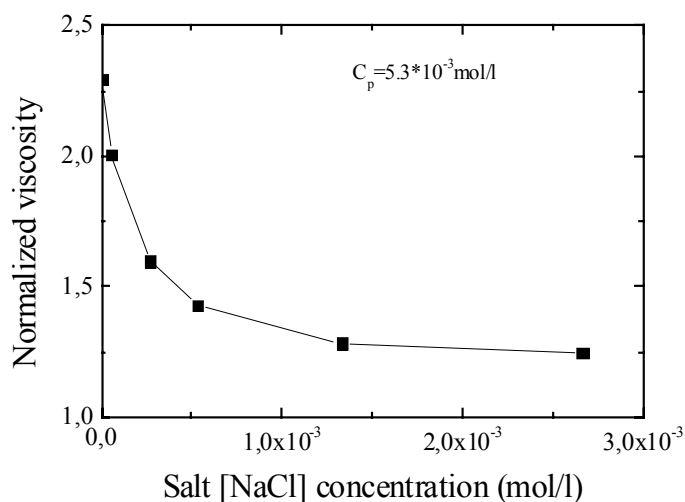


Figure 4.4.3. The normalized viscosity of PDADMAC/APG as a function of salt concentration

Figure 4.4.3 shows the viscosity of PDADMAC as function of the NaCl concentration. The viscosity decreases as the concentration of salt increases.

The results from viscosimetric and TFPB measurements in the present of salt can be explained by the fact that the addition of salt screens the charges along the polyelectrolyte chains and induces a decrease in electrostatic repulsion along the chain and therefore a coiling of the chains start. The screening of charges reduces electrostatic interactions between neighboring chains which causes destruction of the structuring of polyelectrolyte chains within the foam film and in the bulk. Theoretical investigations of polyelectrolytes in poor solvents predict this kind of transition⁷⁸ but a similar model can be applied to the present situation of constant monomer density and high salt concentration. The experiments with the TFPB method show that the steps in film thickness are induced at a lower pressure than in the salt free case which is in good agreement with theoretical calculations of forces between surfaces immersed in polyelectrolyte solution at different salt concentrations⁷⁹.

Nevertheless, experiments with different degrees of charge per backbone and with salt (NaCl) strongly clarified that electrostatic interaction is responsible for the conformation and the structuring of the polyelectrolyte chains in the bulk and within foam films.

5. RESULTS

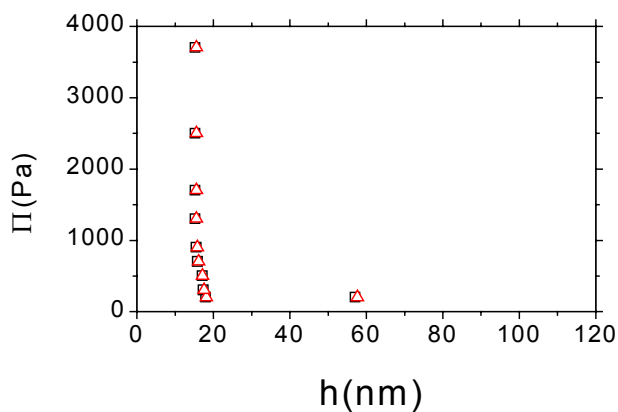
BRANCHED POLYELECTROLYTE

Since weak polyelectrolyte (PEI) was easily synthesized with different molecular architectures (linear and branched) it is chosen as model molecule in our investigation. The structuring of the branched PEI and the influence of molecular architecture on structuring of polyelectrolytes within the foam film is presented in this chapter. In the last section of the Chapter 5, interactions between branched PEI and surfactants are described as well as the influence of these interactions on the properties of the foam films.

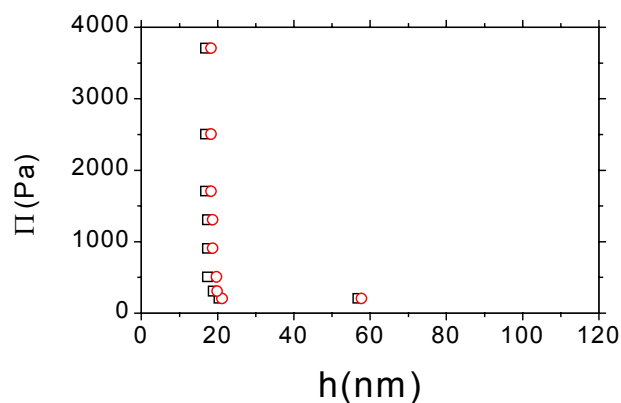
The foam films were formed from solutions of cationic surfactant (C₁₆TAB), because it forms very stable films with PEI.

5.1. LINEAR PEI

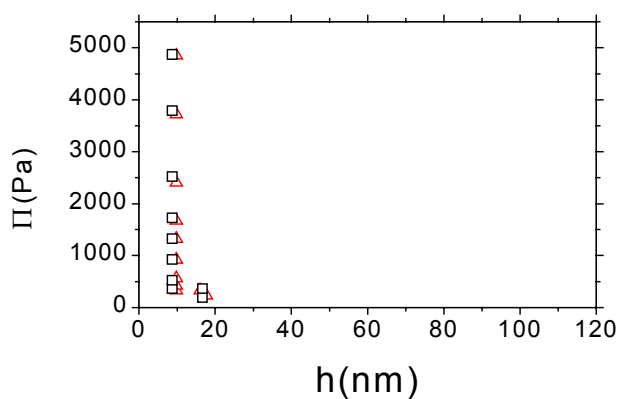
5.1. Influence of pH and PEI concentration on film thickness



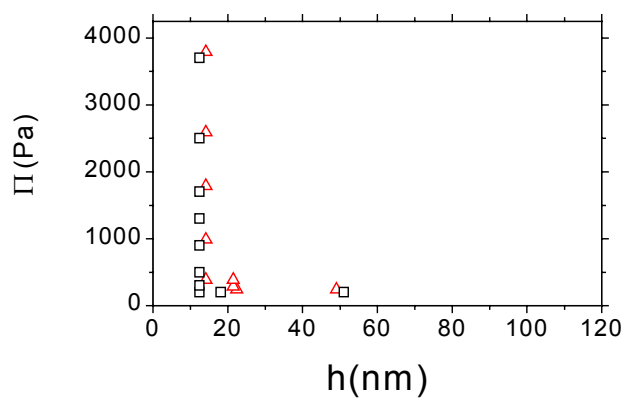
a) $c_p = 0.0212$ mol/l, pH 2-2.5



b) $c_p = 0.0212$ mol/l, pH 4-4.5



c) $c_p = 0.34$ mol/l, pH 2-2.5



d) $c_p = 0.34$ mol/l, pH 4-4.5

Figure 5.1.1 Disjoining pressure isotherms for a mixed system of linear PEI5000/ $C_{16}TAB$ at different polyelectrolyte concentrations and a fixed surfactant concentration ($C_{16}TAB$) is $c_s = 9.2 \cdot 10^{-5}$ mol/l.

Fig 5.1.1 shows the disjoining pressure isotherms for two different concentrations at two different pH values. The isotherms show stratification of the film and the number of steps increases with increasing the polyelectrolyte concentration, which is interpreted as a consequence of structuring of linear PEI within the film core. As the pH decreases the number of steps also decreases. The final thickness of the films corresponds to very thin CBF. The measurements were done at these pH values since at higher pH values the PEI becomes neutral^{64,75} and insoluble in water because of hydrophobicity of the polymer backbone. The solubility increases with increasing electrostatic repulsion along and between chains during the protonation of the imino groups at the polymer backbone. At pH 4 the PEI is fully soluble in water and has approximately a degree of charge of 61%⁸⁶. The degree of charge of 61% at pH 4 corresponds to an effective charge density, since the formal charge density per chain is partially screened by acid (e.g. chlorine ions).

The step size of the transition scales with polymer concentration again as $(\Delta h \propto c^{-1/2})$ ⁸⁶ and it was expected from previous investigation. When the pH value decreases (pH 2) more counterions are introduced in the solution and screening of the formal charge increase. At a value of pH 2 linear PEI has a lower charge density (59%)⁸⁶ than at value of pH 4 due to the concentration of counterions. The electrostatic repulsion along and between chains decreases, the structuring becomes more “soft” and the amplitude of the oscillatory force is reduced. That means that the effect of increasing ionic strength becomes more important for structuring than the influence of increasing charge density. The influence of pH (e.g. additional counterions) on the structuring of PEI is the same as the influence of salt on the strong polyelectrolyte as PDADMAC. These results confirm again that electrostatic repulsion is a decisive force in determining the structuring of linear polyelectrolytes within foam films.

In the next section the structuring of branched polyelectrolyte within foam film is described .

5.2 BRANCHED PEI

5.2.1 Influence of concentration of branched PEI 5000

on film thickness at pH4

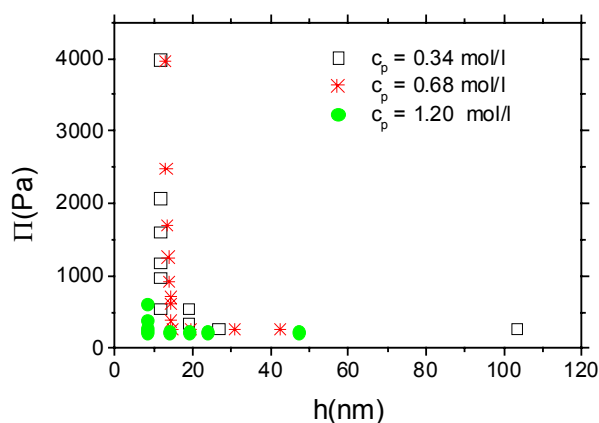


Figure 5.2.1 The disjoining pressure isotherms of a mixed system of PEI5000/ $C_{16}TAB$ as a function of film thickness and different polyelectrolyte concentration and fixed concentration of surfactant $c_s = 9.2 \times 10^{-5}$ mol/l.

Figure 5.2.1. shows stratification of the film containing branched polyelectrolyte. With increasing the polyelectrolyte concentration, the number of steps increases as in the case of the linear polyelectrolyte. The film thickness slightly decreases at highest polyelectrolyte concentration but it still corresponds to the thin CBF. The appearance of a CBF was expected before because of the strong electrostatic repulsion between cationic surfactant at the interface and cationic branched polyelectrolyte.

At pH 4 the degree of charge of branched PEI is 74%, and the branched PEI is described as a charged colloidal spherical particle^{83,88,89} in the bulk solution. In analogy to this model the structuring of the PEI within the foam film can be described as a layering of spherical particles within the film core^{26,30,86}.

The stratification is caused by expulsion of layers of spheres from the film core^{26,30,86}. A similar model is used to describe the stratification of the foam film containing spherical micelles of surfactant molecule and diblock copolymers within the foam^{26,30,85} film. Since the structuring of branched polyelectrolytes is described as layering of colloidal spheres, the size of the jump has to be related to the characteristic length in the bulk solution³⁰. For spherical charged particles characteristic length is related to the diameter of the particles enlarged for screening length ($D_{\text{car}} = d_{\text{par}} + 2\kappa^{-1}$). Since diameter of particles is related to the degree of polymerization, the influence of the molecular weight on the structuring of branched polyelectrolyte was expected.

In order to clarify the presented model which describes the structuring of branched polyelectrolyte within the foam film, as well as to determine the influence of molecular weight on the structuring of branched polyelectrolytes within foam film, the foam films with higher molecular weight of PEI have been prepared.

The influence of molecular weight on the structuring of branched polyelectrolyte is described in the next section.

5.3 INFLUENCE OF THE MOLECULAR WEIGHT

5.3.1. Influence of concentration of PEI 25000 on film thickness at pH4

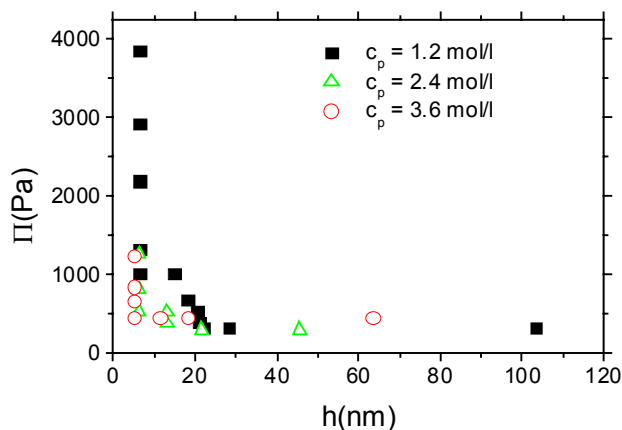


Figure 5 3.1. The disjoining pressure isotherms of a mixed system of PEI 25000 /C₁₆TAB at pH 4 as function of film thickness at different polyelectrolyte concentrations a) $c_p = 1.2$, b) $c_p = 2.4$, c) $c_p = 3.6$ and at a fixed concentration of surfactant C₁₆TAB $c_s = 9.2 \times 10^{-5}$ mol/l.

In order to measure the influence of the polyelectrolyte concentration on the structuring of branched polyelectrolyte with higher molecular weight, disjoining pressure isotherms were measured at these high concentrations because at lower concentrations only one step is detected. As the polyelectrolyte concentration increases, the number of steps also increases due to the structuring of branched polyelectrolyte within the film core. The thickness of the film decreases with increasing polyelectrolyte concentration and at higher concentrations the film thickness corresponds to the NBF. The observed NBFs are very stable and the rupturing of the films occurs at relatively high pressure. Since the branched PEI is almost fully charged at pH 4 (74 %) ⁸⁶ and bear the charges of the same sign as the C₁₆TAB, the appearance of the NBF at pH 4 is related to presence of additional counterions in the film solution.

In order to achieve pH 4 at higher polyelectrolyte concentrations, the amount of acid which is added to the polyelectrolyte solution increases and these additional counterions induce reduce electrostatic repulsion with cationic surfactants at the film surfaces which cause occurrence of a NBF. The occurrence of the NBF at these high polyelectrolyte

concentrations confirm our assumption (Chapter 4) that CBF \rightarrow NBF transition is caused by the reduced electrostatic repulsion between the film core and the film surfaces. The disjoining pressure isotherm for two molecular weights are presented in the figure 5.3.2.

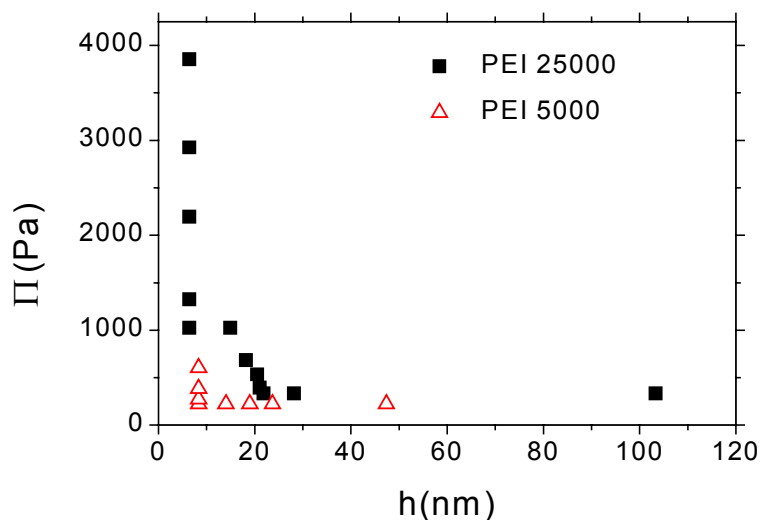


Figure 5.3.2 The disjoining pressure isotherms of a mixed system PEI / C₁₆TAB for two molecular weights 5000 and 25000 as function of film thickness at pH 4, the polyelectrolyte concentration is $c_p = 1.2 \text{ mol/l}$ and the surfactant concentration is $c_s = 9.2 \times 10^{-5} \text{ mol/l}$.

Figure 5.3.2 shows that the number of steps increases with decreasing molecular weight and the size of the jumps are smaller for higher molecular weight. This is due to a smaller diameter of the molecules at higher molecular weight. The structuring of spherical particles within the foam film^{23,26,30,86} regardless their internal structure (colloid, polymeric or surfactant) is described by the same model.

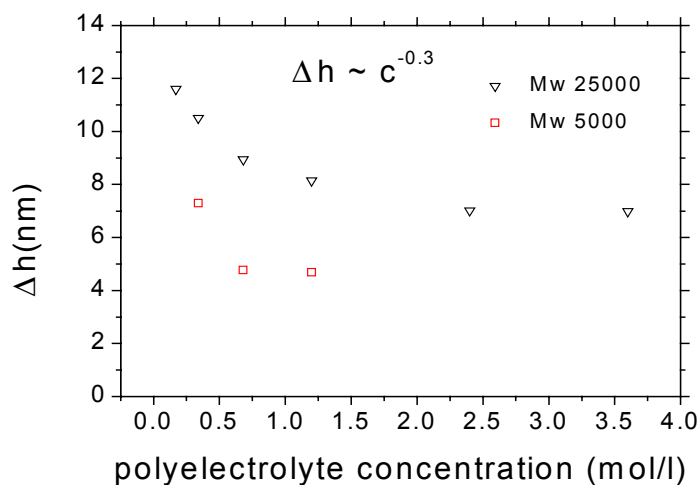


Fig. 5.3.3 The size of the steps as a function of PEI 38% concentration at pH 4.

Fig 5.3.3. shows that the size of the jump of branched polyelectrolyte scales with concentration with exponent (-0.3). This exponent is similar to the exponent -0.33 which confirms that the stratification of the film is caused by structuring of spherical particles inside the film core. As was mentioned before (Chapter 2.) an power law concentration dependence of 1/3 is indication of close packing of charged spherical particles within the film core.

From the results presented in sections 5.2 and 5.3 the structuring of the charge polyelectrolytes spheres within foam film can be described by scheme Fig 5.3.4.

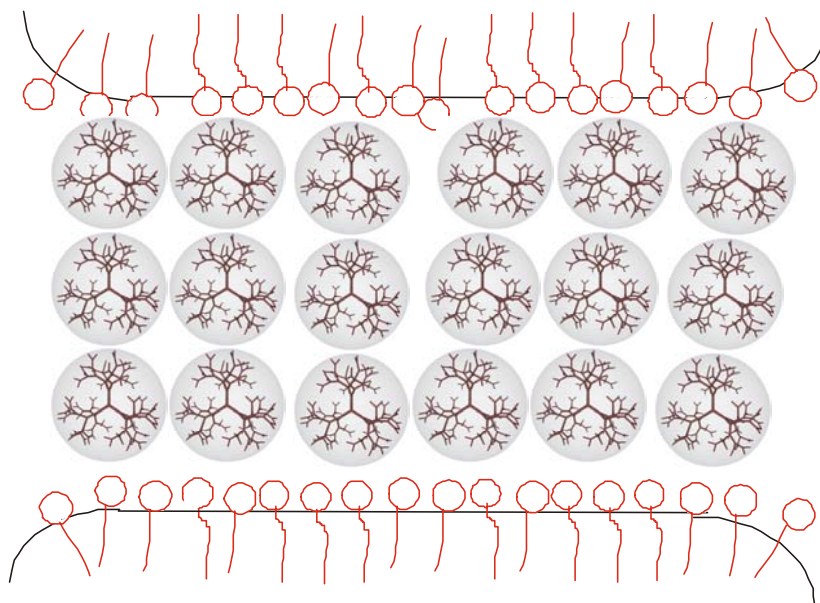


Figure 5.3.4. The structuring of branched polyelectrolyte within a foam film

This scheme shows that the structuring of branched PEI at pH 4 within the foam film is described as layering of *charged colloidal spheres*. The stratification of the foam films is explained by the expulsion of molecules from the film core. The diameter of spheres⁸⁶ is 3 nm and 4.5 nm for PEI with molecular weights of 5000 and 25000 respectively. These values are much more smaller than the measured step sizes in the disjoining pressure isotherms (7nm and 12 nm). The open question is why the step size is not related to the diameter of spheres plus 2x Debye length since the branched polyelectrolytes are charged and electrostatic repulsion between them exist. At an ionic strength of 0.34 mol/l, the Debye length ($\kappa=3.288*\sqrt{c}$) is of the order of 0.5 nm. If all monomers of PEI 5000 would be charged the minimum distance between two molecules would be 4 nm which is factor two below the step size. If we take into account that the molecular distance of about 7 nm would mean the Debye length, of approximately 2 nm, corresponds to the charge density of 12% which is much lower from experimentally observed charge density of 74%.

The discrepancy between experimentally detected charge density (74%) and calculated (12%) can be explained with assumption that that most of counterions are entrapped within the spherical core and the only free counterions (12%) are involved in electrostatic interaction between the chains⁸⁶.

In order to determine the influence of electrostatics on the structuring of the branched PEI within the film core, the foam films which contain the PEI were prepared⁸⁶ at two different pH. These results are described in the next section.

5.4 INFLUENCE OF ELECTROSTATICS ON THE STRUCTURING OF BRANCHED POLYELECTROLYTES

The influence of the electrostatics on the structuring of branched PEI was estimated measuring disjoining pressure isotherms at different pH⁸⁶. The disjoining pressure isotherms of branched PEI at two different pH values 10 and 4 are presented in Fig. 5.4.1.

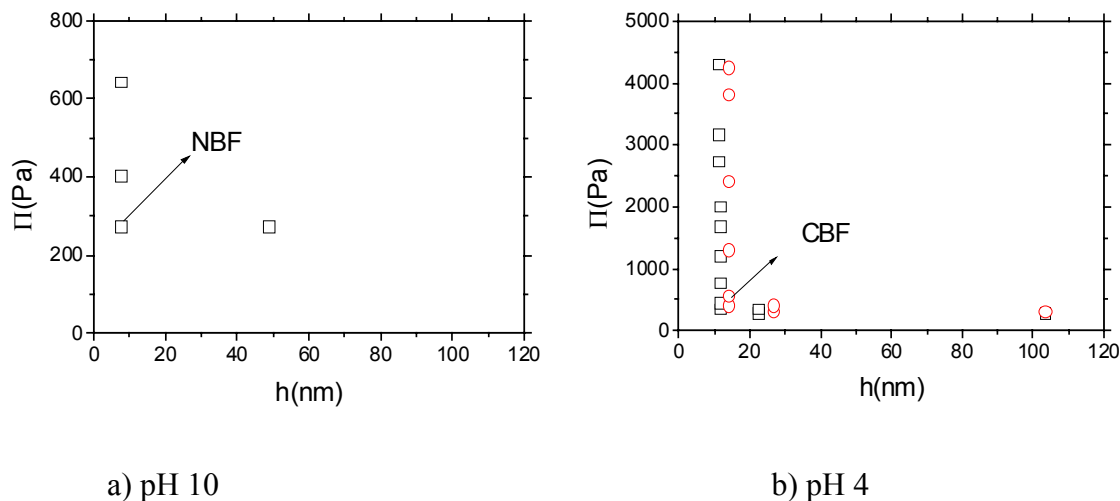


Figure 5.4.1. Disjoining pressure isotherms for a mixed system PEI 25000 /C₁₆TAB as a function of the film thickness at two pH values. The polyelectrolyte concentration is $c_p=0.34$ mol/l and surfactant concentration is $c_s=9.2 \times 10^{-5}$ mol/l.

Figure 5.4.1 shows that at pH 10 the final thickness of the foam film corresponds to the NBF in contrast to the CBF which is observed at pH 4. The appearance of the NBF indicates the presence of attractive forces between the film surfaces. The origin of the NBF at pH 10 is quite different than the origin of NBF at pH 4 at a higher polyelectrolyte concentration. (Section 5.3). At a value of pH 4 two steps are observed and these jumps are related to the structuring of PEI within the foam film. At pH10 only one jump is observed and this jump is unrelated to the structuring of polyelectrolyte within the film core because the size of the jump does not change with polyelectrolyte concentration.

At pH 10 the PEI chains have a degree of charge of 17%. The charges at that pH are related to the appearance of positively charged nitrogen atoms which are created during the branching of polyelectrolyte chains. Since these nitrogen's are predominately located inside the polyelectrolytes sphere the rest of the molecule is less hydrophilic.

Since branched PEI at pH 10 is less hydrophilic it is possible to assume that polyelectrolytes are at the interface of the foam film. The hydrophobic interaction between "neutral" molecules could overcome the electrostatic barrier and leads to the appearance of a NBF. The interaction with surfactant tails can facilitate the organization of the branched PEI at interface⁸² The rupturing of NBF at relatively low pressure can be explained by geometrical reasons, packing of "neutral" spheres in the tiny bilayer of NBF is not complete and the foam film ruptures. Since the NBF of high molecular weight of PEI(25000) is approximately 2 nm thicker from the NBF of the lower molecular weight (5000), the assumption that the branched molecules at pH10 are at surfaces of the foam film is directly supported.

The structuring of branched PEI⁸⁶ is observed only for strongly charged molecules at pH 4 (degree of charges 74%) due to strong electrostatic repulsion along and between molecules. The effect of the increasing ionic strength from pH10 to pH 4 seems to be not so important for the structuring as the increases of the charged density. The last experiments directly shows that electrostatic interactions are responsible for the structuring of the branched PEI.

The difference in the structuring of the linear and branched polyelectrolyte can be also expressed by measuring the dynamical property of the foam film such as drainage Fig. 5.3.5.

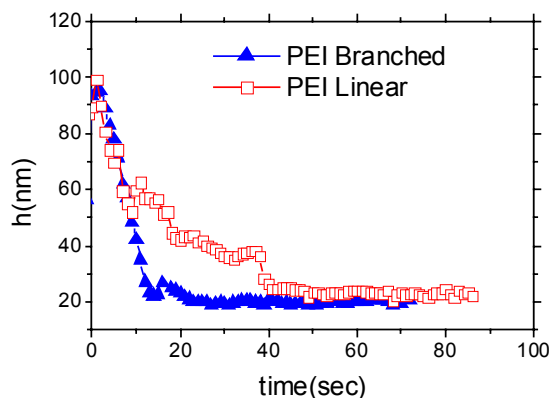


Fig.5.3.5. The drainage of a mixed system of linear and branched polyelectrolyte with cationic surfactant at pH 4, surfactant ($C_{16}TAB$) concentration is $c_s = 9.2 \times 10^{-5}$ mol/l, the PEI concentration is fixed at $c_p = 0.34$ mol/l.

Figure 5.3.5 shows that the drainage of the film which contains linear PEI is much slower than the film with branched polyelectrolyte. As it has been already described before the chains of linear polyelectrolytes in the semi dilute solution interdigitate. According to this picture a slower expulsion of the linear polyelectrolytes from the film core was expected because of the interdigitation of polyelectrolyte chains (slower drainage) in contrast to the faster expulsion of non interdigitating spheres. Since the charge per volume is much higher in branched polyelectrolytes than in linear ones, the repulsion between branched spheres and surfactant of the same charge is much more pronounced and additionally facilitate faster expulsion (drainage) of the branched polyelectrolytes from the film core.

As it was mentioned before the interactions between polyelectrolyte and surfactants determine the film stability^{13,30} and cause CBF→NBF transition⁷⁴. These interactions can be seen from photos of the foam films. In the next section the three most representative photos of branched PEI/surfactants foam films are described and interactions which cause appearance of that photos are discussed.

5.5 BRANCHED PEI – SURFACTANTS

INTERACTION

Interactions between polyelectrolytes and surfactants determine the properties of the foam films such as stability and the final thickness. The three most representative photos of the foam films which contain the branched polyelectrolyte (PEI) are presented in this section with short description of the interactions which cause appearance of these photos.



Figure 5.5.1. The NBF of PEI 5000/C₁₆TAB at pH 10 $c_p = 0.04$ mol /l, $c_s = 9.2 \times 10^{-5}$ mol/l.

Figure 5.5.1 shows that the weakly charged PEI (17%)⁸⁶ at pH 10 and cationic surfactant C₁₆TAB forms a NBF. The assumption about origin of the NBF of branched PEI at pH 10 is described in section 5.4. The drainage of this film is very slowly that spots look like frozen in the short period of the time. The photo from Figure 5.5.1. present approximately 40th min after beginning of transition. The film with so slowly speed of transition was observed for the first

time. Non circular shape of the spots indicates a high surface energy. During the transition the fusion of the spots takes place and new spots become more circular which indicates minimization of the surface energy during the transition. Further investigations of that unusual NBF are not possible due to the relatively low stability of the film. The film breaks before the transition is finished. Up to date the explanation for slowly drainage and non spherical shape of the spots still does not exist.

In the Section 5.2, it is shown that cationic surfactant $C_{16}TAB$ with the PEI at pH 4 form CBF due to a strong electrostatic repulsion between molecules from the film core and at the film surfaces. If the cationic surfactant ($C_{16}TAB$) is exchanged by non ionic ($C_{12}E_5$), the electrostatic interaction between PEI and surfaces becomes attractive^{7,26} due to adsorbed OH^- ions and at pH 4 a NBF appears (see Fig 5.5.2). After a few second the transition is finished and the whole film reaches new equilibrium thickness which corresponds to the NBF.

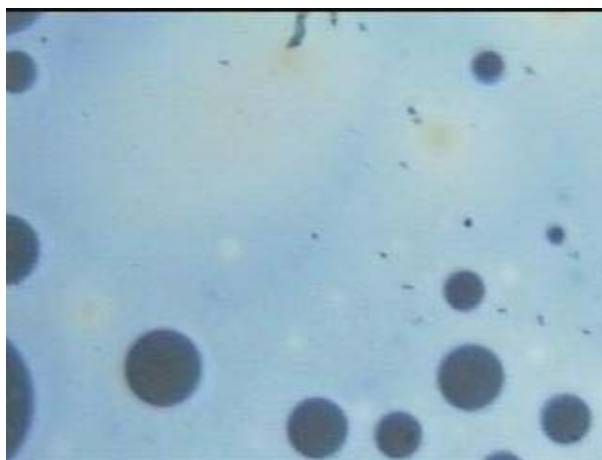


Figure 5.5.2 The snapshot of the NBF transition for mixed system of the branched PEI 25000 / $C_{12}E_5$ at pH 4, $c_p = 0.34 \text{ mol/l}$, $c_s = 9.2 \times 10^{-5} \text{ mol/l}$

This photo again confirms assumption about the electrostatic origin of the CBF→NBF transition described in the section 4.2

In order to complete the investigation of the CBF→ NBF transition for branched PEI, the mixed system PEI 25000 / $C_{16}TAB$ was formed at a higher

pH value between 12-14 (Fig. 5.5.3). This pH value was achieved by adding a few drops of a 1molar NaOH solution to the film solution.

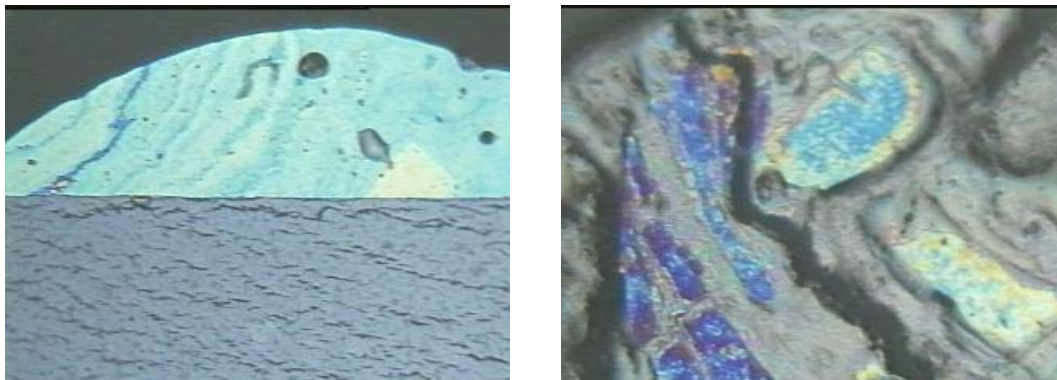


Figure 5.5.3 The photos of PEI 25000 / C₁₆TAB films at pH between 12-14, $c_p = 0.34 \text{ mol/l}$, $c_s = 9.2 \times 10^{-5} \text{ mol/l}$

The photos in Figure 5.5.3 show a solid crystalline structure within the foam film at pH 12. The appearance of these aggregates within the foam film is explained by the interplay of hydrophobic forces (Chapter 5.4) and the electrostatic attraction between hydroxyl ions within the film core and cationic surfactant at the surfaces of the film. These crystal structures are induced only in the film they have not been detected in the bulk. Similar aggregates within foam films are described elsewhere^{29,30,76}. The stability of these films is very high but the appearance of crystals avoids further investigation of these films by the TFPB method.

The presented photos clearly show how interactions between branched PEI, surfactants and additional counterions determine the properties of the foam films such as CBF → NBF transition, stability and drainage.

6. AMPHIPHILIC BLOCK COPOLYMERS

It is known that the properties of diblock copolymers strongly depend on the quality of the solvent. If the solvent is good for both monomers the diblock copolymers behave as “simple” homopolymers in a good solvent^{3,4,56}. If the solvent is only good only for one class of monomers, various aggregates such as micelles, vesicles, worm like micelles appear in solution and a full description of these complex self organized structures is given elsewhere^{56,85,92,93}. If the hydrophilic block is charged, electrostatic interaction together with solvent quality provide additional forces which determine the shape of the aggregates. Potential applications of these structures are enormous, for example stabilization of microemulsions, nanocasting, drug delivery^{2,3,4,27,56,68}, etc. It should be noticed that the foam film presents a unique system for investigation of diblock copolymer in confined space because it is possible to investigate the influence of the second interface on the formation and stability of polymer brushes in comparison to the single air / water interface^{92,95,102}.

In this chapter foam films are stabilized by PSSH-b-PEE.

6.1. INFLUENCE OF PSSH-b-PEE CONCENTRATION

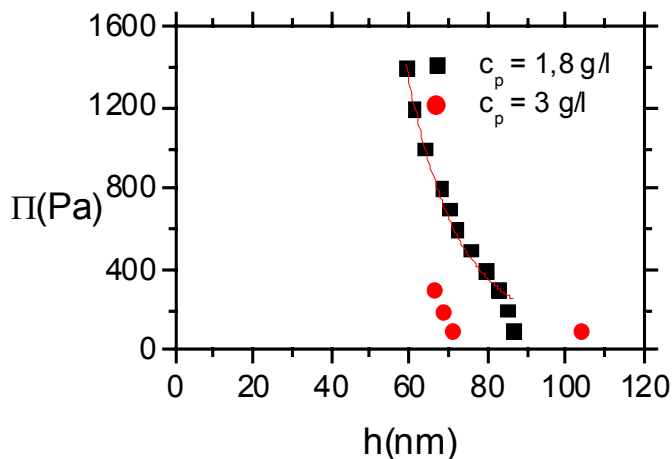


Figure 6.1.1. Disjoining pressure isotherms of PSSH-b- PEE for different polyelectrolyte concentration.

The disjoining pressure isotherm of the PSSH-b-PEE at the lower concentration 1.8 g/l looks like the isotherm of the low molecular weight surfactant molecules below the cmc. The disjoining pressure isotherm at the higher concentration of polymer 3 g/l shows stratification at the film, and the step size is approximately 32 nm. At the higher polyelectrolyte concentration the film breaks at a lower pressure. At that concentration the film is less stable and rupturing of the film occurs at a lower pressure.

Since the foam film drains continuously at polyelectrolyte concentration of 1.8 g/l, the data points can be fitted with exponential function.

$$\Pi_{el} = \Pi_0 \exp[-\kappa(h - 2h_0)] \quad (6.1)$$

where κ is inverse the Debye screening length and h_0 is the brush thickness.

The exponential decay indicates that the film is stabilized by an electrostatic repulsion between the film surfaces. The value of h_0 (22.5nm) was calculated from X –rays curves by Helm⁹³. The disjoining pressure Π_0 is connected with the surface potential by eq. 1.2. [Chapter 1, DLVO theory].

The surface potential (Ψ_0) of around 20mV is calculated from the fitted values, this potential corresponds to the potential of the brush/solution interface⁹³. The sign of potential cannot be determined with the TFPB^{7,26,46,85}.

The fit results in a Debye length (κ^{-1}) of 15 nm and a value for Π_0 of around 2200 Pa. The value of Debye length of 15 nm corresponds to the counterion concentration of 4.4×10^{-4} mol/l. According to the Odijk theory^{50,90} the Debye length of polyelectrolyte consists of two parts, one corresponding to the counterions and the other one to the ions of additional salt. Since PSSH-b-PEE is dissolved in pure water without any additional salt, the screening length is only affected by the counterions of PSSH.

The experimentally determined Debye length for PSSH-PEE is rather large with respect to the counterion concentration since the copolymer concentration of 1.8 g/l corresponds to the counterion concentration of 7.4×10^{-3} mol/l, and the distance between two charges is about 2.5 Å which is almost three times smaller than the Bjerrum length^{50,58}. Therefore, the counterion condensation has to be taken into account in this region^{85,91} and the concentration of free counterions is 1/3 of the total number of charged monomers. With this assumption the Debye length is about 6 nm, which is much more smaller than the experimentally determined value of 15 nm.

The deviation from the experimentally calculated Debye length can be explained with the assumption that the polyelectrolyte brushes in the foam film belong to osmotically swollen brushes, where almost all counterions are situated inside the brush and the concentration of free counterions inside the film is very small.

Particularly, the formation of a brush structure, for a similar system PSSH₈₃-PEE₁₁₄ was confirmed by X-ray measurement^{92,93,94}. The formation of this brush structure could be interpreted in a way that the hydrophobic PEE part of the copolymer is collapsed at the interface in an approximately 1 nm thick layer and the hydrophilic PSS chains were directed towards the film bulk.

Since the foam film has two interfaces, the structure of our diblock copolymer at low concentration within the foam film is described by the scheme presented in Fig. 6.1.2.

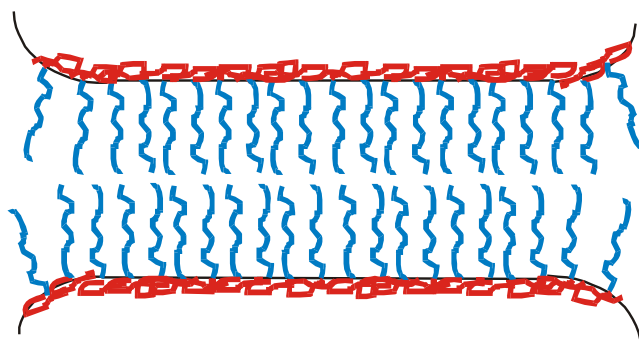


Figure. 6.1.2. Schematic presentation of diblock copolymers within a foam film.

Similar investigations of vertical free standing films of amphiphilic molecules Pt –PSS show interdigitation of brushes at high pressure⁹⁴. The presented PSSH-b-PEE, they do not seem to interdigitate. If they were in contact the electrostatic repulsive force would increase with decreasing h as $1/h$, instead of following an exponential law.

The brush structure appears only when the hydrophilic part is strongly anchored at the interface. Recently Saint Jalmes²⁷ et al, investigated thin films formed from PSS/PtBS copolymer in which the hydrophilic part is much more larger than hydrophobic one. Since the hydrophilic part is much larger, PSS is not strongly anchored at interface and these films cannot be described in terms of brushes.

As was mentioned before at the higher concentration of 3g/l, a transition in the film thickness is observed. The photo of transition is presented in Fig.6.1.3.

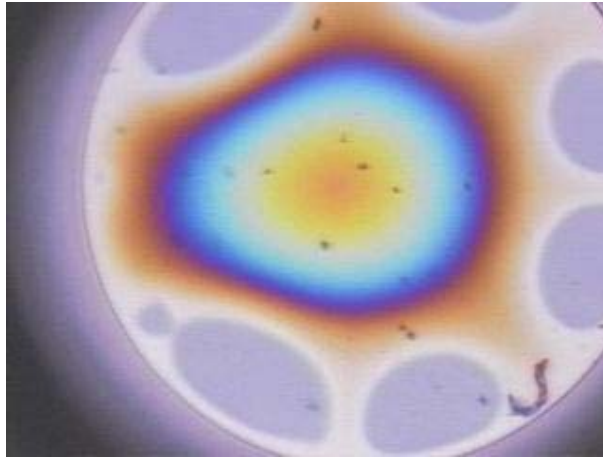


Figure 6.1.1.3. Photo of a transition at a PSSH-b-PEE film, the polyelectrolyte concentration is $c_p = 3$ g/l.

The size of the jump is comparable to diameter of micelles in solution⁹³, therefore a layer of micelles is assumed to be embedded within the film core. In analogy to the solvation forces between spherical particles the interface induces a lateral ordering of the micelles^{26,46}. The micelles are squeezed out of the film²⁶ into the surrounding the bulk phase which leads to a lower concentration in the film which in turn results in the creation of the attractive depletion forces and oscillation of the disjoining pressure^{26,30,85,86}. The multilayer ordering between interfaces for PSSH-b-PEE is not observed and a possible explanation could be that the pressure barrier has to be overcome to squeeze out only one layer is too small to observe a multilayer ordering between interfaces. Since the step in the film thickness and the diameter of micelle are of similar size it is assumed that the micelle is not compressed in the film. Due to similarity in stratification of low molecular weight surfactant and amphiphilic diblock copolymer the PSSH-b-PEE can be considered as giant surfactant.

The decrease in stability and thickness at higher diblock polymer concentration is caused by a decrease in electrostatic repulsion between the interfaces. The free counterions introduced by the PSS part lead to the screening of electrostatic repulsion between the brushes and along one brush. This leads to the coiling of the PSS part and also causes a decrease in the film thickness with increasing polymer concentration.

With respect to the small surfactant molecules, the thinning of the interface layer after increasing the polymer concentration is counterintuitive since usually the packing of the surface active molecules increases with increasing concentration.

In order to obtain information about the influence of electrostatics on the thickness of the films formed of diblock copolymers, experiments with salt (NaCl) were performed.

6.2 INFLUENCE OF IONIC STRENGTH

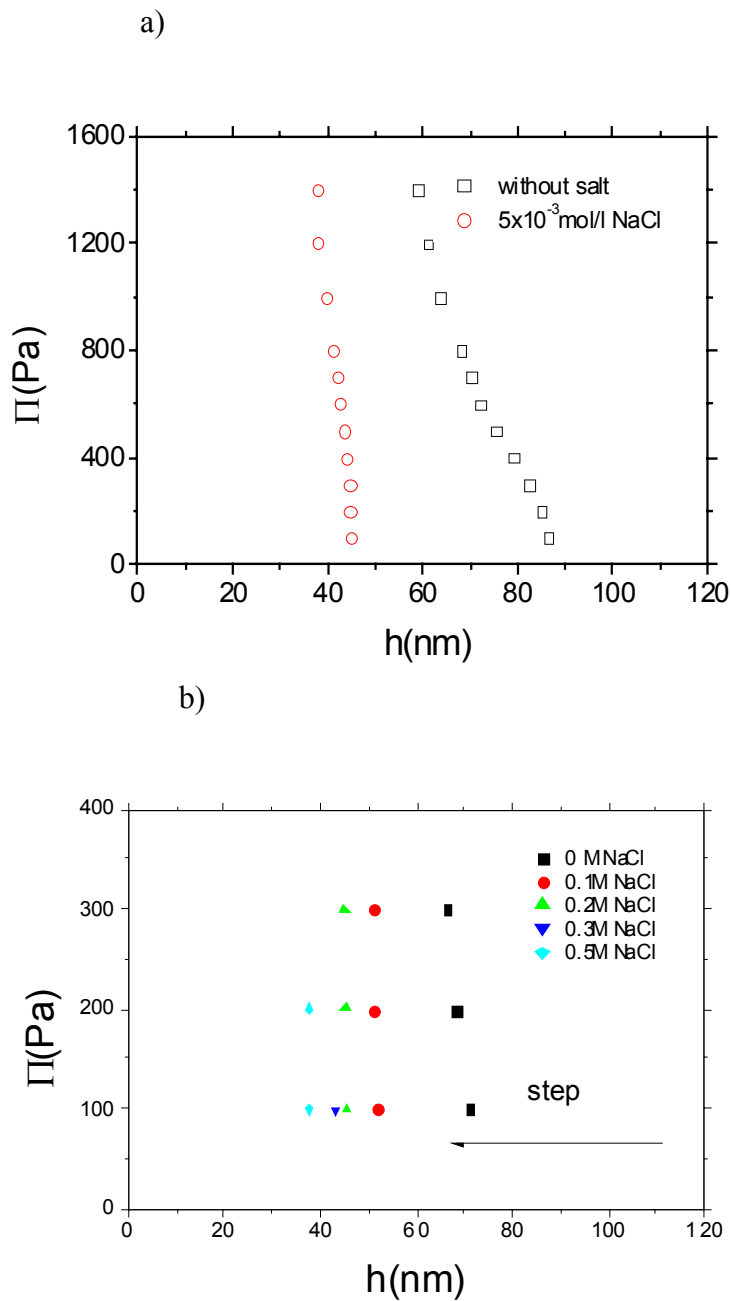


Figure 6.2.1. Disjoining pressure isotherms of PSSH-b-PEE at concentration a) 1.8 g/l and b) 3 g/l without and with salt (NaCl).

Figure 6.2.1. shows disjoining pressure isotherms of PSSH-b-PEE without salt and in the presence of different salt concentrations. The salt influence is observed at both polymer concentrations.

At the lower concentration (1.8 g/l) after addition of salt the film becomes thinner and the isotherm is steeper. This is an additional proof that the film is stabilized by electrostatic repulsion at low ionic strength. The steeper shape of the isotherms at the salt concentration (NaCl) of 50 mmol/l can be explained with a small Debye length of 1.4 nm at that ionic strength⁸⁵. With increasing ionic strength the grafted chains become more coiled which results in the reduction of the film thickness. A decrease in the film thickness after addition of the salt was also observed in the vertical films of the charged diblock copolymers where drainage is driven by gravitation⁹⁴.

At higher polyelectrolyte concentrations with increasing ionic strength the film become thinner after the step and the film becomes less stable. After addition of salt an experimental problem occurred, since the film was not in the equilibrium before the step, the precise estimation of the size of the jumps is impossible. So that only the part of disjoining pressure isotherms after the step is shown in Fig 6.2.1.

On the basis of the presented results from section 6.1 and 6.2 the structure and structuring of PSSH-PEE without and in the presence of salt within foam film, can be described by the following scheme Fig.6.2.2.

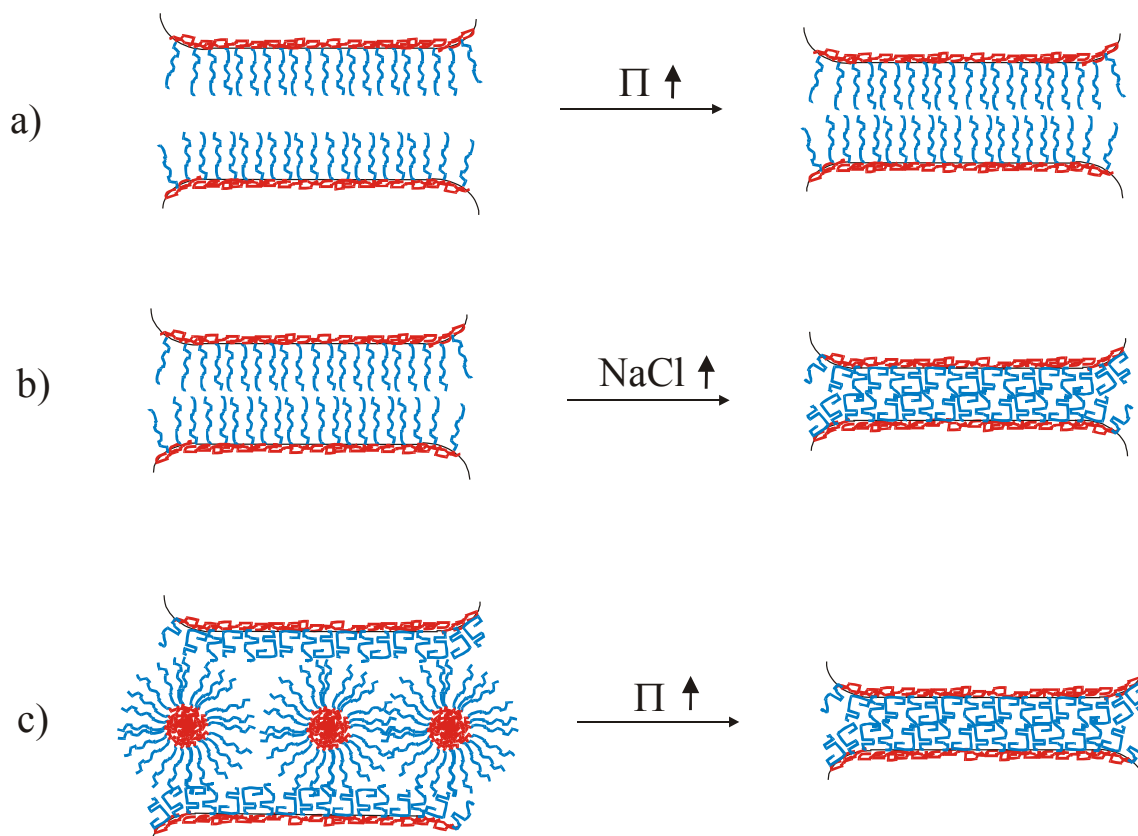


Figure 6.2.2. Schematic view of the amphiphilic copolymer PSSH/PEE within a foam film, a) approach of two brushes at low polymer concentration, b) influence of ionic strength, c) expulsion of one layer of micelles at high polymer concentration.

Figure 6.2.2 shows schematic behavior of the PSSH/PEE foam film. When the pressure increases the two surfaces of the foam films approach each other but steric and electrostatic repulsion prevents interdigitation of brushes and stabilize the film. The salt induces coiling of grafted chains due to “screening effect” and the thickness of the film decreases. At a higher concentration micelles are formed and stratification is related to the expulsion of micelles from the film core.

7. SUMMARY

The stepwise thinning was observed for every foam film which is formed from semidilute polyelectrolyte solution, regardless of differences in the molecular architecture of the single chain. All measurements were done at low surfactant concentration (below cmc.) therefore the polyelectrolyte / surfactant complexes can not be detected and the stratification of the foam films is caused only by the structuring of the polyelectrolytes within the film core.

In the case of PDADMAC and PEI with linear architecture, the step size scales with concentration by the same exponent as the correlation length in the bulk ($\Delta h \sim c^{-1/2}$). SANS measurements additionally show that the step size of the film transition is similar to the correlation length of a corresponding polyelectrolyte solution. On the basis of these results it is possible to conclude that the structuring of the polyelectrolyte chains within a foam film and in the bulk is identical and can be described with the same transient network structure proposed by de Gennes (isotropic model). The fact that the jump size and correlation length are unrelated to the molecular weight of the single chain additionally confirms the isotropic model as the most proper model which describes the structuring of linear polyelectrolytes within the foam film and in the bulk.

The stratification of the film can be explained as a process of destroying and rebuilding of a transient network structures within the film core. Up to a certain pressure the network reorganizes itself with n meshes and the polyelectrolyte chains which do not contribute to the network are pressed out. During the thinning the polyelectrolyte concentration within film is reduced and the film thins until the thickness of the film core fits to the $n-1$ meshes.

The reduction of the polyelectrolyte concentration within the film core with respect to the polyelectrolyte concentration in surrounding meniscus induces the (attractive) depletion forces between the film surfaces and oscillation appears.

At charge densities above the threshold of counterion condensation the step size is constant indicating a renormalisation of effective charge. Below the condensation threshold, the amplitude of the disjoining pressure decreases with decreasing degree of charge and disappears for neutral polymer chains. A decrease in the pressure amplitude is also noticed after addition of salt (change pH) in the solution of linear polyelectrolytes. Both the decrease in charge density and the increasing ionic strength reduced the electrostatic interactions and destroy the structuring of polyelectrolytes within the film core, which confirms that structuring of the polyelectrolytes within foam film is caused by electrostatic interactions between chains. Viscosity and SANS measurements of corresponding bulk solution show that the electrostatic interactions is also responsible for the structuring of linear polyelectrolytes in the bulk.

In the case of branched polyelectrolyte (PEI) the step size of the foam films scales with polyelectrolyte concentration as $\Delta h \sim c^{-1/3}$. This is a typical scaling law for ordering of spherical particles in three dimension. On the basis of the scaling exponent of $-1/3$ the structuring of the branched polyelectrolytes within the foam film can be described as a layering of spheres inside the film core. The stratification of films is explained by expulsion of the spheres during the film thinning. Since the structuring of the branched polyelectrolyte (PEI) is mostly pronounced when the PEI is fully charged, it confirms that electrostatic interactions between spheres determine the structuring of PEI within film core.

In contrast to the foam film of hydrophilic polyelectrolyte (PDADMAC, PEI) the foam films of the amphiphilic polyelectrolyte (PSSH-PEE) are stable without surfactant. Foam films of charged PSSH-PEE have a kind of “sandwich” structure of two opposing polyelectrolyte brushes and are stabilized by electrostatic interactions. The exponential decay of the $\Pi(h)$ isotherms indicates that the brushes do not interdigitate. The film thickness decrease with increasing ionic strength since the electrostatic repulsion between film surfaces is screened as

well as by shrinking of interfacial layer of polyelectrolyte due to screening of charges per polyelectrolyte chain.

At higher polyelectrolyte concentration micelles are formed within the film core and in analogy to the film of small surfactant molecules, stratification of the film is explained by the process of squeezing out the micelles from the film core.

During the film drainage two equilibrium thicknesses (CBF and NBF) of the foam films are observed. The experimental results show that the CBF \rightarrow NBF transition depends only on electrostatic interactions between molecules from the film core and molecules at interface. The macromolecular structure does not play any role. If electrostatic attraction between molecules at film surfaces and within the film core exist the CBF \rightarrow NBF transition occurs and the final thickness correspond to the NBF. In the case of electrostatic repulsion between them film is much stable, breaks at higher pressure and the final thickness corresponds to a CBF.

On the basis of experimental results it is possible to conclude that electrostatic interaction is the force which determine the structuring of polyelectrolytes regardless differences in their architecture. The same interaction determines the properties of the foam films such as final thickness (CBF \rightarrow NBF transition) and stability.

8. OUTLOOK

The structuring of covalently bonded linear and branched polyelectrolytes have been very well investigated in the bulk as well as within the foam film and theoretical models which describe structuring have been established^{30,59,60,66,86,89}. The supramolecular^{98,100} and interlocked^{96,96,101} polymers have to be considered as the promising compounds for future research because their importance in the future technology⁹⁷. The structuring of covalently bonded polyelectrolyte is caused by electrostatic repulsion between the chains but in the case of interlocked polymer, the steric interactions because presence of mechanical bonds can be more pronounced and determine the structuring of these polymers. Up to date the structuring of these polymer is unknown in confined and infinite space,

Since monomers in a supramolecular* polymers¹⁰⁰ are connected by non covalent interactions, geometrical confinement could have a stronger influence on the conformation of single chain as well as on the structuring with respect to the their covalent analogues. The confinement (thin film geometry) can induces degradation of polymers on monomer units. If non covalent bonding is strong enough that supramolecular polymers can survive within the foam the structuring of these polymers within the foam film can be investigated. It is important to stress that the interaction between supramolecular polymer and surfactants is also new and the promising field of research and until now only few papers have been published¹⁰⁰.

The interlocked polymers based on rotaxane and catanane structures have been recently synthesized with single chains of different molecular architectures¹⁰¹⁻¹⁰³. It should be noticed that presence of the mechanical bonds strongly affects properties of these polymers and some basic concept from polymer physics such as entanglement is under the question since the presence of big macrocycles on the polymer backbone strongly influence the entanglement of chains.

*- by definition supramolecular chemistry is chemistry beyond covalen bond and supramolecular polymers,are polymers in which monomers are linked by non covalent interactions

In confined environment the structuring of interlocked chains can be much more affected because the confinement can induce additional treading of these polymers, especially if the interlocked polymer has a large macrocycle group (wheel in rotaxanes compounds). The interlocked polymers are also synthesized with groups which can be shuttled between two segment of polymers under the influence external stimuli (pH, light or voltage), the influence of confinement on this process can be studied by the foam films of these compounds. The shuttling process influences the conformation of a single chain. Changes in the structuring of these polymers within the foam films could be observed by measuring disjoining pressure isotherms.

At the end it should be noticed that the interlocked polymers are one of the most promising compounds for designing a new nanodevices, molecular machines and motors⁹⁷, and the knowledge of their properties at surfaces and in the confined spaces are crucial for their applications.

REFERENCES

- ¹ K. W. Kolasinski, *Surface science*, **2001**, New York Wiley
- ² P. Ball, *Made to Measure*, **1997**, Princeton University Press
- ³ D. F. Evans, H. Wennerström, *Colloidal Domain*, **1999**, New York Wiley VCH
- ⁴ R. J. Hunter, *Introduction to modern colloidal science*, **1993**, Oxford science
- ⁵ J. L. Toca Herera, R. Krustev, H. J. Müller, H. Möhwald, *J. Phys. Chem. B* **2000**, 104, 5486
- ⁶ M. Daune, *Molecular biophysics*, **1999**, Oxford University Press,
- ⁷ D. Exerova, P. Kruglyakov, *Foam and foam films*, **1998**, Elsevier
- ⁸ R. K. Khan, *Foam, Theory Measurements and Applications*, Surfactant Science Series, **1996** New York, Marcel Dekker,
- ⁹ E. M. Scarpelli, *Surfactants and the lining of the lung*, **1998** The John Hopkins University Press Baltimore
- ¹⁰ O. Sonneville-Aubrun, V. Bergeron, *Langmuir*, et all **2000**, 16, 1566
- ¹¹ I. B. Ivanov, *Thin liquid films*, **1988**, New York Marcel Dekker,
- ¹² V. Bergeron, A. Waltermo, P. M. Cleasson, *Langmir*, **1996**, 12, 1336
- ¹³ R. v. Klitzing, H.J. Müller, *Curr. Opinion. Colloid Interface Sci.* **2002**, 7, 42
- ¹⁴ B.V. Derjaguin, *Prog. Colloid and Polymer Sci*, **1987**, 74,17
- ¹⁵ R. Krustev, H.J. Müller, *Langmuir* **1999**, 15, 2134
- ¹⁶ J. M. Corkill, J.F. Goodman, C. P. Ogden, *J. Chem. Soc. Faraday*, **1965**, 61, 583

- ¹⁷ T. Kolarov, R. Cohen, D. Exerova *Colloids and Surfaces*, **1989**, 42, 49
- ¹⁸ J.A. Feijter, A. Vrij, *Adsorption at interfaces ACS Symposium Series*, **1975**, 183
- ¹⁹ I. Newton *in Optics*, 1730, London, **1952** New York
- ²⁰ A. M. Reinold, . A.W. Rücker, *Philos. Trans.*, **1886**, 177 , 1886
- ²¹ E.S. Johnott, *Philos. Mag.*, **1906**. 70,1339
- ²² R. E. Perin, *Ann.Phys.* **1918**, 10, 160
- ²³ P. A. Kralchevsky, A. D. Nikolov, D. T. Wasan. I.B. Ivanov, *Langmir*, **1990**, 6, 1180
- ²⁴ E. Manev, J. E. Proust, L.T.M. Sarraga, *Colloid,. Polym. Sci.*, **1977**, 225,1133
- ²⁵ E. Manev, S.Sazdanova, D. T. Wasan. *J. Dispersion Sci.*, **1984**, 5, 11
- ²⁶ V. Bergeron, C. J Radke, *Langmir*, **1992**, 8, 3020
- ²⁷ A. Saint –Jaimés, et all, *Langmir*, **2002**, 18, 2103
- ²⁸ A. Asnacios, A. Espert, A. Colin, D. Langevin, *Phys. Rev. Lett.* **1997**, 78,4974.
- ²⁹ R. Klitzing, A. Espert, A. Asnacios, A. Colin, T. Helweg, D. Langevin, *Colloids Surf.A*, **1999**, 149, 131
- ³⁰ O. Theodoly, J. S. Tan, C. E. Williams , V. Bergeron *Langmir* **2001** 17, 4910
- ³¹ D. H. Everet, *Specialist Periodicals of Colloid Science, Vol 2*, Chemical Society, **1975**, London
- ³² D. den Engelsen, G. Frens, *J. Chem. Soc. Faraday Tran. I*, **1973**, 70, 237
- ³³ H.J. Müller, Th . Rheinländer, *Langmuir* **1996** 12 2334
- ³⁴ B. V. Derjaguin, N. V. Churaev, V. M. Muller, *Surface forces*, Consultants bureau **1987**
- ³⁵ J. Lyklema, *Recueil*, **1962**, 81, 891

- ³⁶ D. Evert, *Colloids and surfaces A*, **1998**, 141, 279
- ³⁷ E. Mileva, D. Exerova, *Colloids and Surfaces A*, **1999**, 149, 207
- ³⁸ A. Schedulko, *Adv. Colloids. Interface. Sci.* **1967**, 1, 391
- ³⁹ A. Waltermo, P. M. Cleason, S. Simonsson, E. Manev, I. Johansson, V. Bergeron, *Langmir*, **1996**, 22, 5272
- ⁴⁰ N. Krasteva, R. Krustev, H. J. Müller, D. Volhardt, H. Möhwald, **2001**, 105, 1185
- ⁴¹ B. Leciurt et al., *J. Chem. Phys.* **1998**, 108, 1284
- ⁴² F. Lihert, D. Blaudez, C. Heywang, J. M. Turllet, *Langmir*, **2002**, 18, 512
- ⁴³ J. L. Toca-Herera, R. v. Klitzing, *Macromolecules*, **2002**, 35, 2861
- ⁴⁴ K. S. Schmitz, *Langmir*, **1997**, 13, 5849
- ⁴⁵ V. Bergeron, *Ph.D. thesis*, **1992**, University of California Berkeley
- ⁴⁶ J. Isrealchvilli, *Intermolecular and surface Forces*, **1998**, Academic Press, London
- ⁴⁷ I. Langmir, *J. Am. Chem. Soc.*, **1917**, 39, 1848,
- ⁴⁸ M. Manciu, E. Ruckenstein, *Langmir* **2001**, 17, 7582
- ⁴⁹ H. J. Müller, *Langmir*, **1998**, 14, 6489,
- ⁵⁰ H. Dautzenberg, W. Jeager, J. Kötzt, B. Philip, Ch. Seidel. D. Stscherbina, *Polyelectrolytes*; **1994**, Hanser,
- ⁵¹ F. Vögtle, J.F. Stoddart, M. Shibasaki, *Stimulating concept in chemistry*, **2000**, Wiley VCH
- ⁵², F. Caruso, C. Schüler, D. G. Kurth, *Chem. Mater*, **1999**, 11, 3394
- ⁵³ K. S. Schmitz, *Macroions in Solution and Colloidal Suspension*, **1993**, VCH
- ⁵⁴ G. Srobl, *The Physics of Polymers*, **1997**, Springer

- ⁵⁵ G. R. Newkome, C.N. Moorefield, F. Vögtle, *Dendritic Molecules, Concepts, Synthesis, Perspectives*, **1996** Wiley VCH
- ⁵⁶ A. D. Schlüter, *Synthesis of Polymers*, **1999** Wiley VCH
- ⁵⁷ G. S. Manning, *J. Chem. Phys.* **1969**, 51,924
- ⁵⁸ J. L. Barrat, J. F. Joanny, *Polyelectrolytes* **1992**
- ⁵⁹ P. G. de Gennes *Scaling concepts in polymer physics*, **1979**, Cornell University Press
- ⁶⁰ P. G. de Gennes, P. Pincus, R. M. Velasco, F. Brochard, *J. Phys. France*, **1976**, 37
- ⁶¹ A. J. Milling, *J. Phys. Chem.*, **1996**, 100, 8986
- ⁶² H. Dautenzberg, E. Görnitz, W. Jaeger, , *Macromol. Chem. Phys.*, **1998**, 199, 1561,
- C. L. McCormic, R. S. Armentrout, *ACS Polymer preparation* **1998**, 39, 617
- ⁶³ C. R. Dirk, G. E. Ham, *J. Macromol. Sci, Chem*, **1970**, 1301, B.L. Rivas, K. E. Geckeler, *Adv. Polymer. Sci*, **1992**, 102, 171
- ⁶⁴ M. A. Winnik, S. M. Bystryak, Z. Liu, J Siddiqui, *Macromolecules*, **1998**, 31, 6855
- ⁶⁵ V. Bergeron, P. Classon, *Adv in Colloid and Interface Sci.* **2001**, 89-90, 1
- ⁶⁶ B. Kolaric, W. Jäger, R. v. Klitzing, *J. Phys. Chem. B.*, **2000**, 104, 5096
- ⁶⁷ K. J. Mysels, M. N. Jones, *Discussion Faraday Soc*, **1966**, 42, 42
- ⁶⁸ S. Förster, N. Hermsdorf, C. Bötcher, P.Lindner, *Macromolecules*, **ASAP**, 2002
- ⁶⁹ H. G.Elias, *An introduction to polymer science*, **1997**, VCH
- ⁷⁰ P.W. Atkins, *Physical Chemistry*, **1988**, Oxford University Press

- ⁷¹ D. Langevin, *Adv. In Colloid and Interface Sci.* **2001**, 89-90, 467
- ⁷² A.Saint- Jalmes, T. Zemb, D. Langevin, *Progr. Colloid. Polym. Sci.*, **2001**, 118, 1
- ⁷³ R. v. Klitzing , *Tenside Surf. Det.*, **2000**, 37, 338
- ⁷⁴ R. v. Klitzing, B. Kolaric, W. Jäger, A. Brandt, *Phys. Chem. Chem. Phys.*, **2001**, 199, 1561
- ⁷⁵ B. Kolaric, Regime v. Klitzing, *Unpublished results*
- ⁷⁶ V. Bergeron, D. Langevin, A. Asnacios, *Langmuir*, **1996**, 1550
- ⁷⁶ J. Ray, G.S. Manning, *Macromolecules*, **1997**, 30, 5739
- ⁷⁷ W. Essafi, F. Lafuma, C. E. Williams, *Eur. Phys. J. B*, **1999**, 9, 261
- ⁷⁸ U. Micka, C. Holm, K. Kremer, *Langmir*, **1999**, 15, 4033
- ⁷⁹ A.J. Yethiraj, *J. Chem. Phys.*, **1999**, 111, 1797
- ⁸⁰ C. N Likos, M. Schmidt, H. Löwen, M Ballauff, D. Potschke, P. Lindner, *Macromolecules*; **2001**, 34, 2914
- ⁸¹ Y. Tor, *Supramolecular Stereochemistry*, **1995**, 247, Kluwer Academic Publishers, Ed., J.S. Siegel
- ⁸² A.P.H.J. Schinning, *J. Am. Chem. Soc.*, **1998**, 120, 8199
- ⁸³ M. Ballauff , *Topics in Current Chem*, , **2001**, 212, 177,
- ⁸⁴ D. Muscat, R.A.T.M. van Benthem, *Topics in Current Chem.*, **2001**, 212, 42
- ⁸⁵ B. Kolaric, S. Förster, R. v Klitzing, *Progr. Colloid. Polymer Sci.*, **2001**, 117,195
- ⁸⁶ R. v. Klitzing, B. Kolaric, *Progr. Colloid. Polymer Sci*, august **2002** Accepted

- ⁸⁷ K. Inoue, *Prog. Polym. Sci.*, **2000**, 25, 453
- ⁸⁸ V. O. Borisov, M. Daoud, *Macromolecules* **2001**, 34, 8286
- ⁸⁹ W. Burchard, *Advance in Polymer Science Vol.e 143*, **1999**, 113
- ⁹⁰ T. Odijk, *Macromolecules*, **1979**,12, 688
- ⁹¹ R. Sedev, D. Exerova, *Adv. Colloid. Int. Sci.*, **1999**, 83, 111
- ⁹² H. Ahrens, S. Förster, C.A. Helm, *Macromolecules*, **1997**, 30, 8447
- ⁹³ H. Ahrens, S. Förster, C.A. Helm, *Phys. Rev. Letters*, **1998**, 81, 4172
- ⁹⁴ P. Guenon, P. Sealchli, D. Sentenac, J. W. Mays, J.J Benattar, *Phys. Rev. Letters*,**1995**, 74
- ⁹⁵ T. J. Prosa, , B. J Bauer, E. J Amis, *Macromolecules*, **2001**, 34 4897
- ⁹⁶ J. P. Sauvage, D .Buchecker, *Molecular Catanenes Rotaxane and Knots*, **1999**
Wiley-VCH
- ⁹⁷ J. P. Sauvage, *Molecular machines and motors*, Structure and bonding, **2001**, 9,
Springer Verlag
- ⁹⁸ J.van der Gucht, N. A. M Besseling, M. A. Cohen Stuart, *J. Am. Chem. Soc.*
2002, 124, 6202
- ⁹⁹ R. v. Klitzing, A. Espert, A.Colin, D. Langevin, *Colloids and Surfaces A*, **2001**,
176,109
- ¹⁰⁰ P. Lehmann, D. G. Kurth, G. Berzinski, C. Symiez, *Chem. Eur. J*, **2001**,7, 1646
Kurt
- ¹⁰¹ F. M. Raymo, J. F. Stoddart, *Chem. Rev.* **1999**, 99, 1643
- ¹⁰² P. Kekicheff, F. Nallet, P. Richeti, *J. Phys*, **1994**, 735
- ¹⁰³ A. M Elizarov, S.-H Chiu, P. T Glink, J. F Stoddart, *Org. Lett.*, **2002**, 4, 679

BIOGRAPHY

First Name: Branko
Family name: Kolaric
Nationality: Yugoslavian
Date of birth: March 29, 1969
Place of birth: Belgrade, Yugoslavia

Education:

- 1995 University degree, dipl. chem. (MSc in chemistry) specialization in physical chemistry, University of Belgrade
- 2000 Magistratura (candidate for Ph.D.) in Organic chemistry, University of Belgrade,
- 2002 Ph.D. in Physical Chemistry- Colloid and Interface Chemistry, TU-Berlin

Marital status: married, one child

Employment :

1995-1998: Researcher in ICN- Galenika, Yugoslav –American pharmaceutical company, (part of ICN Pharmaceuticals in Yugoslavia), Department for basic research, drug delivery lab

1998-2002 Researcher in the Institute of chemistry, TU-Berlin

RESEARCH GRANTS:

DYNAMICS, STABILITY AND SELF ORGANIZATION OF THE NON-EQUILIBRIUM SYSTEMS, awarded by Ministry of Science of Serbia, 1996-2000,

MOLECULAR ARCHITECTURE OF POLYELECTROLYTES, awarded by DFG, 1998-2000

MOLECULAR ARCHITECTURE OF POLYELECTROLYTES, awarded by DFG, 2000-2002

COMPLEX FLUIDS FROM 3 TO 2 DIMENSIONS, French-German Network, awarded by DFG, 1.03.2002-1.09.2002

PHYSICAL CHEMISTRY OF DYNAMICAL STATES AND STRUCTURES, NONEQUILLIBRIUM SYSTEMS, SELFORGANIZATION, MULTISTABILITY

AND OSCILLATORY PROCESS , awarded by Ministry of Science of Serbia, 2002-2006,

Publications from Ph.D. thesis

B. Kolaric , W. Jäger, R v. Klitzing “*Mesoscopic ordering of polyelectrolyte chains in foam films: Role of the electrostatic forces*”, *The Journal of Physical Chemistry B* volume, **2000**, 104, 5096

B. Kolaric, S. Förster , R v. Klitzing “*Interactions between polyelectrolyte brushes in free standing liquid films: Influence of ionic strength*” *Progress in Polymer and Colloid science*, **2001** 117(195),

R. v. Klitzing, B. Kolaric, W. Jäger, A. Brand, *Structuring of POLY(DADMAC) chains in aqueous media: A comparison between bulk and free standing film measurements*, *Phys. Chem. Chem. Phys.*, **2002**, 1907-1914,

R. v. Klitzing, B. Kolaric, *Influence of the polycation architecture on the oscillatory forces of aqueous free-standing polyelectrolyte/surfactant films*, *Progress in Colloid and polymer Science* **Accepted August 2002**

B.Kolaric, R.v. Klitzing, *Foam films stabilized by Poly(ethylen imine)*, *Tenside Surf, Det*, **Accepted October 2002**