Adsorption of Linear and Star-Shaped Polyelectrolytes to Monolayers of Charged Amphiphiles

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Summary: Adsorption of polyelectrolytes has been studied employing monolayers of ionic amphiphiles at the air water interface as model surfaces. The adsorption of polyelectrolytes from a solution brought into contact with the amphiphile monolayer results in changes of the monolayer structure and properties. Monitoring these changes can be done by recording the changes in surface pressure. The kinetics of the adsorption depends strongly on the nature of the polyelectrolyte. Depending on the structure of the polyelectrolyte a purely diffusion controlled adsorption or a sequence of diffusion controlled adsorption and ordering processes have been identified to determine the kinetics. The influence of the molecular architecture on the polyelectrolyte adsorption has been further studied employing linear and star shaped poly(acrylic acid) and poly(N-propyl-4-vinyl pyridinium bromides), respectively. An unexpected behavior with an induction period in the adsorption kinetics of both polymers has been found. Furthermore, the degree of branching has only very minor effects on the adsorption kinetics.

Keywords: adsorption kinetics; amphiphiles; monolayers; polyelectrolytes; star-shaped polyelectrolytes

Introduction

Polyelectrolyte adsorption onto solid substrates plays an important role in many applications such as modification of surfaces e.g. preparation of antistatic and protective coatings or making artificial organs biocompatible. But also many technical processes like wastewater treatment and paper production are closely connected with polyelectrolyte adsorption.[1] Although there is a big interest in the adsorption process, only a few methods are available for *in-situ* investigation of the polyelectrolyte adsorption onto charged surfaces like ellipsometry[2] or surface plasmon resonance spectroscopy.[3] Monolayers of ionic amphiphiles at the air water interface can be regarded as models for charged surfaces. The adsorption of polyelectrolytes from a solution brought into

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contact with the amphiphile monolayer results in changes of the monolayer structure and properties. Monitoring these changes can be done by different methods and should allow to obtain information about the adsorption process.[4, 5]

Polyelectrolyte-amphiphile complexes are formed spontaneously when an amphiphile solution is spread on a subphase containing the polyelectrolyte.[6, 7] Complex formation may results in a stabilization of monolayers and LB films of ionic amphiphiles, or in a change in the their structure[6, 7] or morphology.[8] Studying the monolayer behavior of the complexes allows to obtain information about the interaction between polyelectrolyte and amphiphile and about the new type of structure that has been formed. In addition the adsorption process can be monitored if preformed monolayers are brought into contact with a polyelectrolyte containing subphase.[9, 10]

There are several methods to prepare a monolayer of an ionic amphiphile on pure water and to bring it subsequently into contact with a polyelectrolyte solution. The polyelectrolyte can be added to the water subphase after compression of the monolayer as a concentrated solution.[11] Drawbacks of this method are that the subphase has to be stirred in order to ensure a homogeneous distribution of the polyelectrolyte and that the polyelectrolyte has to be added as highly concentrated solution. These problems can be avoided if the subphase is continuously exchanged.[12, 13] However, this methods requires a special trough and a fine control of supply and discharge of the subphase, in order to keep the level in the trough constant. Another drawback is that the flow has to be rather low in order to keep the mechanical stress on the monolayer as low as possible. However, at low flow rates there is a laminar flow profile and a concentration gradient perpendicular to the flow direction occurs. Therefore, long exchange times are necessary.[13]

Fromherz has reported a method in which the monolayer is prepared on one compartment of a multi-compartment trough which contains pure water and is subsequently transferred to another compartment which contains a polyelectrolyte or enzyme solution [14, 15, 16, 17] (s. Figure 1). The water level in the compartments is slightly higher than the walls, but due to the meniscus formed at the hydrophobic walls there is no contact between the solutions. During the transfer process, the contact area between the monolayer and the polyelectrolyte solution increases linearly. A minor mixing of the subphases during the transfer cannot be avoided and the transfer speed is limited by the stability of the monolayer.

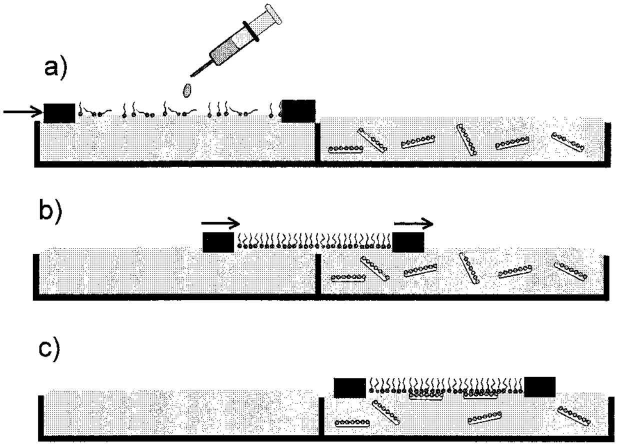


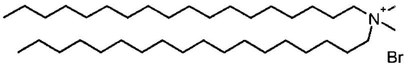
Figure 1. Fromherz method for bringing a preformed monolayer into contact with a subphase containing a polyelectrolyte: a) spreading the amphiphile solution on a compartment with pure water and subsequent compression of the monolayer, b) transfer of the compressed monolayer onto a compartment that contains a polyelectrolyte solution, and c) monitoring the adsorption process

Measuring the surface pressure is a well established method and can be performed easily even on a two compartment trough. So, recording the changes in the surface pressure after transferring the monolayer to the polyelectrolyte containing subphase is a straightforward way to monitor the adsorption. The expected change in surface pressure can be estimated from the comparison of the isotherms recorded on pure water and on a polyelectrolyte subphase (s. Figure 2). Experimental details for this method are given in Ref. [5, 18, 19].

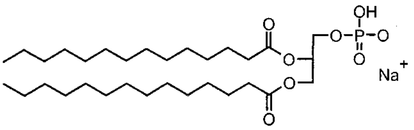
Materials

The amphiphiles forming the model monolayer have to be chosen very carefully. The monolayer has to have sufficient stability to be transferred on the Fromherz trough. Furthermore, the changes in the structure of the monolayer upon adsorption of the polyelectrolyte have to be in such a way that they can be monitored.

Dioctadecyldimethylammonium bromide (DODA) is an amphiphile that is well suited to investigate the adsorption process for anionic polyelectrolytes[19, 20, 21] The isotherm of DODA (Figure 2) shows two regions, an expanded monolayer structure at high area per amphiphile, which turns into a more condensed structure at a surface pressure of approximately 20 mN/m.[22,23,24] The DODA monolayers are stable and suitable for the transfer according to the Fromherz method in both regions.[12,14] The area requirements for DODA on pure water are given by the coulomb interactions of the ionic head groups and the packing of the alkyl chains.[20]



DODA



DMPA

The isotherms for complexes of DODA and the anionic polyelectrolytes like poly(styrene sulfonate) (PSS),[21] carboxymethylcellulose sodium salt (CMC)[21] and polyacrylic acid (PAA)[18] (for the structure of the polymers s.Table 1) are significantly different from the isotherm of DODA on pure water. For complexes with PSS the area per DODA amphiphile is reduced to 0.60 nm^2.[21] The area per amphiphile in the complex is close to the value found in single crystals (0.56 nm^2 [25]). The lower area per amphiphile in the complex monolayer compared to the monolayer on pure water can be ascribed to the charge compensation, which significantly reduces the coulombic interaction of the amphiphiles head groups.

The area per amphiphile is larger for the complex of DODA with PAA complex than for the pure DODA monolayer. For PAA a incorporation of some non ionised carboxylic acid groups into the monolayer has been made responsible for the larger area per DODA molecule found for the complex.[18] It is well known, that PAA shows some surface activity.[26] Furthermore it has been shown by Ishimuro and Ueberreiter that only the protonated carboxylic acid groups are surface active.[27] It is therefore expected that the area per amphiphile in the complex depends on the pH of the subphase. This is in fact the case, as can be seen in Fig. 2. The lower the pH, that is the higher the degree of protonation, the higher is the area per amphiphile in the complex. Indeed at high pH, when all carboxylic acid groups are deprotonated the area per amphiphile is lower for the complex than for DODA on pure water. Thus for a not to high pH a significant change in the surface pressure can be expected when a DODA monolayer prepared on a pure water subphase is brought into contact with a polyelectrolyte solution as subphase.

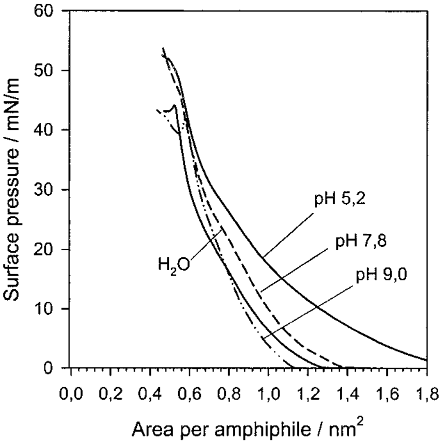


Figure 2. Comparison of the isotherms for DODA spread on pure water, and solutions containing PAS at pH = 5.2 (12 mg/L PAA dissolved in ultrapure water), at pH = 7.8 (12 mg/L PAS dissolved in ultrapure water and 100 μl 1 M NaOH added to 210 ml subphase) at pH = 9.0 12 mg/L PAS dissolved in ultrapure water and 150 μl 1 M NaOH added to 210 ml subphase)

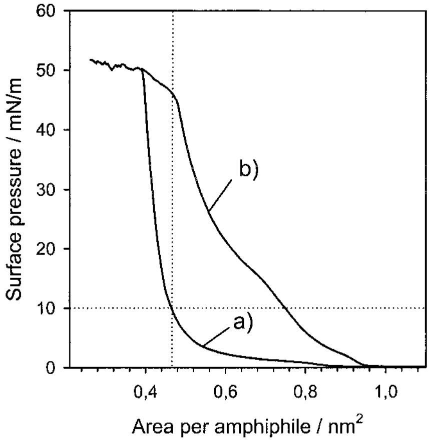
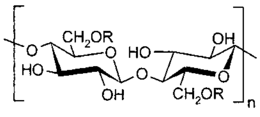
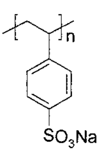
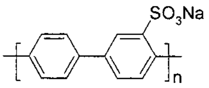
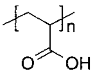
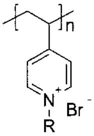


Figure 3. Comparison of the isotherms for DMPA spread on a) pure water, b) on an aqueous solution of poly(N-methyl-4-vinylpyridium bromide) q1PVP (c = 12.2 mg/L)

DMPA is a two chain anionic amphiphile which shows sufficient stability for the transfer in the Fromherz technique and the isotherms on pure water and on cationic polyelectrolytes like poly(N-methyl-4-vinylpyridium bromide) (q1PVP) are significantly different (Figure 3). Again the area per amphiphile is larger for the polyelectrolyte complex compared to the monolayer on pure water. This is believed to be due to the incorporation of hydrophobic parts of the polyelectrolyte into the monolayer. A large change in the surface pressure can be expected when a DMPA monolayer is brought into contact with a polyelectrolyte solution.

Table 1. Polyelectrolytes used for the investigations

polyelectrolyte	structure	molecular weight
sodium salt of carboxymethylcellulose, (CMC)	 R = -CH_2COONa DS = 0.7	M_w ~ 90 000 g/mol[1]
sodium salt of poly(styrol-p-sulfonate), (PSS)		M_w ~ 100 000 g/mol[2]
sodium salt of poly(p-phenylene sulfonate) (PPPS)		P_n = 4, 36, 54 see ref. [19, 20]
polyacrylic acid linear, 4-arm, 6-arm, 12-arm star (PAA)		linear 83 000g/mol [3,5] 4-arm 114 000 g/mol [3,5] 6-arm 111 000 g/mol [3,5] 12-arm 54 000 g/mol [3,5]
quaternized poly(vinylpyridine) linear, 4-arm, 6-arm, 12-arm (R = methyl (q1PVP), R = propyl (q3PVP))	 R = -CH_3, R = -C_3H_7	linear 89 000 g/mol [4,6] 4-arm 95 000 g/mol [4,6] 6-arm 91 000 g/mol [4,6] 12-arm 118 000 g/mol [4,6]

[1]Aldrich, [2]Acros, [3]M_w determined by SEC, [4]M_w determined by light scattering, [5,6] determined for the non-ionic prepolymers [5]poly(tert.-butylacrylate) and [6]poly(vinylpyridine)

The conformation of a flexible polyelectrolyte in solution depends on several factors, among which the charge density and the salt concentration are most important. The repulsion of the charges along the polyelectrolyte chain results in a stretching and an expanded coil is formed. The polymer can be described by the worm-like chain model. However, when the charges are screened or compensated the polymer forms a more compact random coil.[1] Therefore besides poly(styrene sulfonate) and carboxymethylcellulose,[8, 19] which show these changes in their conformation we used polyelectrolytes which have a more fixed conformation.

Polymers with a poly(p-phenylene) backbone have been previously used as model for the completely extended chain situation. Poly(p-phenylene sulfonate) (PPPS) was employed as an anionic polyelectrolyte forming complexes with cationic DODA.[5, 19, 20, 21] Star-shaped polymers have a more globular shape than linear chains. Therefore, in this work we used star-shaped polymers with varying number of arms as approximation of the random coil situation of the polyelectrolytes.

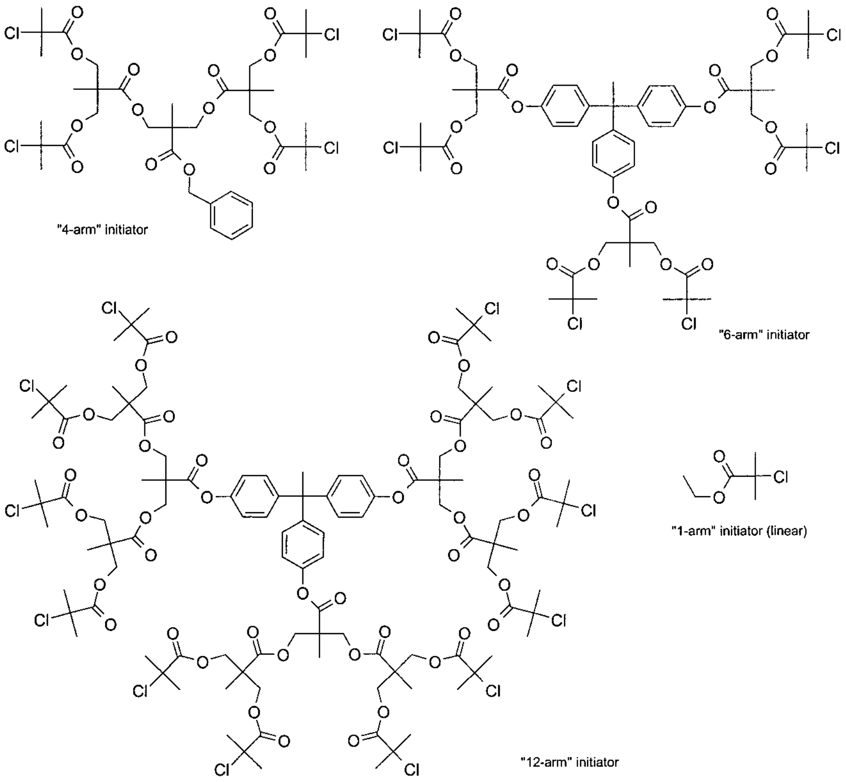


Figure 4. Dendritic initiators used for the synthesis of star shaped poly(vinylpyridine)s

We have synthesized polyacrylic acid[18] and poly(vinylpyridine) by ATRP employing dendritic initiators. The experimental details for the synthesis of the initiators and of star-shaped polyacrylic acid are given in ref. [18]. For the synthesis of the poly(vinylpyridine)s the same initiators were used but with chlorine end groups (s. Figure 4). Details of the synthesis are described in ref. [28].

Surface Pressure/Area Isotherms for the Polyelectrolyte-Amphiphile-Complexes

The isotherms for DODA spread on subphases containing the different PAAs are shown in Figure 5. The isotherms are dissimilar for the different architectures of PAA. There is an increase in the area per amphiphile going from linear to 4-arm or 6-arm PAA. This trend is expected if an insertion of the hydrophobic core is assumed. However, the trend is not continued for the 12-arm PAA which has the largest hydrophobic core, but the area per amphiphile is only slightly higher than for the linear PAA. This unexpected behavior is can be correlated with the pH which is reached when the corresponding PAA is dissolved in pure water. The pH is the lowest for the 12-arm PAA (pH = 4.95) followed by the linear PAA (pH = 5.2), but higher for the 4-arm and 6-arm (both pH = 5.4). This slight differences in the pH of the solution might have a small but significant impact on the structure of the monolayer (Figure 2).

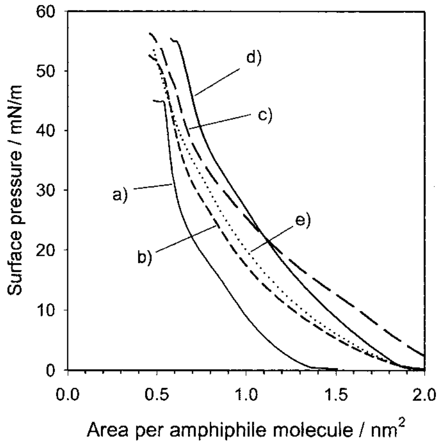


Figure 5. Surface pressure / area isotherms of DODA spread on a) pure water and solutions containing b) linear (c = 13.2 mg/L, pH = 5.2), c) 4-arm (c = 11.8 mg/L, pH = 5.4), d) 6-arm (c = 12.2 mg/L pH = 5.4), and e) 12-arm polyacrylic acid (c = 11.6 mg/L pH = 4.95)

The cause for the different pH of the PAA solutions has not yet been identified unambiguously, but may be related to the differences in ionisation behavior of linear and star shaped molecules. However, theories would predict a reduced ionization for the higher branched weak polyelectrolyte, that is a higher pH for the 12-arm polymer.[29, 30]

Poly(N-propyl-4-vinylpyridinium bromide) (q3PVP) is a strong polyelectrolyte which degree of ionisation does not depend on the pH of the solution. The isotherms for linear and star-shaped q3PVP are shown in Figure 6. The same trend as with the star shaped PAA can be observed. The higher the degree of branching the larger is the area per amphiphile. Furthermore, the trend is continued for the 12-arm q3PVP. Thus in this case there is just the expected increase due to the larger hydrophobic core.

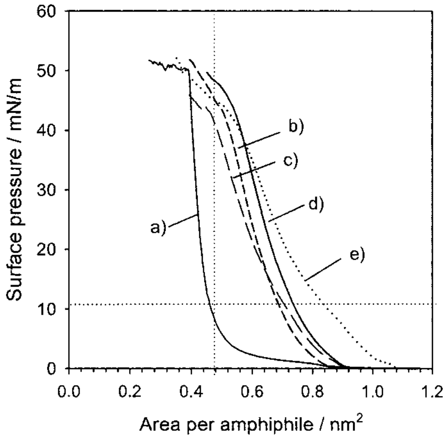


Figure 6. Surface pressure/area isotherms of DMPA spread on a) pure water and solutions containing b) linear (c = 12.8 mg/L), c) 4-arm (c = 12.2 mg/L), d) 6-arm (c = 11.8 mg/L), and e) 12-arm quarternized poly(vinylpyridine) (c = 12.1 mg/L)

Adsorption Experiments

The adsorption of the polyelectrolyte to an amphiphile monolayer brought into contact with the polyelectrolyte solution in Fromherz experiment can be monitored by recording the surface pressure as function of time (π-t-isotherms).[5, 18, 19, 31] It has been shown previously that there are significant differences between the π-t-isotherms for the different polyelectrolytes, while in the case of PSS and CMC, the surface pressure change seems to be a direct measure for the adsorption and the π-t-isotherms show a concentration dependence as expected for a diffusion controlled process,[19] this is not the case for PPPS. The π-t-isotherms show an inflection. Reducing the concentration of the polyelectrolyte in the subphase or increasing the molecular weight, the inflection becomes more pronounced and an induction period is found in which no change in the surface pressure takes place (Figure 7). In this case the change in the surface pressure is obviously no longer a direct measure of the adsorbed amount, but additional effects like the interactions of the polymer chains with each other, with the interface itself, and with the amphiphiles at the interface have to be taken into account.[19, 32, 33] Indeed it was possible to describe the dynamics of the adsorption process assuming a two-dimensional "crystallization" process.[19] Employing this approach the π-t-isotherms can be fitted nicely with an expression derived from the AVRAMI-equation, which has been developed to describe crystallization behavior of polymers.[34]

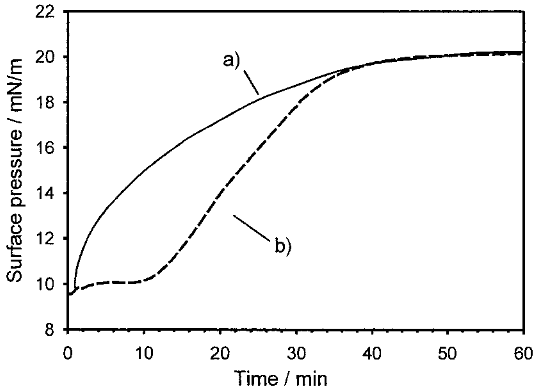


Figure 7. Comparison of the π-t-isotherms a) expected for an diffusion controlled adsorption (schematic) and b) those found for PPPS($P_n = 36$, C = 20.0 mg/L ($0,8\cdot 10^{-5}$ mol/L ionic sites)[19]

According to the results with PSS and CMC on one side and the rigid rod like polymers PPPS on the other side the adsorption process has to be divided in several steps: (1) the diffusion of the polymer chain to the monolayer, (2) the change in conformation and adsorption, (3) organization or "crystallization". For PPPS – that is the model for the extended chain situation – it has to be assumed that the ordering (step 3) is the rate determining step.[19]

As mentioned already star-shaped polymers have a more globular shape than linear chains. It can be anticipated, that these more globular shaped polymers do not show ordering phenomena upon adsorption as observed for the rigid rod polymers. However, as shown in Figure 8 the π-t-isotherms for the different polyacrylic acids also show a kind of induction period, in which the surface pressure even is reduced compared to the original pressure.

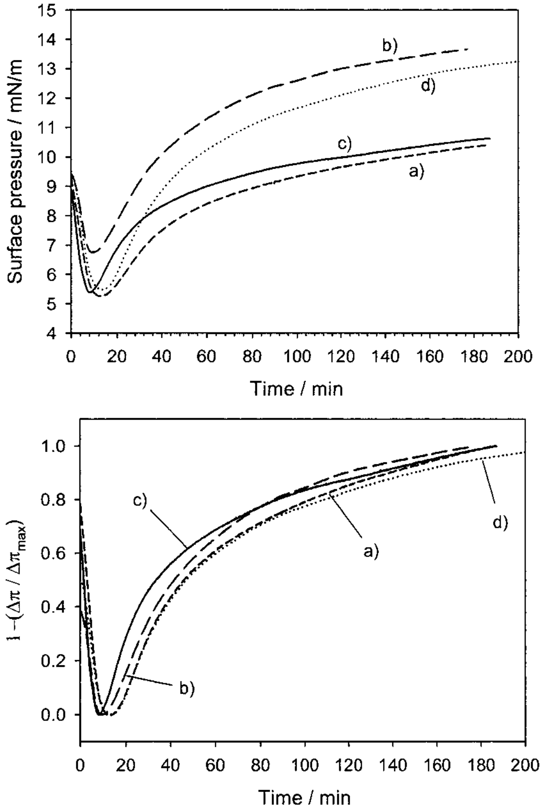


Figure 8. Change in surface pressure (π) upon transfer of a DODA monolayer onto a solution containing a) linear (c = 2.0 mg/L), b) 4-arm (c = 1.8 mg/L), c) 6-arm (c = 3.1 mg/L), and d) 12-arm polyacrylic acid (c = 1.5 mg/L) as function of time (top) and normalized change in surface normalized to the maximum change in surface pressure (bottom) (transfer of the monolayer at 10 mN/m)

The extent of the surface pressure drop seems not to depend on the number of arms. It is somewhat less pronounced for the 6-arm polyacrylic acid, but for the linear, the 4-arm-, and the 12-arm-polymer it is almost the same. Furthermore, the π-t-isotherms show only a slight scattering when normalized to the maximum surface pressure change (s. Figure 8 bottom). Thus, there is an unexpected induction period for PAA, which does not significantly depend on the degree of branching.

The situation for the branched q3PVP is very similar. Again all polyelectrolytes show an unexpected behavior in the adsorption kinetics with an induction period in which the surface pressure drops. This is unexpected since the comparison of the π-A-isotherms suggest an increase in the surface pressure and no ordering phenomena are anticipated for q3PVP as it is the case for PPPS. Furthermore, the π-t-isotherms for the star-shaped polymers are very similar. Thus, there are no differences in the adsorption kinetics due to the degree of branching. However, for this class of polymers the linear polymer shows a different behavior (Figure 9), but the difference is merely quantitative than qualitative.

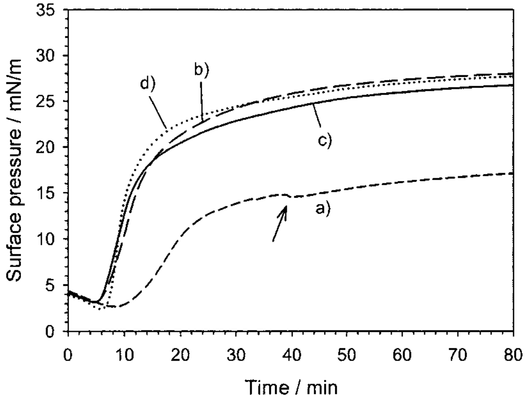


Figure 9. Change in surface pressure (π) upon transfer of a DMPA monolayer onto a solution containing a) linear (c = 1.9 mg/L), b) 4-arm (c = 1.8 mg/L), c) 6-arm (c = 1.9 mg/L), and d) 12-arm poly(N-propyl-4-vinylpyridium bromide) (c = 1.9 mg/L) as function of time (transfer of the monolayer at 5 mN/m), the arrow marks a partial collapse

The π-t-isotherm for the linear q3PVP has the same shape than those for the star-shaped q3PVP, but the final surface pressure is somewhat lower and the induction period slightly longer. The origin of the quantitative differences remain elusive. It can be speculated that a partial collapse of the monolayer upon adsorption and the concomitant increase in surface pressure limits the final surface pressure. The π-t-isotherm for the linear q3PVP show an indication for a partial collapse (discontinuity at approximately 45 min marked by an arrow in Figure 9).

The investigation of linear and star-shaped poly(acrylic acid) and poly(N-propyl-4-vinylpyridium bromide) indicate that the influence of the degree of branching on the kinetics of adsorption of the polyelectrolyte to a monolayer of charged amphiphile is not very significant. Furthermore, for the DODA/PAA as well as for the DMPA/qPVP a significant induction period is found in the π-t-isotherms, which is completely unexpected. The explanation for this behavior remains elusive at this moment, but it can be supposed that beside ordering effects also hydrophobic interaction may play a role in the adsorption process. The surface pressure change can be due to a incorporation (partly or completely) of the polyelectrolyte into the monolayer. This process is most likely the rate determining step after diffusion and adsorption.

Conclusions

We have shown that it is possible to use monolayers of ionic amphiphiles as model surfaces to study the polyelectrolyte adsorption. Previously rigid rod-like polymers were investigated as model for completely extended chain situation. Star-shaped polymers have a more globular shape than linear polymers and can be regarded as approximation of the random coil situation of the polyelectrolytes. In this study linear and star-shaped poly(acrylic acid) and poly(n-propyl-4-vinylpyridium bromide) with varying number of arms were used to study the influence of an increasing degree of branching on the adsorption kinetics. Previous results with rigid rod-like polyelectrolytes have indicated that the adsorption process is a multi-step process in which the adsorption itself is followed by an ordering process in the complex monolayer. Such an ordering process resulting in a liquid crystalline phase can be ruled out for a globular system. However, the experimental results with the linear and star-shaped polyelectrolytes clearly show that the also highly branched 12-arm polyelectrolytes can show an induction period in the adsorption kinetics measured as π-t-isotherm. The influence of the degree of branching on the adsorption kinetics seems to be small for both polyelectrolytes and merely quantitative.

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