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INVESTIGATION OF POLYELECTROLYTE ADSORPTION BY MEANS OF A NOVEL CONCEPT BASED UPON THE USE OF MODEL SURFACES AND MODEL POLYELECTROLYTES

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Abstract: A concept to study the influence of molecular parameters in the adsorption of polyelectrolytes is presented. Characteristic for this approach is the use of model surfaces and model polyelectrolytes. The properties of both the surfaces and polyelectrolytes can be varied in a well defined way and over a broad range. First experiments show that the method is able to give structural information about the adsorbed polyelectrolytes. The method is very sensitive, adsorption experiments with polyelectrolyte concentrations in the region of micromoles per litre are possible.

INTRODUCTION

The adsorption of polymers and especially the adsorption of polyelectrolytes is a phenomenon of both industrial and scientific importance (Refs. 1,2). Especially the cationic surface modification of organic and inorganic materials with non-stoichiometric polyelectrolyte complexes (Ref. 3) is an interesting field. A number of questions, based upon the molecular properties of the surfaces as well as of the polyelectrolytes, are still open. This paper presents a concept to study the influence of molecular interactions in the adsorption process by the use of model surfaces and model polyelectrolytes. First experiments on this basis were carried out with the aim to proof the useability of this concept and to find out the limits of the techniques.

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It is necessary, that the model surfaces have a well defined structure. Additionally, the introduction of different functional groups (ionic and non-ionic) should be possible. Moreover, their density and distribution should be varied in a simple way. The Langmuir-Blodgett (LB) technique (Ref. 4, 5) fulfils these requirements and was therefore chosen as method for the preparation of the model surfaces. With respect to their stability, amphiphilic polymers should be applied.

Starting point of the search for appropriate model polyelectrolytes was the formulation of the requirements on these compounds. Mainly, these polymers must make it possible to get information on their conformation in solution and in the adsorbed layer. In addition, data to quantify the adsorbed amounts are essential. Furthermore, polyelectrolytes with a variety of functional groups should be accessible from the same basis polymer.

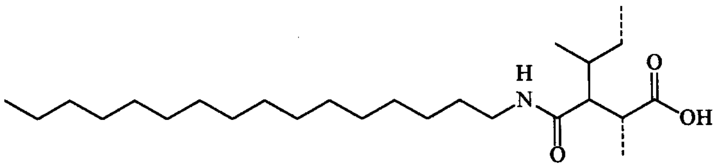
The usefulness of fluorescence marked polymers (Ref. 6) for the investigation of interpolymer interactions in solution was demonstrated for instance by Kabanov (Ref. 7), Somasundaran (Ref. 8) or Turro (Ref. 9). So it was obvious to adapt the method for the investigation of polyelectrolyte adsorption and adsorbed layers.

EXPERIMENTAL PART

Materials

All solvents were dried before use. The reactions were carried out under a nitrogen atmosphere. Polymer concentrations were related to the repeating units.

Poly(maleic acid hexadecyl monoamide-alt-propylene) (**12**, see structure 1). A solution of 0.021 mole hexadecylamine and 0.014 mole Poly(maleic anhydride-alt-propylene) (Leuna AG, Germany, M_w 24.000) in 100 ml pyridine was heated at 90°C for 20 hours. The product was precipitated in acetonitrile and dried. Then the polymer was twice dissolved in tetrahydrofurane and precipitated in acetonitrile. IR and NMR spectra agree with the proposed structure.



structure (1)

Poly((ethylene)$_{0.5}$*-co-(maleic acid pyrene monoamide)*$_{0.025}$*-co-(maleic anhydride)*$_{0.475}$*)* **(189,** see structure 2). This polymer was prepared by heating a solution of 0.0025 mole 1-amino pyrene (purum, Fluka Chemie AG, Switzerland) and 0.05 mole Poly(ethylene-alt-maleic anhydride) (Polyscience Inc., USA, M_w 106.000) in 95 ml pyridine at 95°C for 5 hours. The crue product was precipitated in ethyl acetate. Then the polymer was twice dissolved in tetrahydrofurane and precipitated in hexane again. IR and NMR spectra agree with the proposed structure.

Poly((ethylene)$_{0.5}$*-co-(maleic acid)*$_{0.475}$*-co-(maleic acid pyrene monoamide)*$_{0.025}$*)* **(189h,** structure see figure 1). Hydrolysis of 2g **189** was performed for 40 hours in 60 ml of a 1:1 mixture of water and tetrahydrofurane at 60°C. The solvent was removed with a vacuum rotation evaporator. Then the polyelectrolyte was dissolved in ethanol and precipitated in ethyl acetate. IR and NMR spectra agree with the proposed structure.

Poly((ethylene)$_{0.5}$*-co-(maleic acid)*$_{0.355}$*-co-(maleic acid-picolyl monoamide)*$_{0.12}$*-co-(maleic acid pyrene monoamide)*$_{0.025}$*)* **(199,** structure see figure 1). 0.007 mole **189** and 0.0028 mole 4-picolylamine (purum, Fluka Chemie AG, Switzerland) in 50 ml tetrahydrofurane were heated at 50°C for 5 hours. The crue product was filtered off. Then the polymer was dissolved in pyridine and precipitated in hexane.

The water used for the monolayer and adsorption experiments was purified using a Milli-Q Plus system (Millipore, USA; 18.2 MΩ/cm) feeded by a Milli-RO-5 instrument (Millipore, USA).

Transparent supports for LB film preparation were synthetic quartz plates Spektrosil B (TQS GmbH, Germany). The quartz plates were purified in a mixture of H_2SO_4 and potassium peroxodisulphate. If required, they were hydrophobized with hexamethyldisilazane (98 vol.-%, Aldrich, Germany).

For the preparation of the polyelectrolyte stock solutions the polymers were dissolved first in a small amount of an organic solvent (**189h**, ethanol, 1 vol.-%; **199**, dimethyl sulphoxide, 1 vol.-%). Then the solutions were filled up with water. At the day of use the stock solutions were mixed with buffer solution by a factor of 10 in minimum so that the final content of the organic solvent was 0.1 vol.-% or less. The buffer solutions were prepared with NaOH, citric acid, phosphoric acid, boric acid and HCl according to Theorell and Stenhagen (Ref. 10). Only in the case of the experiments shown in figure 7 a commercial phosphate buffer (Merck, Germany) was applied.

Methods

The monolayer and deposition experiments were carried out in a clean room (class 10 at the working place) with commercial film balances KSV 3000 (KSV Instruments, Finland) and FW 2 (Lauda Dr. R. Wobser GmbH, Germany). Monolayer depositions were carried out with a dipping speed of 1 mm per minute and with an upper delay of 16 minutes at 23°C. The pressure was held to be constant at 33 mN/m.

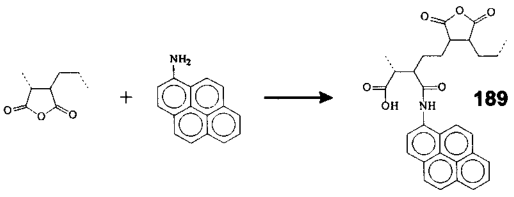
U.v./vis. spectra were recorded on a Lambda 2 spectrophotometer (Perkin-Elmer, Germany). Fluorescence Spectra were measured with a LS 50 fluorescence spectrometer (Perkin-Elmer, UK). A modified sample cell was used. The incident angle of the excitation beam was 45°. Excitation and emission slit widths were 5 and 15 nm, respectively.

Adsorption experiments were carried out in beakers with approximately 100 ml of the stirred adsorption solution. Afterwards, the supports were washed in water for three minutes under stirring and dried on air.

RESULTS AND DISCUSSION

Concept

The Poly(maleic anhydride-alt-ethylene) copolymer was selected as the basis polymer because a variety of functional groups can be introduced in a similar way, including the fluorescence probes. Structure 2 shows the synthesis of the fluorescence marked basis polymer. The pyrene content was adjusted to 5 mol-% (related to the maleic anhydride units). This product was the basis for the synthesis of a number of polyelectrolytes with different functional groups but with the same backbone and chain length.



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Structure (2)

Figure 1 illustrates the manifold of accessible polymer structures without the demand of completeness (not all of them has been realised yet). Hydrolysis yields a relatively weak polyacid. Reaction with aniline sulfonic acid leads to a strong polyacid. The conversion with 4-aminomethyl pyridine yields polyampholytes. After imidization and quaternization a strong polycation will be available, whereas through the conversion with aliphatic amines the balance between hydrophilic and hydrophobic parts in the molecule may be varied. The polyelectrolytes used for the experiments of this paper are indicated by the corresponding product numbers.

Figure 2a shows an introduction into the photochemical aspects of this work (Ref. 11). To simplify matter's pyrene was chosen as an example, and only the most important reaction pathways were included. After absorption of a photon the molecule passes into an excited singulett state, which can deactivate to the ground state by thermal processes or emission of fluorescence light. In a competing reaction with another pyrene molecule in the ground state an excited dimer can be formed. This is a so-called excimer, which can deactivate by fluorescence emission and thermal processes, too. The fluorescence of the excimer is red-shifted and can be observed beside the fluorescence of the monomeric pyrene. The formation of the excimer is a bimolecular reaction. Therefor, the ratio of monomer and excimer fluorescence intensities depends strongly on the average distance between the molecules and on the diffusion coefficients.

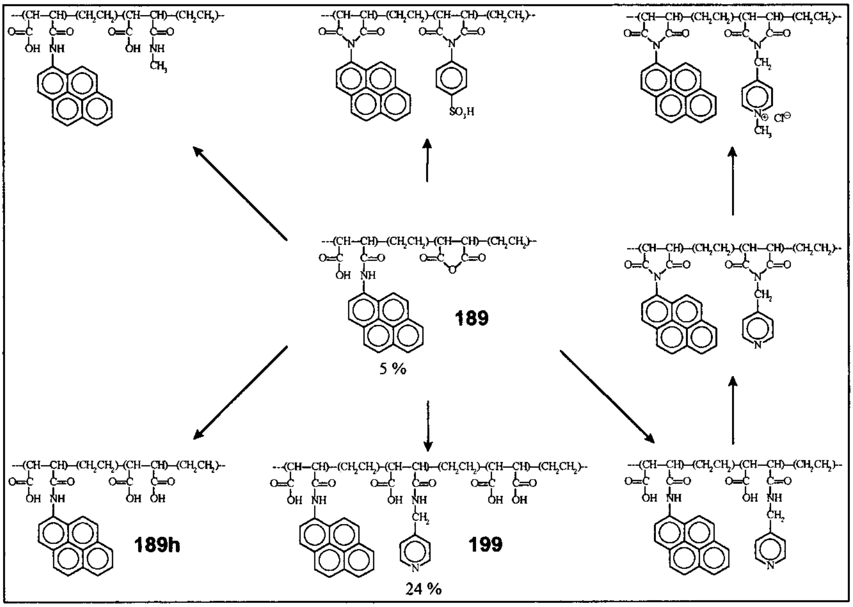

Figure 1: Synthesis of polyelectrolytes starting from the basis polymer

In the case of polymer bound pyrene, the relations are more complex: the polymer conformation has an influence on the local pyrene concentration as can be seen in the figure 2b. In a coiled polymer conformation the probability for the excimer formation is much higher than in the case of an expanded macromolecule. The ratio of excimer and monomer fluorescence intensities can be used to get information about the polymer conformation[5,6].

The polyampholyte **199** shows at pH 4.8 a higher excimer fluorescence than monomer fluorescence (figure 3). An increase of the pH to 6.5 causes a higher monomer fluorescence indicating a more expanded polymer conformation. The behaviour of **199** is determined by the coexistence of the carboxylic acid groups and the pyridine units. For poly(maleic acid-co-ethylene) pK_{S1} values between 3.65 (Ref. 12) and 4.0 (Ref. 13) were reported. In the case of

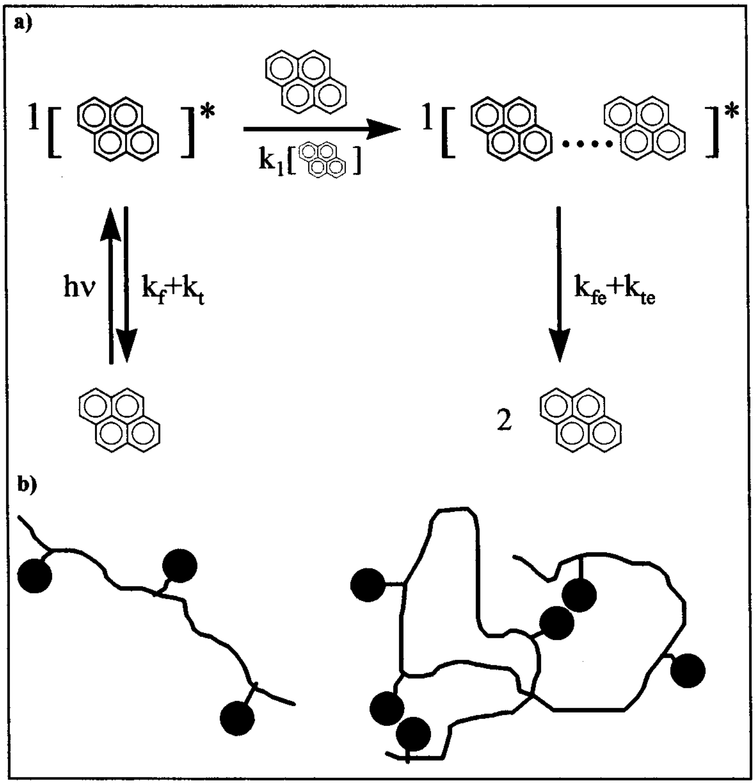

Figure 2: An introduction to pyrene photochemistry

pyridine a pK_B value of about 8.75 is known (Ref. 10). With these values, for the change of the pH from 4.8 to 6.5 an increase of the number of dissociated carboxylic acid groups of about ten percent may be assumed. This results in enhanced repulsive forces within the macromolecule. Otherwise, at pH 6.5 the number of pyridinium moieties is decreased to a value of about 15% in comparison to pH 4.8. Because the pyridinium cations compensate the repulsive forces of the carboxylate anions in part, this leads also to higher repulsive forces in the maromolecules causing a more expanded chain conformation.

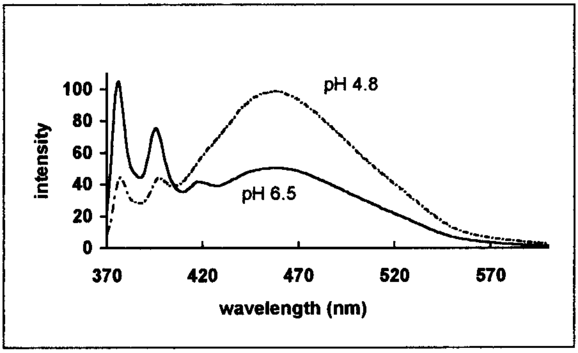

Figure 3: Fluorescence spectra of **199** ([**199**] = 0.001 M in water, pH was adjusted with NaOH or HCl)

For the preparation of the model surfaces the LB technique has been used. A solution of the amphiphilic polymer was spread on an aqueous subphase. After evaporation of the solvent the molecules were compressed to a highly ordered monolayer. By dipping an appropriate substrate upwards through this monofilm the monolayer could be transferred to the substrate with an orientation of the polar groups towards solid support, a following dipping downwards yielded an opposite orientation of the molecules in the second transferred monolayer. Consecutive repetitions of this process lead to multilayer assemblies with a high supramolecular order of the molecules. In dependence on the last transfer direction, the top layer was either polar or not. In the following text, a LB multilayer with polar groups on the top will be designated as a „hydrophilic" LB layer (■●═...═●), otherwise it is called a „hydrophobic" (■●═...═●●═) one.

To realise different surface properties the same principles in synthesis were used as in the case of our model polyelectrolytes (figure 1). Here, maleic anhydride copolymers with long hydrophobic side chains serve as basis for the preparation of cationic, anionic or non-ionic surfaces. Amphiphilic copolymers of this kind have been introduced for the preparation of LB multilayers by Tredgold and Hodge (Ref. 14). Among the chemical nature of the functional groups in the surface, their density is an important parameter which may be varied by different ways (figure 4): On the one hand, for instance the charge density may be changed through the variation of the degree of substitution. On the other hand, mixing of the homopolymers in an appropriate ratio should result in the same surface charge but perhaps in a different charge distribution. In the last case one has to distinguish between a homogenous distribution and the formation of domains with varying compositions.

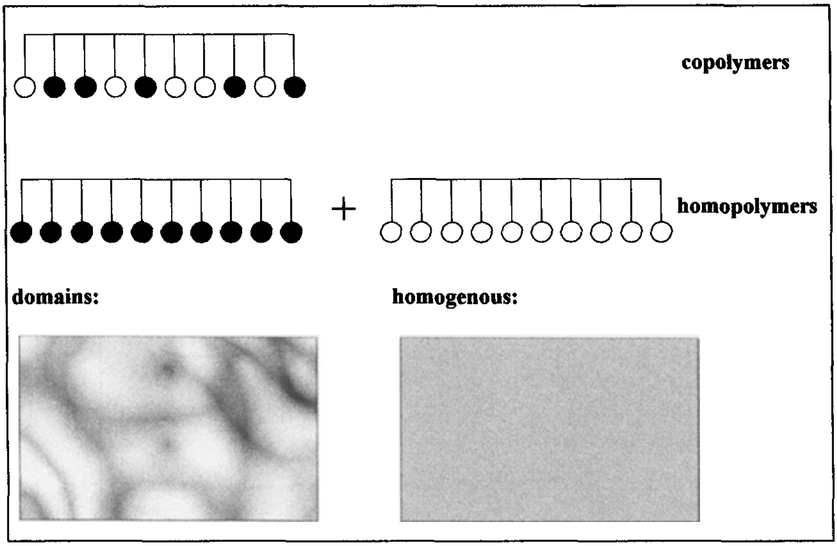

Figure 4: Density and distribution of functional groups (schematically)

First results

In the following experiments LB multilayers of poly(maleic acid hexadecylamide-co-propylene) (**12**) were used. Figure 5 shows in the inset the isotherm of this polymer obtained during compression on a pure water subphase. The polymer forms highly stable monolayers as can be seen from the high collapse pressure of about 70 mN/m. The collapse area is approximately 23 Å^2 and thus a little bit higher than for similar low molecular weight amphiphiles. Monolayer transfer to quartz supports were carried out at a film pressure of 33 mN/m, the transfer ratios were between 0.9 and 1. The bottom figure shall illustrate the reproducibility in the multilayer preparation and contains the u.v./vis. spectra of four different quartz supports with three monolayers of **12**. Only minor differences between the curves are detectable.

In preparatory experiments the stability of LB layers (two monolayers of **12** on hydrophilic quartz) was tested at pH 4.8 and pH 8. The pH was adjusted by addition of HCl or NaOH as well as by use of buffer solution. The supports were immersed in the stirred solutions for one hour. The u.v./vis. spectra showed no loss of polymers due to the experiment.

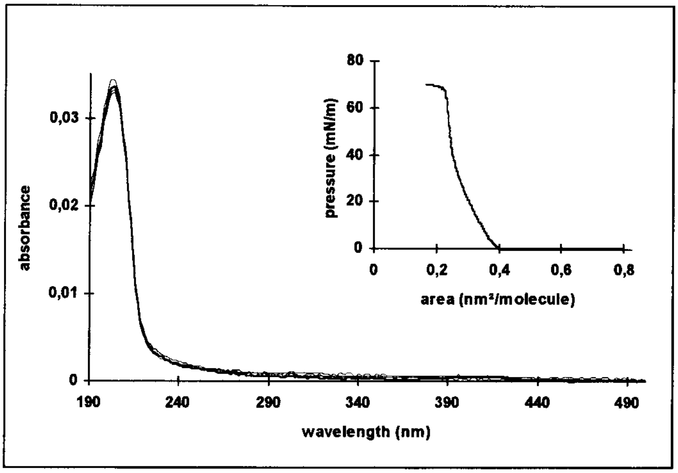

Figure 5: Absorption spectra of 3 monolayers of **12** (■•══••═) on four different hydrophilic quartz supports, in the inset: π-A isotherm of **12** on water at 22°C

In one of the very first adsorption experiments with the polyelectrolyte **199** (10^{-3} M) in pure water four different surfaces were used: hydrophilic and hydrophobic LB layers of **12** and hydrophobized and hydrophilic quartz plates. Firstly, these supports were immersed in the polyelectrolyte solution. After three minutes they were washed with water (3 minutes) and dried on air. Then, the fluorescence spectra were recorded. For the non-coated substrates only a negligible fluorescence was detectable. In the experiments with the LB films significantly enhanced fluorescence signals were visible. Unfortunately, these experiments were not reproducible. As a reason it was found out, that the fluorescence spectra of the polyelectrolyte solutions showed drastic changes with the time. This may be explained in part by the adsorption of CO_2 and therefor an altered pH value. Until now, these changes can suppressed only by use of buffers. This is a disadvantage because it is a restriction for the variation of solvent polarity and composition. The following experiments were carried out with buffered solutions.

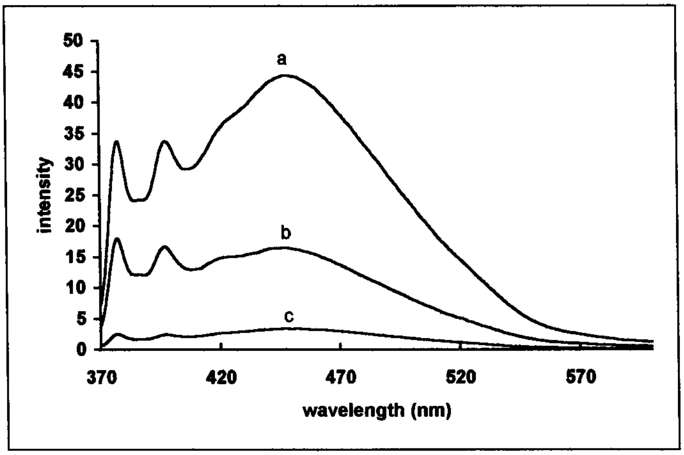

Figure 6: Adsorption of **199** on different supports (adsorption time: 1 min, [**199**] = 10^{-3} M pH 4.9):

a) 3 layers **12** on hydrophilic quartz (■═══)
b) 2 layers **12** on hydrophilic quartz (■══)
c) hydrophilic quartz

Figure 6 shows the adsorption of the polyelectrolyte **199** (10^{-3} M) on different surfaces. First of all, clear differences between the various surfaces are visible. In the case of a hydrophilic quartz plate only a small fluorescence was observed (curve c). On a hydrophilic LB layer a significantly enhanced fluorescence was detectable (curve b). The strongest fluorescence exhibited the polymer adsorbed on a hydrophobic LB layer (curve a). Because the polyelectrolyte exhibits a dominant negative charge, repulsive forces between them and the likewise negatively charged surface prevent a more effective adsorption. Otherwise, in solution hydrophobic materials have negatively charged surfaces (Ref. 15), too. Contradictory to polar surfaces with dissociating groups here, the surface charge is a result of the specific adsorption of anions. In the case of the hydrophobic LB layer the polyelectrolyte was able to replace the adsorbed low molecular anions. Additionally, hydrophobic interactions between surface and polymer are quite possible. This can explain that the hydrophobic LB layer shows a higher excimer fluorescence then the hydrophilic one. With the actual knowledge a more coiled conformation of the adsorbed polyelectrolytes may be assumed. In comparison to the solution spectrum (see figure 3) the excimer part of the fluorescence is lowered. This behaviour points to a conformational change in the adsorption process or by drying, respectively.

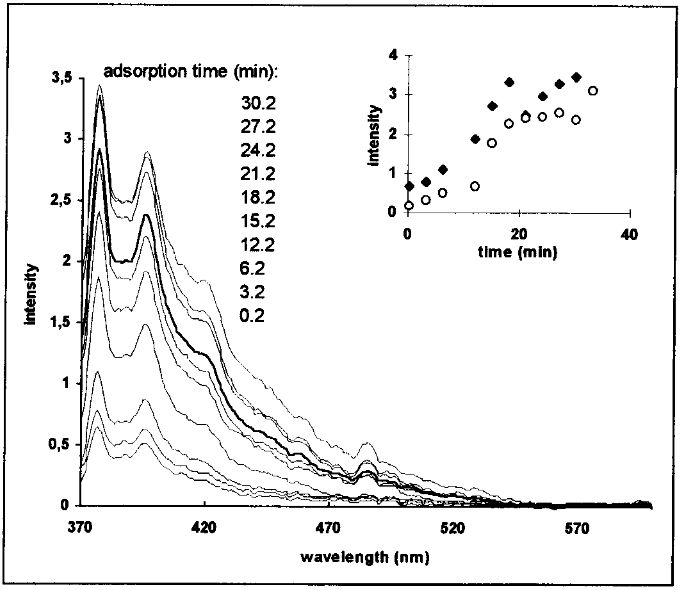

Figure 7: Fluorescence spectra of **189h** adsorbed on 3 monolayers (■≡≡≡≡) of **12** on quartz ([**189h**] = 10^{-3} M, phosphate buffer, pH 7, parameter: adsorption time; in the inset: squares-this series, circles-independent series for reproduction)

It was very interesting to learn how sensitive is the method. For the experiments shown in figure 7 the polyacid **189h** was used at a concentration of $5*10^{-7}$ M. The model surface was a hydrophilic quartz substrate with three monolayers of the polyamphiphile **12**, the pH value of the adsorption solution was 7. The figure shows the fluorescence spectra with the adsorption time as parameter. The spectra illustrate that the noise was acceptable. The squares in the inset correspond to the fluorescence intensities at 377 nm in the presented series of spectra, the circles were results of an independent parallel experiment under the same conditions. Until now the reproducibility is not satisfactory but the results show that the method will work even in the case of very small concentrations. By determination of the decrease of the solution concentration of the polyelectrolyte the adsorbed amount was estimated. It should be pointed out, that the amount of adsorbed polymer in these experiment is less then required for a densely packed monolayer of **199**, in which the molecules has been adsorbed without loops and tails (approximately 0.1 „monolayers" were adsorbed in each adsorption step). Therefor, the investigation of the first steps in the adsorption process should be possible.

CONCLUSIONS

In this paper a concept to study the adsorption of model polyelectrolytes on model surfaces was introduced. This approach is characterised by two main features:

1. A basis polymer serves as starting point for the synthesis of a variety of polyelectrolytes with different functional groups but the same backbone. This basis polymer was marked with pyrene to investigate the adsorbed polyelectrolytes by means of fluorescence spectroscopy. Beside the quantitative aspect (fluorescence intensity) structural information are available (monomer/excimer equilibrium).
2. Langmuir-Blodgett multilayers as model surfaces give the possibility to vary the kind of functional groups in the surface as well as their density. Amphiphilic polymers with different functionality can be synthesised in a similar way like the model polyelectrolytes.

First experiments showed, that the method is able to detect adsorbed polymers in amounts much less than required for a densely packed flat monolayer of the polyelectrolyte. The conformation of the adsorbed polymers may differ from that in the adsorption solution as indicated by the different ratios of monomer and excimer fluorescence in solution and in the adsorbed layer. The conformational changes can be dominated by molecular interactions of the polyelectrolyte with the surface or by drying of the samples. However, further investigations should be extended to wet surfaces and the adsorption/formation of polyelectrolyte complexes at the surfaces. Additionally, supporting analytical methods like reflection/absorption FTIR, spectroscopy with polarised light, surface plasmon resonance and AFM will be applied. Actually, the use of buffered polyelectrolyte solutions is necessary. In the future alternatives for the work in salt free solutions should be find out.

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