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Surface Modification by Polyelectrolytes: Studies on Model Systems

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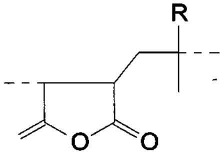
SUMMARY: An improved method for the preparation of uniform dispersions of non-stoichiometric polyelectrolyte complexes on the basis of maleic acid copolymers and poly(diallyldimethylammonium chloride) was developed. The dispersed particles showed a narrow size distribution on the nm scale and were used as model systems for the investigation of their adsorption on different model surfaces. A combination of ATR-FTIR, SPR, ellipsometry and SEM was useful for the monitoring of the adsorption process of individual colloid particles and may lead to a quantitative description of the adsorption process. For a better understanding of the underlying principles and interactions organic model surfaces which meet the requirements of the different methods are required.

Introduction

Surface modification by polyelectrolytes (PEL) and polyelectrolyte complexes (PEC) is a field of both practical and scientific interest[1,2,3]. One aim is the introduction of cationic surface charge. For this, polyelectrolyte complexes made from maleic acid copolymers (**1**) and poly(diallyldimethylammonium chloride) (PDADMAC, **2**) are of special interest[4,5,6].



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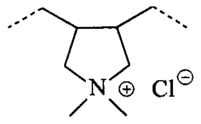
a R = -H

b R = -Ph



2

Polyelectrolyte complex dispersions can be easily prepared by mixing solutions of the oppositely charged polymers. However, the process and structure formation is not fully understood in detail. An important question is that of the influence of the molar mixing ratio (n_-/n_+) between the base units of polyanions (PA) and polycations (PK) on the composition of the polyelectrolyte complex and it's structure.

Fig.1 illustrates some difficulties, which may arise in the handling of the dispersions prepared by the straightforward mixing of PDADMAC and poly(maleic acid-co-propylene) (P(MS-P), **1a**) solutions. The initial ratio n_-/n_+ was 0.6 in these experiments. The dispersions of the polyelectrolyte complex were characterized by their optical density at 500 nm and their particle size. They were stable only in a very small concentration range. At low concentrations soluble polyelectrolyte complexes were formed. The solution was clear, no colloid particles could be detected. Above PDADMAC concentrations of 0.004 mole/l the complex precipitated. It was not possible to characterize the equilibrium between free PEL and PEC particles in a sufficient manner. Other difficulties result from the influence of pH and inorganic salts leading to changed properties. To get more insight in the formation of the PEC's and their adsorption, uniform dispersions have to be prepared and used in combination with model surfaces.

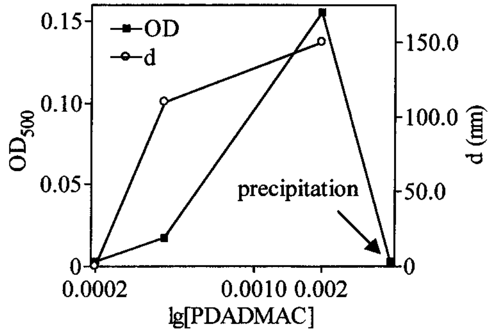


Fig.1: Optical density (OD_{500}) and particle size d of PEC dispersions made from P(MS-P) and PDADMAC in dependence on the initial PK concentration ($n_-/n_+ = 0.6$)

Materials and methods

PDADMAC of $M_W \approx 250.000$ g/mole ($M_W/M_n \approx 1.6$) was synthesized and characterized by W. Jaeger (Fraunhofer-Institut für Angewandte Polymerforschung, Teltow, Germany). Copolymers of maleic acid with propene (P(MS-P)) and α-methylstyrene (P(MS-α-MeSty)) were prepared by hydrolysis of the corresponding anhydrides in the presence of NaOH. These polyanhydrides with $M_W \approx 50.000$ g/mol (P(MS-P)) and $M_W \approx 24\ 000$ g/mol (P(MS-α-MeSty)) were obtained from Leuna AG (Germany).

The *preparation of the initial PEC dispersions* was carried out by direct mixing of solutions of the oppositely charged PEL. In all experiments, a constant amount of PK ($n_+ = 0.25$ mole) was used. The desired amount of the PA solution was added dropwise to the stirred solution of the cationic PEL. The procedure to obtain uniform dispersions will be described as a result.

The *turbidity* of the PEC dispersions was characterized by the optical density OD_{500} at 500 nm. The measurements were carried out with a Lambda 2 UV/VIS spectrometer (Perkin Elmer, Germany).

Quasi-elastic light scattering was used to determine the *z*-average diffusion coefficient of the PEC particles and to calculate their *z*-average hydrodynamic radius. The measurements were carried out at a fixed angle of 90 ° by means of a Zeta Master S device (Malvern, UK).

ATR-FTIR measurements for polyelectrolyte complex adsorption at SiO_x surfaces were performed on the *in-situ-ATR-FTIR Apparatus for Sorption Measurements* (U. P. Fringeli, University of Vienna, OPTISPEC, Zürich) as described elsewhere[9,10], using a commercial rapid scan FTIR-spectrometer (IFS 28, BRUKER) equipped with the globar source and MCT detector. ATR-FTIR spectra were recorded by the SBSR-(Single Beam-Sample Reference)-method, whereby single channel spectra $I_{S,R}$ were recorded of both the upper (S) and lower (R) half ($50*10*2mm^3$) of the silicon internal reflection element (IRE, $50*20*2$ mm^3). A transparent *in-situ* sorption cell (IPF) was used sealing the IRE halfs separately by O-rings (Viton) to form the sample compartment (S), which was filled with PEC dispersion, and the reference compartment (R), which contained water, respectively. Convenient background compensated absorbance spectra (A_{SBSR}) were obtained by ratioing the single channel spectra according to $A_{SBSR} = -\log (I_S/I_R)$.

For spectroscopic ellipsometry a rotating analyzer type variable angle multi wavelength ellipsometer (M-44, J.A. Wollam Co., Lincoln, NE, USA) was applied. An optical two-layer-model was used to fit the experimental data: Si-substrate/SiO_2 layer/adsorbed PEC layer/ambient (air or water). The theoretical constants of Si and SiO_2 were taken from the literature to determine the thickness of the thermal silicon oxide layer from the initial values Δ_0 and Ψ_0 before the adsorption experiments. The average refractive index n and the thickness d assuming a non-absorbing (k=0) uniform adsorbed PEC layer were calculated from the experimental values of Δ and Ψ in the equilibrium state. The measurements of PEC adsorption onto oxidized silicon wafers were carried out in situ in an ellipsometric liquid cell at an angle of incidence of 67,9° or after drying in air at 65, 70 and 75°.

Surface plasmon resonance (SPR) data were recorded with an in-house designed SPR system consisting of a HeNe laser (632.8 nm), a theta/2 theta goniometer and a silicon photodetector.

The laser was coupled through a semi-cylinder onto a glass slide. The semi-cylinder and the glass slide were made from the same high refractive index (1.723) material. The glass slide was covered with a 50 nm evaporated gold film. A liquid-flow cell with a volume of 2.5 ml was mounted on the glass plate and sealed with an O-ring. The solution was continuously circulated through this flow cell by a peristaltic pump with a rate of 10 ml per minute. Instrument control, data collection and modeling of the resulting reflectivity curves to Fresnel's equations were done by self-made software package using Borland Delphi as programming language.

Scanning electron micrographs were taken with an LEO Gemini field emission SEM operated at 1 KeV. Under these conditions charging of samples could be avoided and the low penetration depth of low energy electrons guaranteed high resolution imaging of near surface areas.

AFM micrographs were obtained with an AFM system integrated into an optical microscope (Zeiss Ultraobjective®). Particles examined by AFM were pre-selected in the light microscope under dark field illumination.

Results and discussion

A special procedure was developed to get uniform PEC dispersions. At first, the PEL solutions were mixed in a well defined manner. Then the obtained initial dispersion was centrifuged at 11.000 rpm for 20 minutes. After centrifugation three fractions were obtained: The supernatant fraction showed only a weak turbidity and was with nearly 80...90 vol% the largest fraction. Between this and a solid precipitate a concentrated disperse fraction was visible. The boundary between the supernatant and the concentrated dispersion was not very sharp, the supernatant was removed very carefully. Then the beaker was filled up with water and centrifuged again in order to remove free PEL's and soluble PEC's, respectively. Now the concentrated disperse fraction was isolated and diluted to a definite volume. Table 1 shows the data for the different fractions. The solid precipitate had a nearly stoichiometric composition, approximately 15 % of the polyelectrolyte input were in this fraction. In the supernatant with about 10 % of the initial polymer amount, the particle size distribution showed two maxima at 90 nm and 210 nm. In the disperse fraction an average particle size of 232 nm with a narrow size distribution has been observed (polydispersity: 0.07). The ratio n_-/n_+ was 0.63. Approximately 75 % of the applied polymers were in this fraction. Below pH 9 the particles exhibited a positive surface charge. In the following experiments only dispersions prepared from these concentrated fractions were used and designated as model dispersions. The exact determination of the concentration was not so convenient. So the concentration will be indicated in terms of dilution of the model dispersions.

Table1: Preparation of a model dispersion (n_-/n_+ of the initial dispersion: 0.6)

	particle size (nm)	optical density (500 nm)	n_-/n_+	content[a] (%)
supernatant	86 (15%) 212 (85%)	0.009		≈ 10
concentrated disperse fraction	232	0.09	0.63	75
precipitate			0.95	15

[a] related to the PEL input

In Fig. 2 the determined molar ratios n_-/n_+ in the model dispersions are shown as a function of n_-/n_+ in the initial dispersion. Initial ratios of n_-/n_+ between 0.4 and 0.8 did not have a significant influence on the composition in the model dispersion ($n_-/n_+ \approx 0.63$). In this region the PEC's were positively charged, the isoelectric point was above pH 9. At high initial ratios n_-/n_+ a negatively charged PEC could be obtained, too. In that case the PK was added to the PA solution. First adsorption experiments were carried out with thermal oxidized Si wafers for one hour in water as well as in the presence of sodium chloride. Different concentrations of the model dispersion were applied. The oxide layer was 50 nm thick. After adsorption, the samples were washed with water and analyzed by means of ellipsometry. Surface concentrations of the adsorbed PEC layer under water and in the dry state were determined using the equations of de Fejter[7] and Filippova[8] using a mean value for the refractive index increment dn/dc of PEC and the PEC density, respectively. Values between 1 and 8 mg/m² were obtained. With the assumption of a density of 1 g/cm³, one can derive a layer thickness of 1 and 8 nm if an uniform,

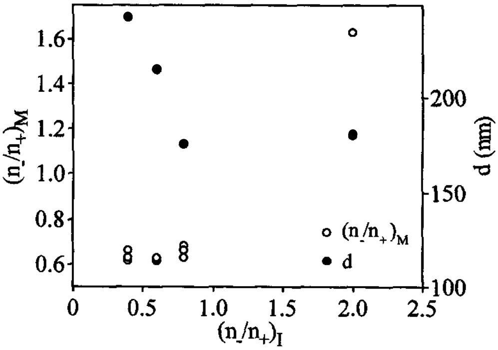


Fig. 2: Molar ration PA/PK and particle size d in the model dispersion ($(n_-/n_+)_M$) in dependence on the initial molar ratio PA/PK ($(n_-/n_+)_I$)

homogeneous PEC layer is assumed. This was a little bit surprising with respect to the particle size in the dispersions.

With an in-situ-ATR-IR technique[9,10] further information should be acquired. In Fig. 3 the integrated band area of the carboxylate stretching vibration of the polyanion component is plotted versus time, showing that the PEC adsorption was relatively fast. Possibly an additional long term process was superimposed. Furthermore the adsorption process was accompanied by the desorption of water molecules from the surface, which could be evidenced by the increase of the negative ν_{OH} band.

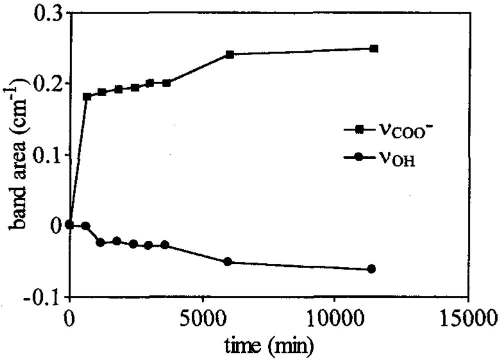


Fig. 3: In-situ ATR-IR spectra monitoring the adsorption of a model PEC dispersion from PDADMAC and P(MS-co-α-MeSty) on SiO_x internal reflection elements (undiluted, $n_-/n_+ = 0.63$)

Interesting details were visible in an electron microscopic image of the ATR plate after adsorption (Fig. 4): Only a part of the surface was covered with the polyelectrolyte complex, approximately 35 %. The diameter of most of the adsorbed particles was between 300 and 450 nm. One can assume that these particles are the result of the adsorption of an individual colloid particle. An average diameter of 230 nm was determined. Some aggregates are visible, too. However, the aggregate formation seems not to be preferred. Possibly, this aggregation is connected with the long-time process mentioned before. With these findings, the low surface concentrations determined by ellipsometry become more understandable. With electron microscopy one can derive a particle density parameter from the number of adsorbed particles on a defined area. Within eight different adsorption experiments a good correlation between this particle density parameter and the integrated band area of the carboxylate

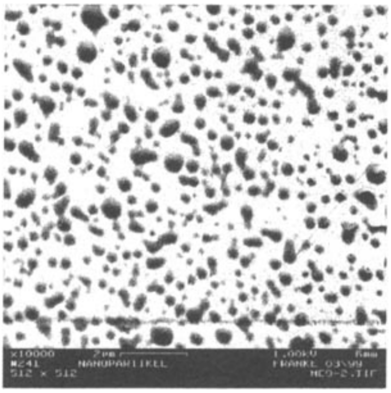


Fig. 4: SEM micrograph of the adsorbed PEC layer on a SiO_x internal reflection element (after the experiment from Fig. 3)

groups was observed. So both experimental values may serve as measure for the adsorbed polyelectrolyte complex.

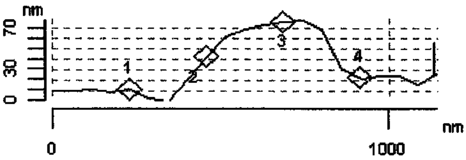


Fig. 5: Surface profile taken from an AFM micrograph of an individual adsorbed PEC particle (PDMADAC/P(MS-α-MeSty), $n_-/n_+ = 0.63$, undiluted)

In Fig. 5 an AFM integrated into an optical objective was used to determine the height of the adsorbed particles in the dry state. The figure is typical for the adsorbed particles which are assumed as the result of the adsorption of an individual colloid particle. Their height is approximately 60 nm. In a very rough approximation one can calculate the volume of such a particle (approximated as a cylinder with a diameter of 330 nm and 60 nm height): $5.1*10^6$ nm^3. This value agrees well with the volume of the initial colloidal particle ($6.5*10^6$ nm^3). With the surface coverage or the particle density parameter one gets an average thickness of the adsorbed layer. In the case of the experiment shown in Fig. 3 and 4 this thickness is of about 16 nm.

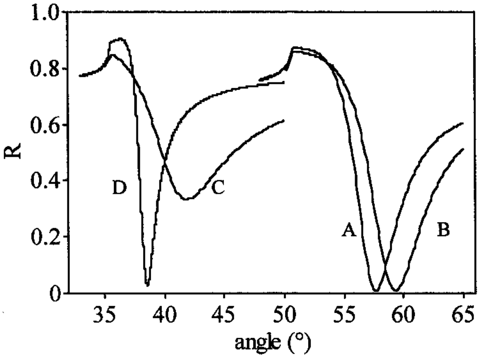


Fig. 6: Angle dependent reflectivity R of adsorbed PEC on two monolayers (■≡≡) on gold ($n_-/n_+ = 0.63$, dilution 1/10, A: LB layer under water, B: LB layer with adsorbed PEC under water, C: dry LB layer with adsorbed PEC, D: dry LB layer (model calculation))

In-situ surface plasmon resonance (SPR) is another method which can give quantitative information about the adsorption. In Fig. 6 the results of an adsorption experiment of a model dispersion with $n_-/n_+ = 0.6$ onto a Langmuir-Blodgett double layer is shown. As amphiphile poly(maleic acid hexadecylmonoamide-co-propylene) was used. The carboxylic acid groups of the top layer were oriented to the dispersion. Curve A was monitored under water before the adsorption experiment. As consequence of the adsorption the minimum of the reflection curve was shifted towards higher angles (B). The left curves (D, C) represent the situation in the dry state. For a kinetic measurement the change of reflectivity at a fixed angle (56.8°) was observed. Model calculations have shown that in the reflectivity range between 0.15 and 0.5 the reflectivity is direct proportional to the adsorbed layer thickness. With curve B of fig. 6 a thickness of 10 nm has been determined for the adsorbed PEC layer (under water), calculated with a refractive index of 1.5.

In the experiments shown in Fig. 7 the adsorption of three different model dispersions on gold and on a silicon wafer were compared. In the case of the gold surface SPR was used, whereas the adsorption on the wafer was recorded with ATR-IR spectroscopy. At pH 6 and pH 9, no significant adsorption occurred on gold. Only in the presence of sodium chloride an adsorption was detectable. In the case of the wafer the smallest adsorption took place in the presence of the sodium chloride. This result emphasizes an important point: For an enhanced quantification and generalization of the results obtained with different methods, the same model surfaces have to meet the requirements of the different methods. Spin coating, Langmuir-Blodgett, self assembled or polyelectrolyte multilayers may be suitable and shall be used in the future.

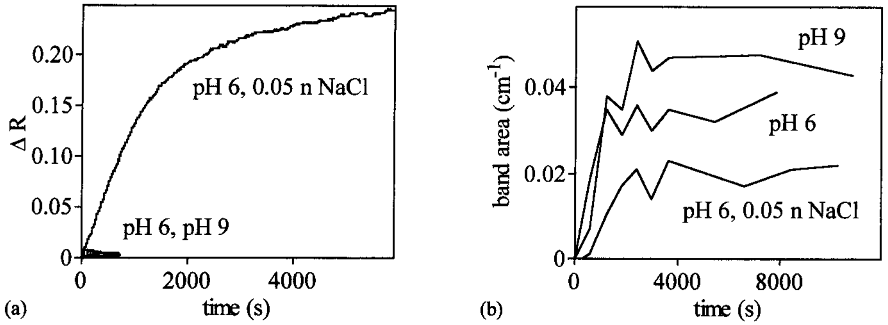


Fig. 7: Adsorption of model dispersions made from P(MS-α-MeSty) and PDMDAAC (dilution 1/10, $n_-/n_+ = 0.63$) on gold (a) and silicon (b) monitored by SPR (a, at 56.8°) and ATR-FTIR (b) spectroscopy

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