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Langmuir–Blodgett layers from polymer–metal complexes: behaviour of monolayers and preparation of multilayers

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Amphiphilic polymers with two different alternating functional units along the main chain were synthesized and their monolayer behaviour was investigated. When they have a ligand group adjacent to a carboxylic acid group, two different metal complexes can be introduced into a monolayer: a complex with a free coordination site can be bound via the ligand group, and a cationic complex as counter-ion. These polymer–metal complexes were prepared in an interfacial reaction between the polymer monolayer and the complex dissolved in the aqueous subphase. The resulting monolayers can be transferred onto solid substrates. The presence of the different complexes was proved by means of ultraviolet/visible spectroscopy.

(Keywords: Langmuir–Blodgett layers; polymer–metal complexes; interfacial reaction)

INTRODUCTION

Langmuir–Blodgett (LB) multilayers have often been used for the construction of highly ordered ultra-thin films with special properties owing to their supramolecular structure. A lot of different functionalities may be introduced in such films. Examples are sensor groups[1] or moieties with non-linear optical properties[2,3]. Otherwise, LB layers may be used for modelling of biological or interfacial processes[4,5]. Different kinds of amphiphiles are available for the design of such an LB multilayer. Generally, polymeric amphiphiles are preferred in comparison to low-molecular-weight substances due to their enhanced stability.

Metal complexes are compounds with fascinating chemical, optical, electrical, thermal and electro-optical properties. With the exception of some phthalocyanine and porphyrin complexes[6,7], polymer–metal complexes have not been used for the construction of LB multilayers. So the first aim of this work is to attach metal complexes to polymeric amphiphiles and to build up LB multilayers with them.

For some applications it is necessary to integrate two functionalities into one monolayer of the LB multilayer system, for instance the components of a redox couple. In the case of low-molecular-weight amphiphiles, some restrictions are valid due to the immiscibility of the amphiphiles on a microscopic level resulting in phase separation in the monolayer. This is the second topic of this work: different metal complexes should be attached to one amphiphilic polymer with two functional groups, each of them selective for one metal complex. A proper starting point is maleic anhydride copolymers. The amphiphilic properties may be introduced by using a long-chain α-olefin as comonomer. Conversion of the anhydride group with an amino compound leads to a maleic acid monoamide structure. The carboxylic acid group should be able to bind a positively charged metal complex as counter-ion. If 4-aminomethylpyridine is applied in the ring-opening reaction, a typical ligand (pyridine) will be attached to the polymer. To prove this concept, the polymers **1** and **2** were synthesized. As metal precursor complex the well known tris(phenanthroline) iron(II) sulfate ($[Fe(phen)_3]SO_4$) and bis(salicylidene-aminopropyl)aminecobalt(II) (**3**) were used. The iron complex has a positive charge and may act as counter-ion of the carboxylic acid group of the polymer. The cobalt complex is not charged and the attachment to the polymer by pure electrostatic interactions is less probable. On the other hand, this complex has a free place in the coordination shell (maybe it is initially occupied by a solvent molecule). Here the pyridine group of the polymer may join the precursor complex as new ligand. For easy working, ligand and counter-ion binding was performed in a reaction at the air–water interface between the spread amphiphilic polymer and the metal complexes in the aqueous subphase.

EXPERIMENTAL

Preparation of the polymers

All solvents were dried before use. All of the reactions were carried out under argon atmosphere. Hexadecylamine and arachidic acid were used as received from Fluka without further purification.

Poly(maleic acid pyridine monoamide-co-*octadecene) (1).* This was synthesized by heating a solution of 7 g poly(maleic anhydride-*co*-octadecene) (Polyscience Inc., USA; M_w 30 000–50 000, molar ratio 1:1) with 2.82 g 4-aminopyridine (Fluka Chemie AG, Switzerland) in 50 ml pyridine for 14 h at 90°C. The raw product was

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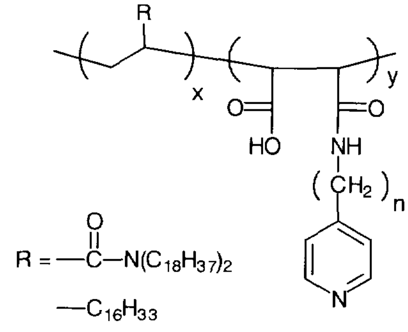
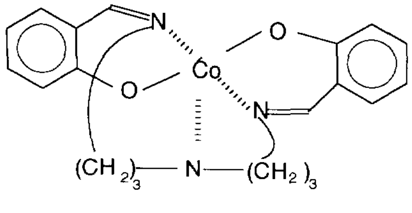


polymer	n	R	x/y
1	0	$-C_{16}H_{33}$	1
2	1	$-CO-N(C_{18}H_{37})_2$	2



complex **3**

precipitated in methanol and water (1:1), dried, dissolved in toluene and precipitated again in ethyl acetate. Infra-red and nuclear magnetic resonance spectra were in agreement with the proposed structure.

Poly(maleic acid picoline monoamide-co-*octadecene) (P(MSPic*-co-*O)).* This was synthesized by heating 7 g poly(maleic anhydride-*co*-octadecene) with 3.24 g 4-aminomethylpicoline in 35 ml pyridine for 7 h at 50 °C. Isolation and analysis were performed as in the case of **1**.

N,N-Dioctadecyl acrylamide (DOAA). A solution of 3.6 g acryloyl chloride (Aldrich Chemie, Germany) in 100 ml toluene was slowly added to a solution of 20.9 g *N,N*-dioctadecylamine (DOA) (Fluka) in 400 ml toluene and stirred for 2 h at 50°C. The cold mixture was filtered to remove the hydrochloride of DOA. The filtrate was reduced to 25% and the reaction product was precipitated by adding an excess of acetonitrile. M.p. 42°C. I.r. analysis concurs. Elemental analysis: C 80.02 (calc. 81.3), H 13.19 (13.47), N 2.63 (2.43).

Poly(maleic anhydride-co-N,N-*dioctadecyl acrylamide) (P(MSA*-co-*DOAA)).* First 6.7 g DOAA were copolymerized with maleic anhydride in the molar ratio of 1:1.2 in 105 ml toluene with 2% azobisisobutyronitrile as initiator. The mixture was then stirred for 10 h at 60°C. The polymer was precipitated in acetone, dried, dissolved in tetrahydrofuran and precipitated again in acetonitrile. Elemental analysis: C 77.41 (calc. 76.65), H 12.23 (11.77), N 2.49 (2.1).

Poly(maleic acid picoline monoamide-co-N,N-*dioctadecyl acrylamide) (***2***).* First, 2.4 g P(MSA-*co*-DOAA) and 4-aminomethylpyridine (Fluka) in the molar ratio 1:1.5 in 20 ml toluene were heated to 50°C for 7 h. The product was then precipitated in acetonitrile, dried, dissolved in tetrahydrofuran and precipitated again in nitromethane. The molar ratio between maleic acid monoamide and *N,N*-dioctadecyl acrylamide for **2** was determined to be 38:62 by inverse gated n.m.r. spectroscopy (delay 30 s).

Metal complexes

*Bis(salicylideneaminopropyl)aminecobalt(II) (***3***).* This was applied as precursor complex. The synthesis was performed according to the procedure given in ref. 8.

Tris(phenanthroline)iron(II) sulfate ($[Fe(phen)_3]^{2+}SO_4^{2-}$). The complex was prepared in aqueous solution by mixing $FeSO_4$ (Laborchemie Apolda, Germany) with 1,10-phenanthroline (Chemapol Prag, Czech Republic) in the molar ratio 1:3 without separation.

Methods

The water used for the monolayer experiments was purified using a Milli-Q Plus system (Millipore, 18.2 $M\Omega\,cm^{-1}$) and adjusted to pH 10 with potassium hydroxide.

The monolayer and deposition experiments were carried out on a Lauda Filmwaage FW2 (Lauda Dr. Wobser GmbH, Germany) with Langmuir system and on a KSV 3000 trough with symmetrical compression and Wilhelmy plate (KSV Instruments, Finland). In most cases the polymer–metal complexes were prepared directly at the water–air interface by spreading the polymer at subphases containing the precursor complex. The concentrations of the spreading solutions were about 1 mg polymer per millilitre of solution.

The isotherms were recorded at 20°C. The monolayer compression speed was 76 $cm^2\,min^{-1}$ (KSV 3000) and 92 $cm^2\,min^{-1}$ (FW 2), respectively.

For Brewster-angle microscopy (BAM 1, Nanofilm Technology, Germany) a Nima 601 S trough (Nima Technology, UK) was used. The method is given in ref. 9. Monolayer deposition from various subphases was carried out with a dipping speed between 0.5 and 1 $mm\,min^{-1}$ and with an upper delay of 30 min at 15°C. The pressure was held at 25 $mN\,m^{-1}$ for polymer **1** and 30 $mN\,m^{-1}$ for polymer **2**. Transparent supports for spectral investigation were synthetic quartz plates Suprasil 2 (Heraeus Quarzglas GmbH, Germany). The quartz supports were purified in a mixture of H_2SO_4 and potassium peroxodisulfate. U.v./v.i.s. spectra were recorded on a Lambda 2 spectrophotometer (Perkin–Elmer).

RESULTS AND DISCUSSION

Monolayer behaviour of the polymers

Figure 1 shows the π-A isotherms of the polymers studied. As in the article of Winter *et al.* concerning a series of similar amphiphilic maleic acid copolymers[10], the isotherms are relatively steep and show a high collapse pressure. Phase transitions cannot be detected. The areas at the collapse point are above 25 nm^2, indicating a head-group-determined arrangement of the octadecene copolymers. Compared to the results given in the literature[10] for poly(maleic acid-*co*-octadecene), a collapse point was observed at a significantly greater area (0.37 nm^2) than in the case of poly(maleic anhydride-*co*-octadecene) (0.25 nm^2). This behaviour can be explained by electrostatic repulsion between the carboxylate groups of the polyacid, and it is in agreement with the results[11] obtained for the change in the molecular area at 30 mN m^{-1} of poly(hexadecene-*co*-maleic anhydride) (0.222 nm^2) during hydrolysis (final value 0.323 nm^2). For the *N,N*-dioctadecyl acrylamide copolymers the arrangement is mainly determined by the packing of the aliphatic tails, as shown by areas of about 0.74 nm^2 at the collapse point.

The lateral organization of a monolayer of **1** was studied by Brewster-angle microscopy during compression. As can be seen in *Figure 2* for polymer **1** the domain structure at higher areas per repeat unit disappears with decreasing area and a homogeneous film is formed.

With the commonly used model of LB multilayers from polymers, a two-phase system is assumed: crystalline packing of the aliphatic tails and an amorphous region of the polymer backbone[12]. Therefore, the *N,N*-dioctadecyl acrylamide copolymers should agree more with this idea, and the order of LB multilayers of these polymers is expected to be higher in comparison to those of the octadecene derivatives. On the other hand, interactions of the polymer with components dissolved in the aqueous subphase should be more easily detectable in the isotherms of the octadecene copolymers. For this reason, the polymer **1** was used in most of the following experiments concerning complex formation at the air–water interface.

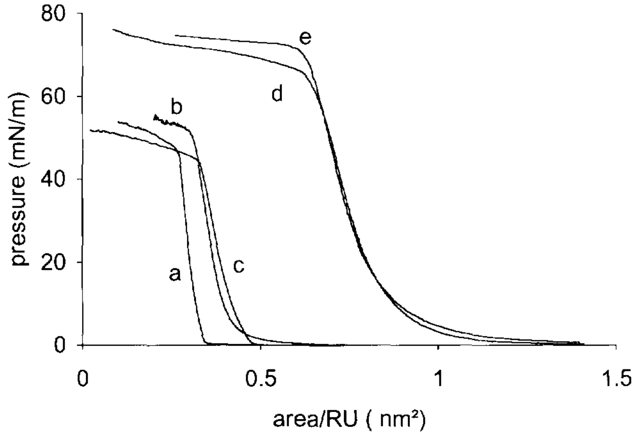


Figure 1 Isotherms of different amphiphilic polymers on a water subphase: (a) P(MSA-O), (b) polymer **1**, (c) P(MSPic-*co*-O), (d) polymer **2**, (e) P(MSA-*co*-*N,N*-DOAA)

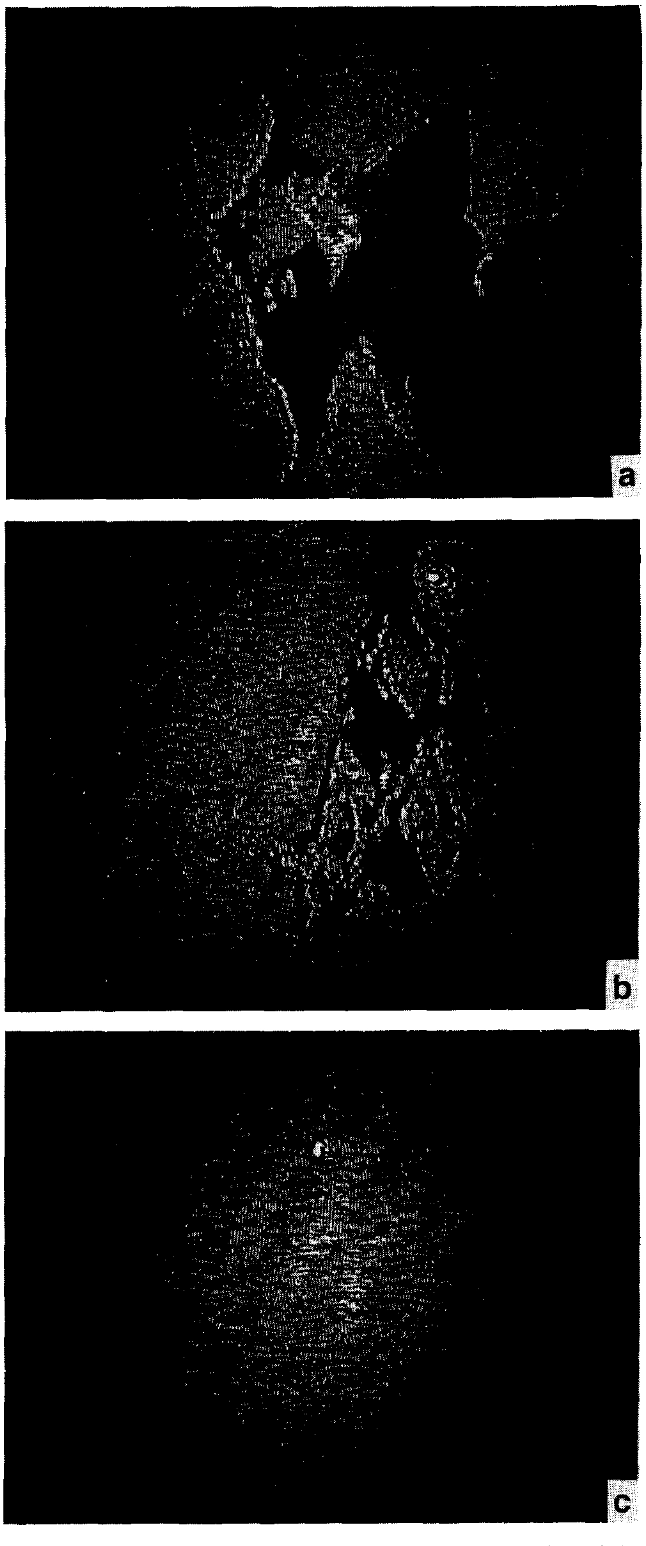


Figure 2 Lateral organization of a monolayer as a function of the area per repeat unit (RU): (a) 1.0 nm^2/RU; (b) 0.6 nm^2/RU; (c) 0.4 nm^2/RU. Brewster-angle microscopy of polymer **1** on a Millipore water subphase at 25°C

Formation of the polymer–metal complex

The experiments dealing with complex formation at the air–water interface were carried out at a subphase pH of 10 to avoid protonation of the pyridine moiety.

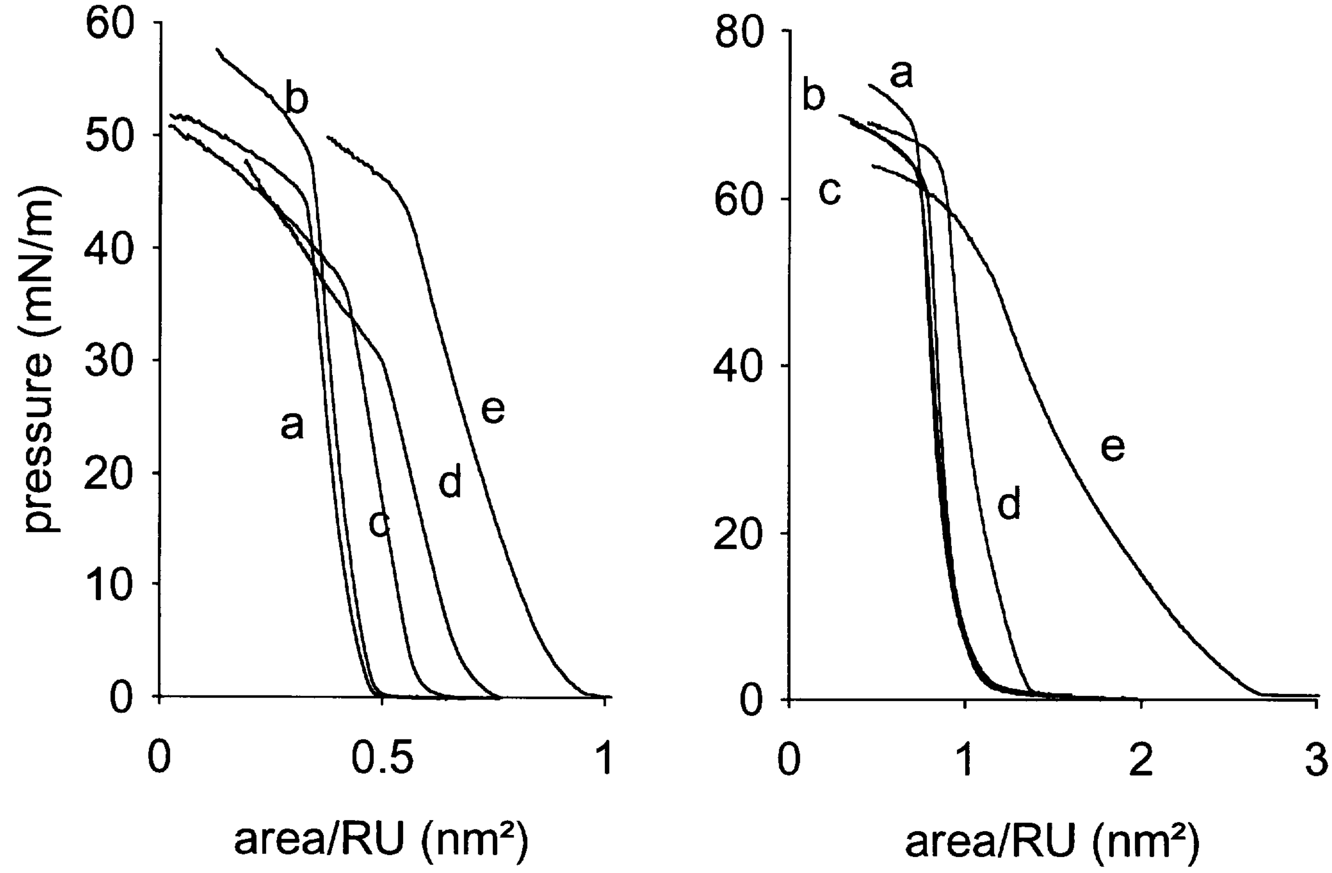


Figure 3 Isotherms of polymer **1** (left) and polymer **2** (right) on different subphases: (a) pure alkaline water (pH 10), (b)–(e) a solution of complex **3**, (b) 10^{-7}, (c) 10^{-6}, (d) 10^{-5}, (e) 10^{-4} mol l^{-1}

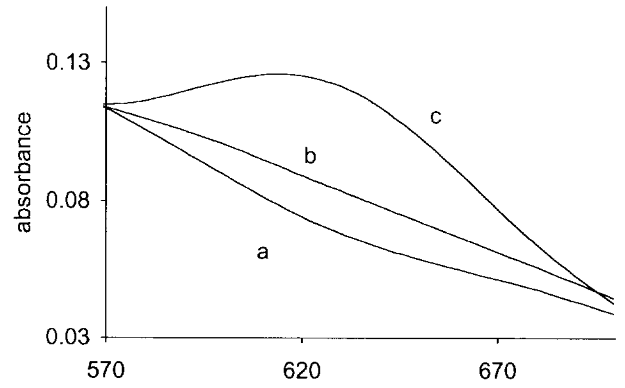


Figure 4 Formation of a new complex from complex **3** and polymer **1** in toluene solution: (a) complex **3**, (b) [polymer **1**]/[complex **3**] = 10, (c) [polymer **1**]/[complex **3**] = 100

Spreading polymers **1** and **2** on subphases containing complex **3**, the isotherms are mainly determined by the complex concentration (*Figure 3*). This is a result of the interaction between the polymers and the precursor complex **3**. The isotherms are determined by the area occupied by the polymer-bound complex. There are two possibilities for interactions of the polymer with the complex molecules, via the acid group and via the pyridine moiety. To distinguish between these possibilities, monolayers of hexadecylamine and arachidic acid were studied as low-molecular-weight model compounds on subphases containing complex **3**. In the case of arachidic acid a significant influence of complex **3** is not observed. Hence, the incorporation of carboxylic acid groups in the coordination shell as sixth ligand or electrostatic interactions may be excluded. Otherwise the monolayer behaviour of hexadecylamine is influenced in qualitatively the same manner by complex **3** as in the case of the polymer **1**. Therefore we assume that the pyridine group of the polymer and the amino group of hexadecylamine were introduced into complex **3** as new ligands.

The entrance of a ligand into the coordination shell of a transition-metal atom induces a splitting of d orbitals of the metal. As a result, the visible absorption spectrum exhibits a new band, showing the electron transition between the split d orbitals, the d–d transition. The extinction coefficient for such transitions is usually of the order of 100 l mol^{-1} cm^{-1}. The reaction of complex **3** with polymer **1** was carried out in toluene and the result is recorded in *Figure 4*. An extinction coefficient of about 80 l mol^{-1} cm^{-1} was obtained. This value was observed in the case of pyridine as ligand, too. Using the Lambert–Beer law to calculate the concentrations, a complex-formation constant of about 10^4 l mol^{-1} was estimated. This value is higher than those given for some simple cobalt–pyridine complexes[13].

The monolayer behaviour of the polymers on subphases containing complex **3** is mainly determined by the complex concentration of the subphase (see *Figure 3*). This can be explained by the greater area required by the complex, in comparison with the area occupied by a repeat unit of the polymer. The complex molecule can be considered as a cuboid with the side areas of 0.34, 0.62 and 1.03 nm^2 (estimated from molecular models), with the empty coordination site in the centre of the largest area. Consequently, the complex molecule can be supposed to lay nearly parallel to the water surface. Further studies will deal with the orientation of the complex molecules with respect to the polymer structure. In observation under the Brewster-angle microscope, the polymer–metal complex has shown a similar behaviour to the polymer, i.e. a homogeneous monolayer was formed after compression.

The concentration dependence of the isotherms can be explained as follows. There exists a point where the influence begins. Above a relatively small concentration of 10^{-7} mol l^{-1} the organization of the monolayer will be more and more determined by the complexes. Complete conversion does not occur, obviously, owing to the steric protection of pyridine rings by complex molecules bound in the neighbourhood. In most cases a stable monolayer at constant pressure (25 mN m^{-1}) was obtained. The time until stability is reached depends strongly on the complex concentration in the subphase. At 10^{-4} mol l^{-1} the monolayer was not stable within 1.5 h, whereas this time for polymer **1** in pure Millipore water is about 20 min. An optimum subphase concentration was found to be 10^{-5} mol l^{-1} in consideration of a high content of the complex and of the stability of the monolayer.

Polymer-metal complexes via ion-ion interactions

Additionally, the polymers contain one carboxylic group per repeat unit. It should be possible to attach a cationic complex molecule as counter-ion to the monolayer. $[Fe(phen)_3]^{2+}$ was used as cationic complex. For example, the interactions were observed on isotherms of polymer **1** on subphases containing cation. The resulting collapse area for a concentration of 10^{-5} mol l^{-1} was obtained to be 0.37 nm^2. Contrary to the results with complex **3**, the influence of the $[Fe(phen)_3]^{2+}$ concentration on the isotherms of the polymers is much lower. Two reasons may be advanced. First, it is possible that the binding of complex **3** is more effective than the counter-ion interaction, resulting in higher amount of polymer-bound complex. Secondly, the steric requirements for counter-ion binding or their influence on the polymer conformation are not as high as in the case of complex formation between the polymer and complex **3**. However, the binding of metal complexes to the polymers was possible in both ways.

Multilayers of polymer–metal complexes

Polymer **1** can be transferred from subphases containing complex **3** onto solid substrates as *Y*-type or *Z*-type multilayers. The orientation depends on the deposition conditions. The multilayers under discussion here were of *Y* type and the monolayers were prepared by spreading the polymer on a subphase with $[\mathbf{3}] = 10^{-5}$ mol l^{-1}. U.v./v.i.s. spectroscopy of such multilayers on quartz shows an absorption with a maximum at 380 nm. This absorption can be attributed to complex **3** in the multilayer. *Figure 5* shows the absorbance of the polymer-bound complex in multilayers as a function of the concentration of complex **3** in the subphase and the layer number. For both complex concentrations studied, a linear relationship between layer number and absorbance is observed. The deviation of some experimental values from the line in *Figure 5* may be the result of fluctuations of the transfer ratio, which varies between 0.6 and 0.9. As expected, the absorbance of the multilayers prepared from the subphase with $[\mathbf{3}] = 10^{-5}$ mol l^{-1} is higher than in the case of $[\mathbf{3}] = 10^{-7}$ mol l^{-1}. This indicates a higher degree of conversion. Analogous results were obtained with multilayers from polymer **1** and $[Fe(phen)_3]^{2+}$.

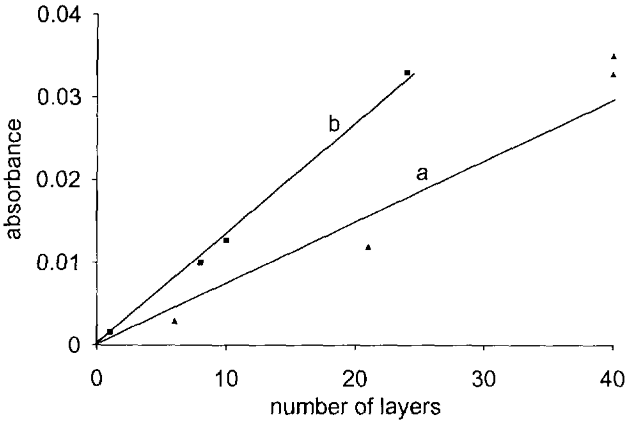


Figure 5 Absorption at 380 nm of multilayers from complex **3** and polymer **1** on a quartz support, deposited from subphases with different concentrations of complex **3**: (a) 10^{-7}, (b) 10^{-5} mol l^{-1}

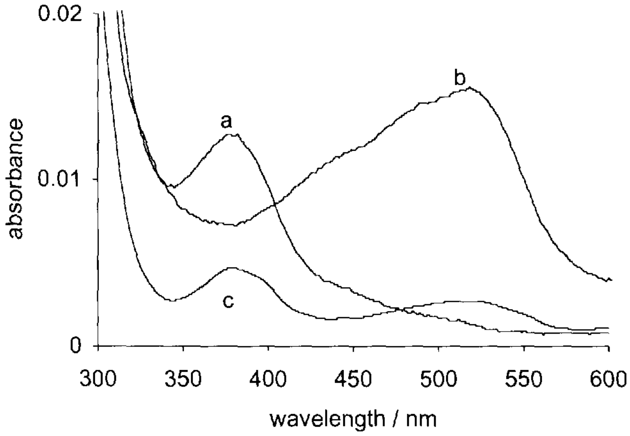


Figure 6 Absorption spectra of multilayers of polymer **1** with different metal complexes on a quartz support: (a) 10 monolayers, subphase 10^{-5} mol l^{-1} complex **3**; (b) 8 monolayers, subphase 10^{-5} mol l^{-1} $[Fe(phen)_3]^{2+}$; (c) 18 monolayers, subphase 10^{-5} mol l^{-1} complex **3** + 10^{-5} mol l^{-1} $[Fe(phen)_3]^{2+}$

In another experiment, multilayers should be built up with monolayers containing the complex **3** as well as $[Fe(phen)_3]^{2+}$ ions. This was performed by dissolving complex **3** and the iron complex in the same subphase. Multilayers using polymer **1** were prepared in the usual manner on quartz plates. In *Figure 6* the absorption spectrum of such a multilayer (curve c) is shown in comparison to the spectra of multilayers with either complex **3** or $[Fe(phen)_3]^{2+}$. The absorptions of both complex **3** (at 380 nm) and $[Fe(phen)_3]^{2+}$ (at 520 nm) are clearly visible in curve c. This means that both complexes were transferred into one multilayer simultaneously.

Experiments in solution demonstrated that the molar extinction coefficients of **3** and $[Fe(phen)_3]^{2+}$ are not affected by the presence of the other complex. Assuming the same behaviour in the multilayer, the data from *Figure*

6 allow one to derive that the total amount of polymer-bound complex decreases due to the introduction of the second complex in the same monolayer or multilayer, respectively. The reason for that may be of steric nature, indicating a competition of complex **3** and $[\mathrm{Fe(phen)_3}]^{2+}$ for space under the monolayer.

CONCLUSIONS

The homogeneous distribution of two functional compounds in one monolayer is often required to realize special optical, electrical or other properties in LB multilayer systems. As has been shown, the introduction of two different metal complexes in one monolayer as part of a multilayer system is possible when using the polymers **1** and **2**. The binding onto two alternating functional groups within the polymers avoids phase separation processes, which may dominate in the case of low-molecular-weight amphiphiles. Monolayer and multilayer investigations as well as reflections by means of molecular models have shown that the density of functional groups of the used polymers is too high with respect to the dimensions of the metal complexes. An improvement of the situation will be realized in further work by reduction of the part of functional groups in the copolymers and by the introduction of a spacer between polymer chain and pyridine ring. The last option opens the possibility to organize the two metal complexes in separate sublayers of one monolayer. Further investigations concerning the orientation and distribution of the complexes and the realization of optical and electrical functionalities are planned.

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