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Communications to the Editor

Layered Nanostructures with LC-Polymers, Polyelectrolytes, and Inorganics

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Recently, part of our work has been devoted to the functionalization of liquid crystalline (LC) polymers with ionic groups.[1−3] The aim of the work was to combine the self-organization properties of LC polymers and of ionomers. In fact, the LC ionomers we investigated show a combination of the properties of liquid crystals and ionomers.[4,5] On the one hand, they exhibit a behavior analogous to that of isotropic ionomers, i.e., the formation of clusters of ionic groups that belong to different polymer chains. This results in the gelation of the polymer and the formation of a temporary network structure. On the other hand, the liquid crystallinity gives rise to an organization by ordering of mesogenic fragments.

To date, investigations have been focused on the bulk properties of such LC ionomers and their behavior in blends with isotropic polyions. Now, our interest is the fabrication of layered nanostructures of these two types of charged polymers. The layering will force the two polymers into a closer contact, due to the high surface to volume ratio in these arrangements. Therefore new and interesting properties may be expected from such structures. The fabrication of multilayers by alternating physisorption of charged species was recently developed by Decher and co-workers.[6] Not only did this method prove to be efficient for polyelectrolytes carrying a number of different functionalities,[7−9] but also a variety of other charged materials can be employed, e.g. bolaamphiphiles,[10] membrane-forming low molar mass amphiphiles,[11] delaminated layered inorganic clays,[12,13] and colloidal particles.[14] In addition to its versatility concerning the materials used, this technique is fast compared to chemical self-assembly and is independent of the substrate size and topology, which is a considerable advantage in comparison to the Langmuir−Blodgett technique.

Layered nanostructures assembled with liquid crystalline ionomers promise to be particularly interesting in two aspects: due to the low charge density, they may permit insight into the limits of this method concerning the lowest possible ionic group content. On top of this, the presence of mesogenic groups may lead to an internal ordering of the assembly, which is rarely encountered in polyelectrolyte multilayers.[8] In this work, we present the buildup of multilayers with liquid crystalline ionomers and amorphous polyions and multilayer assemblies of two oppositely charged liquid crystalline polymers, as well as multilayers with LC polymers and inorganic layered minerals.

In Scheme 1, the chemical formulas of the polymers employed in this investigation and their phase transitions are shown.

1a and **1b** are main-chain LC polymers carrying mesogenic groups consisting of three aromatic cores and brilliant yellow[15] groups bearing negative charges which are linked by flexible C_{12} alkyl spacers. The ratio of the two comonomers were varied in order to obtain information on the influences of the charge density on the phase behavior and on the lower charge limits of the multilayer assembly.

Viologen-containing polycation **2** does not exhibit a thermotropic liquid crystalline phase in the presence of bromine counterions, but in combination with tosylate counterions, main chain polymers containing viologen units separated by alkyl spacers are reported to be thermotropic liquid crystals,[16] therefore it is resonable to regard **2** as mesogenic. The positive charges allow the assembly of multilayer structures entirely made of mesogenic polymers; e.g., polymer **2** can be combined with polymer **1a**.

In the case of liquid crystalline polymer **3**, phosphonic acid salt groups[15] are attached to the central aromatic ring of the mesogenic core via alkyl spacers. This permits a structural variation in comparison to the polyanions **1** and **2**, where the charges are directly fixed to the polymer main chain.

Azoxy LC polymer **4** bears ferrocenium ions attached to the polymer main chain by a flexible alkyl spacer. In contrast to polyanion **3**, the spacers with the charge are not attached to the mesogenic core, but to the main chain spacer.

Poly(choline methacrylate) (**PCM**) was used as isotropic organic polycation in order to build up multilayers in combination with the negatively charged LC polymers **1b** and **3**.

Successive adsorption of the layer pairs was followed by UV−visible spectroscopy. In Figure 1a the absorbance for the polymer **1b**/**PCM** multilayer system at 400 nm is plotted vs the number of deposition cycles.

This plot shows a linear relationship between the number of the cycle and the absorbance. The deposition process could at least be repeated 70 times. This hints at an extremely reproducible deposition for the system **1b**/**PCM**, although **1b** is an example for a polymer with a remarkably low content of ionic groups (one charge per 80 carbon atoms in comparison to one charge per eight carbon atoms in the case of the frequently used poly(styrenesulfonate)). This example highlights the great versatility of this deposition method. However, concentration, solvent mixture, and immersion time for the deposition of anionic ionomer **1b** have to be carefully

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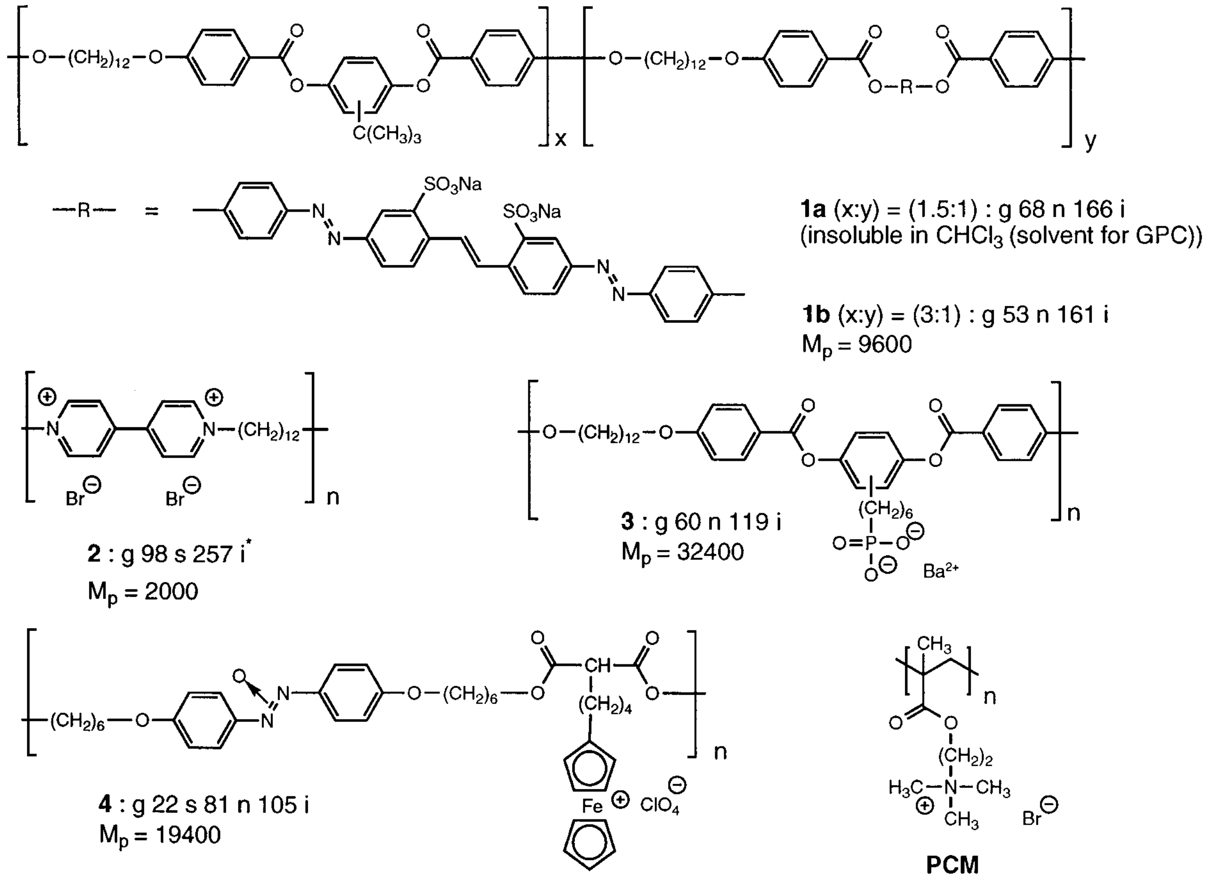
Scheme 1. Chemical Formulas of the Polyions and Their Phase Transition Data As Determined by the Second DSC Heating Run (10 K/min)[a]



Hydrotalcite: $[AlMg_2(OH)_2(OH)_4]^+\ [0.5CO_3,OH,Cl]^-$ **Montmorillonite:** $[AlMg(OH)_2(O)_4]^{5-}\ [Si_2O_3]^{4+}\ [Na, nH_2O]^{1+}$

[a] For polymer **2** the phase transition data for the analog with tosylate counterions according to reference 16 is given. Molecular weights were determined by GPC against PS standards (peak maximum). The molecular weight of polymer **2** was obtained by ^{1}H-NMR end group analysis.

chosen in order to obtain satisfactory assembly results. Presumably the low charge density in this polymer is already very close to the limiting case of the method.

Another example of multilayer assembly with an LC polymer and a polyelectrolyte is given by the **3**/**PCM** system for which absorbance measurements are depicted in Figure 1b. The first deposition step results in low absorbance, but after this, the absorbance increases linearly with the number of deposition cycles. As for the system **1b**/**PCM**, a regular and reproducible deposition may be concluded. The position of the charge in these polymers seems not to be of significant importance for the success of the assembly.

But not only combinations of liquid crystalline and isotropic polymers are possible options for the buildup of multilayers; the assembly of a structure containing only mesogenic polymers was also successful. In Figure 1c the increase in absorbance with the number of deposition cycles is shown for a multilayer structure composed of polymers **1a** and **2**. As for the previous examples, a linear growth of the absorbance is encountered.

The great versatility of this method lead us to investigate the buildup of multilayer assemblies with some of our LC polymers and inorganic layered minerals in exfoliated form.

Since we investigated both negatively and positively charged LC polymers, we also needed negatively and positively charged inorganic materials as partners for the assembly. Therefore we employed the positively charged hydrotalcite and the negatively charged montmorillonite. Success of the multilayer buildup with polymer **1a** and hydrotalcite is confirmed by UV–visible measurements (Figure 1d). Again, a linear increase in absorbance indicates the regular proceeding of the deposition process.

Evidence for the multilayer assembly from polymer **4** and the negatively charged montmorillonite is given in Figure 1e. The observed linearity of the curve points to a reproducible deposition process.

The further characterization of the assemblies by additional analytic methods is exemplified by the system **3**/**PCM**.

FTIR spectroscopy allowed us to confirm the results obtained from the UV–visible spectroscopy. The monitoring of the multilayer buildup with LC polymer **3** and **PCM** on a silicium wafer is shown in Figure 2a.

The spectra of the sample taken after every five deposition cycles demonstrate the increase of different characteristic bands (for instance the carbonyl band at 1730 cm^{-1} and the aromatic band at 1600 cm^{-1}) with the number of deposition cycles. The plot of the absorbance of the bands at 1730 and 1600 cm^{-1} vs the number of adsorption cycles confirms the results from UV–vis spectroscopy, demonstrating the regularity of the deposition process (Figure 2b). This method is

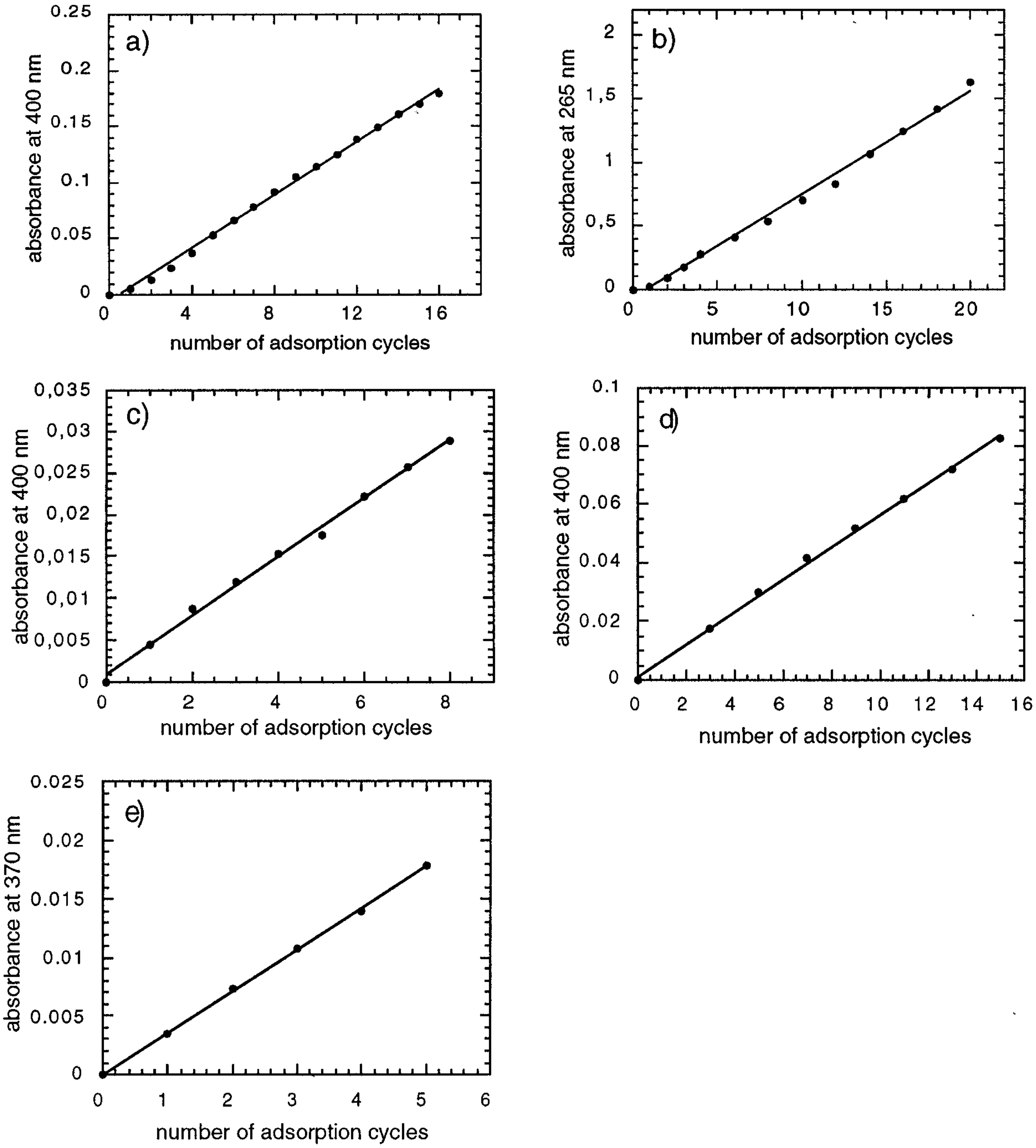


Figure 1. Plot of the absorbance vs the number of deposition cycles for the systems (a) **1b**/**PCM** (b) **3**/**PCM** (c) **1a**/**2** (d) **1a**/hydrotalcite, and (e) **4**/montmorillonite.

especially interesting, because it opens the possibility to determine the relative amounts of each polymer in the multilayer.[17]

Multilayer assemblies were characterized by X-ray reflectivity measurements in order to confirm UV−vis and infrared results and to estimate the thickness of these layers. Reflectivity spectra of samples with different numbers of layer pairs for **3**/**PCM** are presented in Figure 3a. Typical Kiessig fringes[18] resulting from interference of the X-ray beam reflected at the support/film interface and the film/air interface are observed.

This shows that the multilayer buildup proceeds homogenously and produces a smooth surface. A Bragg peak, which would result from scattering between defined layers, is not observed. The results of the calculation of the thickness from the fringes according to Bragg's equation were plotted vs the number of adsorbed layers (Figure 3, inset). In accordance with the UV−visible spectroscopy results, a linear relationship between these parameters is found pointing once more to a regular adsorption process. An average value of 4.9 nm per layer pair can be estimated.

In consequence, the electrostatic assembly with various polyelectrolytes is a versatile new technique to prepare thin films of liquid crystalline polymers. Given the extreme thinness of the layers obtained, the close contact of the combined polymers and the possibilities for molecular organization, this technique may offer an access to new types of liquid crystalline structures with new properties.

Experimental Section. UV−visible measurements were performed on a SLM-AMINCO DW-2000 or a Shimadzu UV-2102 PC spectrometer.

The FTIR-spectra were recorded with a Nicolet 5DXC spectrometer using a transmission geometry.

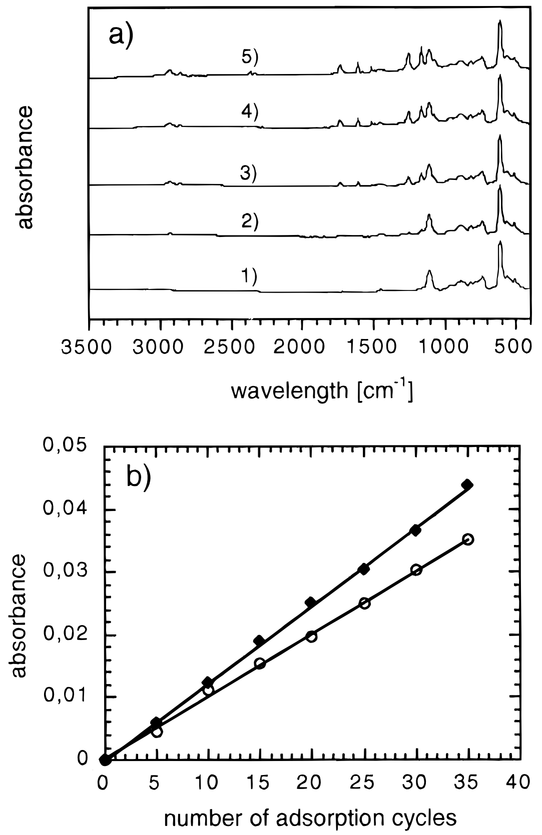


Figure 2. (a) Infrared spectra taken from multilayers prepared from **3**/**PCM**: (1) after PEI and PSPM buffer layers adsorption; (2) after five adsorption cycles; (3) after 15 adsorption cycles; (4) after 25 adsorption cycles; (5) after 35 adsorption cycles. (b) Plot of the infrared absorbance at 1600 cm^{-1} (◆) and 1730 cm^{-1} (○) vs the number of deposition cycles for **3**/**PCM**.

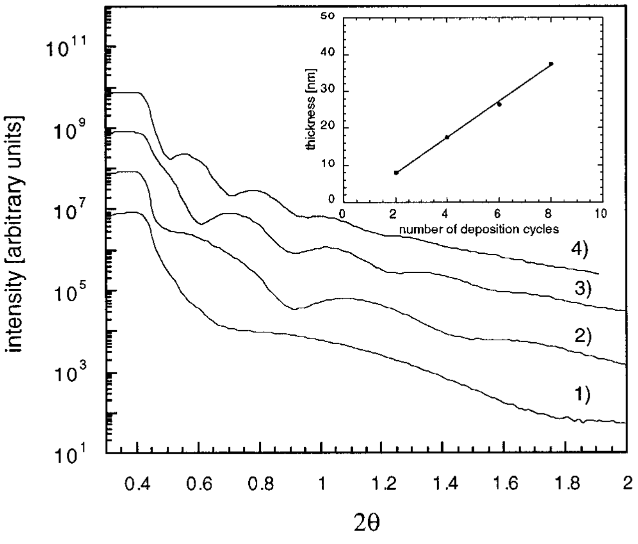


Figure 3. Small angle X-ray diffraction curves for multilayer assemblies of **3**/**PCM** after different numbers of deposition cycles: (1) after two adsorption cycles; (2) after four adsorption cycles; (3) after six adsorption cycles; (4) after eight adsorption cycles. Inset: Thicknesses for multilayer assemblies of **3**/**PCM** as calculated from the X-ray diffraction data.

X-ray reflectivity experiments were performed on a Siemens D-500 diffractometer using Cu Kα radiation (λ = 1.54 Å) and a single-crystal graphite monochromator.

Materials. Ultrapure water (Millipore, 18.2 MΩ) was used for all experiments. Branched poly(ethylene imine) (PEI) was purchased from Aldrich and was used without further purification. The synthesis of poly(sulfopropyl methacrylate) (PSPM) and poly(choline methacrylate) (**PCM**) was already described elsewhere.[13] The synthetic procedure for the preparation of the LC polymers **1a** and **1b** is described in ref 4. Polyion **2** was synthesized in analogy to ref 19 with *N*,*N*-dimethylformamide as solvent. Description of the synthesis of **3** is given in ref 5. LC-polymer **4** was prepared by oxydation of the nonoxidized ferrocene-containing analog described in ref 20 using a procedure described by Wieseman et al.[3]

Aqueous suspensions of deliminated montmorillonite clay ($Al[Si_2O_5](OH)$ containing Na, K, Mg, and Ca ions) and hydrotalcite ($[AlMg_2(OH)_2(OH)_4]^+$ $[0.5CO_3,OH,Cl]^-$) were kindly provided by Dr. Nicolas A. Khotov.[21]

Preparation of Multilayers Assemblies. Quartz or glass supports or silicium wafers were used as substrates. Cleaning of these substrates was achieved using a classical procedure:[10] The substrate was immersed for 20 min in a H_2SO_4/H_2O_2 (1:1) mixture at 80 °C and then extensively rinsed with water. Then the substrates were treated with a $NH_3/H_2O_2/H_2O$ (1:1:5) mixture at 75 °C and thoroughly rinsed with water.

PEI (deposited from an acidified solution) and PSPM were used as buffer layers for all experiments. Concentrations of **PCM** and PSPM were 10^{-2} mol·L^{-1}. LC polymer solutions were prepared by dissolution of polymer in the appropriate organic solvent mixture. Then 10 mg of polymer **1a** was dissolved in a mixture of 7.5 mL of water and 7.5 mL of dimethyl sulfoxide. A solution of polymer **1b** was prepared by dissolving 5 mg in 40 mL of a DMSO/water 1:1 mixture. In the case of polyion **2**, a saturated solution (approximately 30 mg of polymer in 12 mL of water and 3 mL of dimethyl sulfoxide) was prepared. Then 5.1 mg of polymer **3** was dissolved in 8 mL of a 1:1 mixture of DMSO and THF. Preparation of the polymer **4** solution was obtained by dissolution of 5.1 mg of polymer in 6 mL of DMSO and 2 mL of CH_2Cl_2.

The polyelectrolytes were adsorbed on the support by alternating dipping in the cationic and then in the anionic solution, the substrate being rinsed three times with water between these two steps. A rinsing step in a solvent mixture identical to that used to prepare the LC polymer solution is added for the substrate before and after adsorption of the LC polymer. Dipping times for the building of the **1b**/**PCM** system were 20 min in both polymer solutions. Typical 20 min dipping times were used for the **3**/**PCM** system except for the X-ray reflectivity and infrared experiments for which supports were kept in both solutions for 5 and 1 min respectively. In the case of **1a**/**2** multilayers, the support was kept in the **1a** solution for 10 min and in the solution of **2** for 50 min for each cycle. For the system **1a**/hydrotalcite the immersion time was 1 min in the polymer **1a** solution and 20 min in the hydrotalcite solution. Multilayer assemblies with polymer **4** and montmorillonite were prepred by dipping the support for 10 min in the polymer **4** solution and 20 min in the montmorillonite solution.

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