Production of Polyacrylic Acid Homo- and Copolymer Films by Electrochemically Induced Free-Radical Polymerization: Preparation and Swelling Behavior

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Summary: Films of polyacrylic acid hydrogels were produced on a conducting substrate by means of electrochemically initiated polymerization (EIP). An electrochemical quartz crystal microbalance was used to monitor film growth in situ. Homopolymer and copolymer films of polyacrylic acid and poly-*N*-isopropylacrylamide were characterized by FTIR spectroscopy. The degree of swelling of these films could be tuned via the pH.

Keywords: electrochemically initiated polymerization; hydrogels; polyelectrolytes; stimuli-sensitive polymers; surfaces

Introduction

The preparation of hydrogels at solid surfaces has attracted much scientific interest in recent years. Surface-attached gels strongly modify the surface, affecting properties such as hydrophilicity and biocompatibility of the substrate. Thin films of hydrogels are also extensively used in sensing,[1,2] microfluidics,[3] drug release,[4,5] and tissue engineering.[4,6]

There are numerous ways of attaching polymers to a solid surface. Examples are photo cross-linking of pre-formed polymer chains,[7] in-situ atom transfer radical polymerization (ATRP),[8] electron beam irradiation,[9] and plasma polymerization.[10] Electrochemical techniques are particularly suited for conducting substrates. For example, Palacin et al. have grafted vinylic monomers from anhydrous solutions.[11,12] This technique is mainly based on an anionic polymerization and leads to a covalent link between the polymer and the metal. Schuhmann et al. produced coatings by electrochemically induced precipitation of polyelectrolytes.[13]

Our work employs electrochemically initiated polymerization (EIP) which is an easy and flexible method to produce surface coatings of various kinds.[14–17] The technique makes use of the decomposition of an electro-active initiator at an electrode to start a free-radical polymerization. The polymer is formed directly at the electrode surface. As a consequence, the films adhere tightly to the surface. Adhesion is based on physisorption of the hydrogel to the metal. Note in this context that EIP is different from electrografting of conductive polymers. In EIP, the initiator is the electro-active species, rather than the monomer. Recently, we reported on the formation of thermoresponsive poly-*N*-isopropylacrylamide (pNIPAm) hydrogel coatings on gold surfaces based on this approach.[18]

In this work we use electrochemically initiated polymerization to produce coatings of polyacrylic acid (pAA) and copolymer coatings consisting of pAA and pNIPAm[19] on gold surfaces. The films were characterized by Fourier transform infrared (FTIR) spectroscopy. Swelling and deswelling were measured as a function of

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pH using a quartz crystal microbalance (QCM).

The literature contains a few reports on EIP of pAA containing copolymers. Teng and Mahalingam deposited such a copolymer of pAA and polyacrylonitrile (pAN) by EIP in aqueous sulfuric acid.[20] Kolzunova et al. studied the EIP of AA and AN in aqueous ammonium persulfate solutions.[21]

Polyacrylic acid is a pH-sensitive polymer. At low pH, the carboxylic acid groups of pAA are protonated and therefore uncharged. When increasing the pH, the side groups become charged and render the polymer more hydrophilic. Copolymerization with hydrophobic monomers diminishes this effect. When using NIPAm as comonomer, the film thickness becomes sensitive to temperature changes in addition to its pH sensitivity.[22]

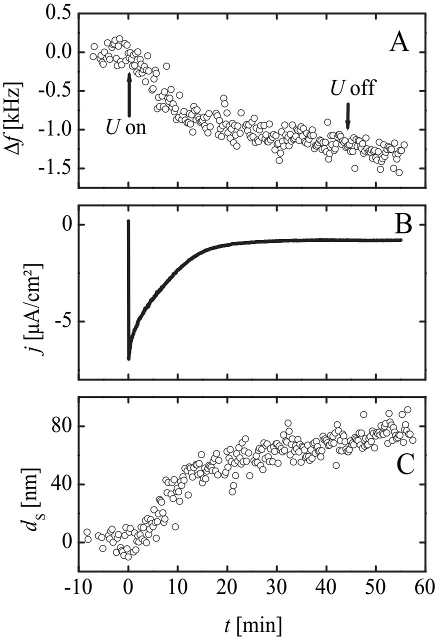


Figure 1.

A: Frequency shift Δf on the 5th overtone (25 MHz), B: current density *j*, and C: Sauerbrey thickness d_S measured when depositing polyacrylic acid on the front electrode of a quartz crystal. A voltage *U* of −0.8 V was applied for 45 minutes, as indicated by the arrows. The resulting film had a Sauerbrey thickness of about 75 nm in the reactant solution.

Production of Hydrogel Films

Films of polyacrylic acid were produced in an aqueous solution containing 0.3 mol/L acrylic acid, 0.4 mol/L potassium sulfate as supporting electrolyte, 6 mmol/L *N,N′*-methylenebisacrylamide as cross-linker, and 10 mmol/L potassium persulfate as electro-active initiator. A voltage of −0.8 V vs. saturated calomel electrode (SCE) was applied for 45 minutes. The deposition was performed at room temperature. For further experimental details see ref. 18. The deposition process was investigated in situ with an electrochemical quartz crystal microbalance (EQCM).[23] Figure 1 shows the frequency shift Δ*f* of the quartz crystal (panel A), the current density *j* (panel B), and the Sauerbrey thickness d_S (panel C). The frequency shows a significant decrease. This decrease is correlated to an increase of mass on the front electrode of the quartz crystal. The Sauerbrey Equation (1) allows for the determination of film thickness of a laterally homogeneous, rigid film:[24]

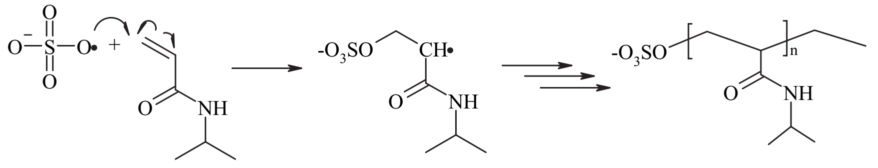
$$\Delta f = -\frac{2nf_f^2}{Z_q} m_S = -\frac{2nf_f^2}{Z_q} \rho_f d_S, \qquad (1)$$

where n is the overtone order, f_f is the fundamental frequency, m_S is the mass per unit area of the film, $Z_q = 8.8 \times 10^6$ kg m^{-2} s^{-1} is the acoustic impedance of AT-cut quartz, $\rho_f \approx 1$ g/cm^3 is the density of the film, and d_S is the film thickness in the Sauerbrey sense, also called "Sauerbrey thickness". The Sauerbrey thickness of a pAA film in dependence on polymerization time is displayed in panel C. The final film thickness was about 75 nm in the reactant solution. Presumably, some free polymer is generated during EIP as well. However, the solution remained clear and there was no precipitate at the bottom of the flask.

Panel B shows the current density which results from the reduction of initiator according to Equation (2). After reduction, most of the radical anions take up another electron from the gold surface (3). Only a few radicals initiate the polymerization according to Equation (4).[25,26]

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} \quad (2)$$

$$SO_4^{\bullet -} + e^- \rightarrow SO_4^{2-} \quad (3)$$



(4)

In the current trace shown in Figure 1B, there is an initial peak, followed by a plateau. The reactivity of the surface drops quickly after the polymerization has started. The reduced reactivity may be either due to poisoning of the active sites or to a reduced initiator diffusion coefficient inside the newly formed gel. Note, however, that the current is not necessarily an indicator of polymer growth, but rather an indicator of initiator decomposition.

Usually, the films show good adhesion to the gold surface. Delamination of the films did not appear in water or salt solutions at room temperature, even over months. The films were heated in water up to 40°C and they remained stable.

An FTIR spectrum taken in reflection on a gold electrode covered with pAA is displayed in Figure 2. It shows all the characteristic bands of the polymer and clearly proves that pAA was deposited on the surface.

Copolymer films were deposited from a reactant solution with a monomer concentration of 0.2 mol/L AA and 0.2 mol/L NIPAm. The film growth was performed in a similar way as described above. The FTIR spectrum (Figure 3) proves that both monomer units are present in the film. Both homopolymers show distinct bands. The band at 1726 cm^{-1} stems from a vibrational motion of the pAA acid groups. The amide group of the pNIPAm homopolymer causes a characteristic peak at 1540 cm^{-1}.

The FTIR spectra do not allow to distinguish between copolymers and a mixture of homopolymers. We have indirect evidence in favor of the formation of copolymers (or at least a very intimate mixture), which is based on the fact that the

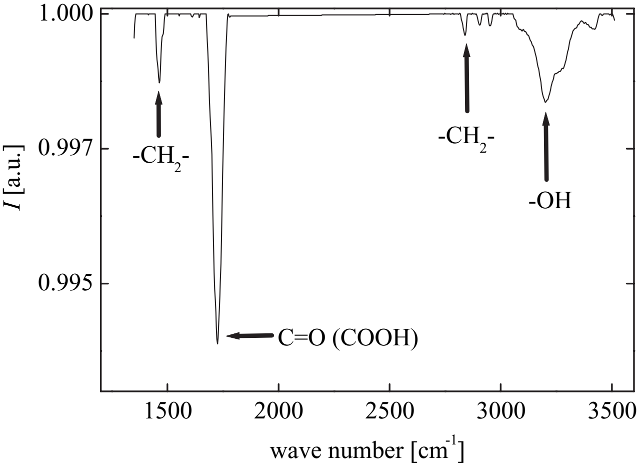


Figure 2.
FTIR spectrum taken on a gold electrode covered with polyacrylic acid – it shows the typical pAA bands.

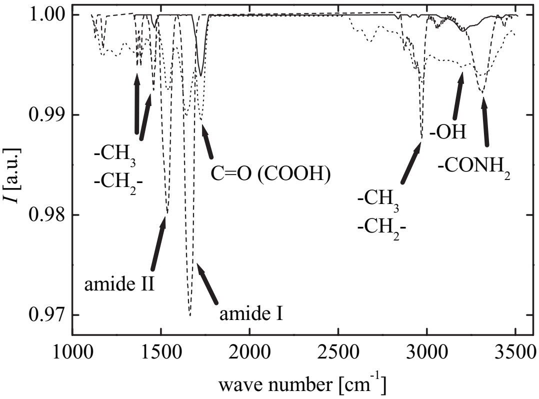


Figure 3.
FTIR spectra of a pAA film (—), of a pNIPAm film (- - -), and of a pAA-co-pNIPAm film (· · · ·) taken on the gold surface in reflection – the spectra demonstrate that EIP is useful to produce pAA and pNIPAm homopolymer films as well as the corresponding copolymer films.

films do not display a temperature driven swelling transition. Had we produced segregated domains of pAA and pNIPAm, the pNIPAm domains would collapse at the lower critical solution temperature (LCST) of 32 °C. It is known that copolymerization of pNIPAm with pAA increases the LCST. Should we have produced copolymers with an LCST above 45 °C (which was our instrumental limit) this would explain the experimental findings. For practical application, the question of whether or not copolymers were produced is of minor importance, as long as the material shows uniform properties.

Swelling Behavior of the Films

The swelling of the films in dependence on the solution pH was investigated. For this purpose, we used aqueous solutions of 0.025 M sulphuric acid and 0.05 M potassium hydroxide at room temperature. The pH was varied by addition of the acid to the base. Figure 4 shows the results obtained with a pure pAA hydrogel film. The frequency shift Δf was measured during pH induced swelling (see panel A). After addition of an aliquot of acid, the quartz was allowed to equilibrate.

The increase of the frequency shift with decreasing pH is caused by water leaving the network when the polymer becomes uncharged. Both the frequency shift and the shift of half bandwidth at half maximum (bandwidth, for short) of the resonance curve were determined by impedance

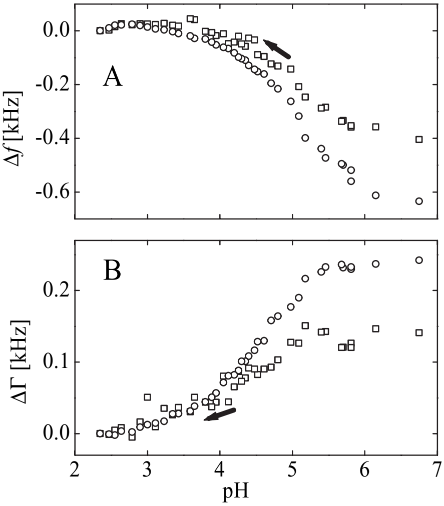


Figure 4.
A: Frequency shift Δf and B: bandwidth shift $\Delta\Gamma$ on the third (□, 15 MHz) and 5th overtone (○, 25 MHz) overtone during the pH dependent swelling of a pAA film deposited on the front electrode of a quartz crystal. The pH was high in the beginning of the experiment and was lowered by addition of acid (as indicated by the arrows). The film collapsed at low pH. This becomes evident by the low mass (low amount of water) and by the high stiffness at low pH. At high pH, the hydrogel is swollen and softer.

analysis. The bandwidth is an indicator of the film's softness. At high pH, the film was soft and the bandwidth was large (right-hand-side in panel B). When decreasing the pH, the film deswelled and became stiffer, resulting in a decreased bandwidth. We observed reswelling when subsequently varying the pH from low to high, but the behaviour was not entirely reversible. Part of the irreversibility may be caused by the fact that the ionic strength of the solution increased during the experiment.

Figure 5 displays the results obtained when using a pAA-co-pNIPAm film. The frequency shift decreases slightly with increasing pH. The shift is much smaller than the one observed when swelling the homopolymer film. We attribute this observation to the fact that the copolymer contains less pH sensitive groups than the homopolymer. A response of the copolymer sets in at around pH 4.5. The homopolymer of pAA shows the first shift at around pH 3. This off-set of the copolymer response indicates that the comonomer influences the pK_A of the hydrogel.

In future experiments, the influence of the ionic strength on the swelling should be investigated. Monomer ratio in the feed as well as cross-linker and initiator concentration should be varied. The method may then open up an easy route to coat sensors with *multi*-stimuli responsive hydrogels.

Conclusions

We demonstrated that electrochemically initiated polymerization is suited to produce polyacrylic acid coatings on gold. The film thickness was about 75 nm after a polymerization time of 45 min. FTIR spectroscopy proved that polyacrylic acid films and films consisting of polyacrylic

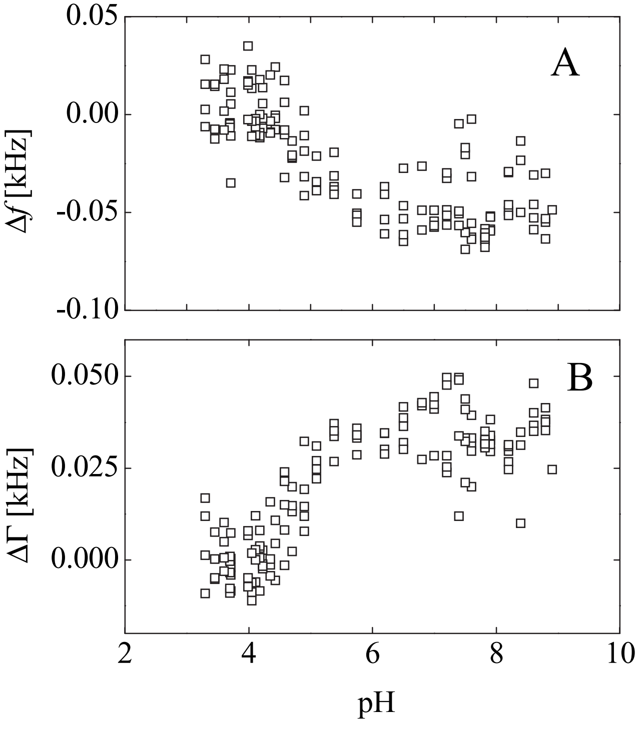


Figure 5.

A: Frequency shift Δf and B: bandwidth shift $\Delta\Gamma$ of a quartz crystal covered with a pAA-co-pNIPAm film as a function of pH – a small shift when increasing the pH proves that the copolymer is sensitive to pH. The response is much smaller as compared to the pAA homopolymer (see Figure 4).

acid and poly-*N*-isopropylacrylamide were formed on the gold surface. The investigation of the LCST behavior indicates the formation of a copolymer. The swelling of the films as a function of pH was investigated with a quartz crystal microbalance. The pAA homopolymer showed a strong response at pH $>$ 3. The swelling ratio decreased strongly when incorporating NIPAm as comonomer. In addition, the copolymerization influenced the pH at which the first conformational variations appeared. The method is useful to produce smart hydrogel films of defined properties.

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[1] J. Heo, R. M. Crooks, *Anal. Chem.* **2005**, *77*, 6843.
[2] J. Kim, N. Singh, L. A. Lyon, *Angew. Chem. Int. Ed.* **2006**, *45*, 1446.
[3] M. E. Harmon, M. Tang, C. W. Frank, *Polymer* **2003**, *44*, 4547.
[4] N. A. Peppas, J. Z. Hilt, A. Khademhosseini, R. Langer, *Adv. Mater.* **2006**, *18*, 1345.
[5] Y. Qiu, K. Park, *Adv. Drug. Deliver. Rev.* **2001**, *53*, 321.
[6] A. Kikuchi, T. Okano, J. Control. *Release* **2005**, *101*, 69.
[7] O. Prucker, C. A. Naumann, J. Rühe, W. Knoll, C. W. Frank, *J. Am. Chem. Soc.* **1999**, *121*, 8766.
[8] X. Kong, T. Kawai, K. Abe, T. Iyoda, *Macromolecules* **2001**, *34*, 1837.
[9] N. Yamada, T. Okano, H. Sakai, F. Karikusa, Y. Sawasaki, Y. Sakurai, *Makromol. Chem. Rapid Commun.* **1990**, *11*, 571.
[10] Y. V. Pan, R. A. Wesley, R. Luginbuhl, D. D. Denton, B. D. Ratner, *Biomacromolecules* **2001**, 2, 32.
[11] S. Palacin, C. Bureau, J. Charlier, G. Deniau, B. Mouanda, P. Viel, *Chem. Phys. Chem.* **2004**, *5*, 1468.
[12] G. Deniau, J. Charlier, B. Alvado, S. Palacin, P. Aplincourt, C. Bauvais, *J. Electroanal. Chem.* **2006**, *586*, 62.
[13] C. Kurzawa, A. Hengstenberg, W. Schuhmann, *Anal. Chem.* **2002**, *74*, 355.
[14] N. Baute, C. Jérôme, L. Martinot, M. Mertens, V. M. Geskin, R. Lazzaroni, J.-L. Brédas, R. Jérôme, *Eur. J. Inorg. Chem.* **2001**, 1097.
[15] G. Yildiz, H. Çatalgil-Giz, F. Kadirgan, *J. Appl. Electrochem.* **2000**, *30*, 71.
[16] C. S. Lee, J. P. Bell, *J. Mater. Sci.* **1995**, *30*, 3827.
[17] S. L. Cram, G. M. Spinks, G. G. Wallace, H. R. Brown, *J. Appl. Polym. Sci.* **2003**, *87*, 765.
[18] J. Reuber, H. Reinhardt, D. Johannsmann, *Langmuir* **2006**, *22*, 3362.
[19] F. Xia, L. Feng, S. Wang, T. Sun, W. Song, W. Jiang, L. Jiang, *Adv. Mater.* **2006**, *18*, 432.
[20] F. S. Teng, R. Mahalingam, *J. Appl. Polym. Sci.* **1979**, *23*, 101.
[21] L. G. Kolzunova, N. Y. Kovarsky, A. S. Inberg, *Russ. Chem. Bull.* **1994**, *43*, 227.
[22] M. J. Serpe, L. A. Lyon, *Chem. Mater.* **2004**, *16*, 4373.
[23] D. A. Buttry, M. D. Ward, *Chem. Rev.* **1992**, *92*, 1355.
[24] G. Sauerbrey, *Z. Phys.* **1959**, *155*, 206.
[25] A. N. Frumkin, N. V. Nikolaevafedoro, N. P. Berezina, K. E. Keis, *J. Electroanal. Chem.* **1975**, *58*, 189.
[26] Z. Samec, K. Doblhofer, *J. Electroanal. Chem.* **1994**, *367*, 141.