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Influence of Polymer Architecture on the Electrochemical Deposition of Polyelectrolytes

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ABSTRACT

This study demonstrates the effect of polymer topology and molar mass on the electrodeposition of preformed polyelectrolytes. The polyelectrolyte solubility is manipulated electrochemically using a counterion switching approach. Upon this, a triggered film formation occurs upon oxidation of hexacyanoferrate(II). The resulting Pt-electrode deposit consists of polycationic chains, namely poly[[2-(methacryloyloxy)ethyl]trimethylammonium chloride] (PMOTAC), which are physically crosslinked by polymer-complexing ferricyanides. Within this study the architecture of the polyelectrolyte is varied from monomeric units over linear and star-shaped polymers to network-like microgel colloids. Film deposition is observed only for linear and star-shaped polymers being pronounced for shorter linear chains at equimolar charge ratios. Quantification is achieved by help of the deposition efficiency *DE* obtained by analyzing the currents of a rotating ring disk electrode (RRDE) during hydrodynamic voltammetry. *DE* relates the amount of deposited ferricyanides to the total amount of electrochemically-produced ferricyanides. *DE* is used to estimate the deposited mass and film thickness showing good agreement with the film thickness determined experimentally by Scanning Force Microscopy. For future applications these results might help optimizing beneficial film formation or minimizing detrimental film formation during other procedures.

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1. Introduction

Since decades the formation of complexes between polyelectrolytes and low molecular ions [1] is of considerable interest due to their successful use in the development of drug-delivery systems [2,3], selective absorbents [4], mineral containing materials and plastics [5], as well as in purification technologies [6–8]. Polycationic species are well suited to accommodate anions. As an example, Kim et al. [9] studied the ability of quaternary amine polymers to complex and release anionic drugs such as sodium sulfathiazole and diclofenac sodium. By taking anions of switchable valency (charge), stimulisensitivity toward e.g. light [10] and electrochemical stimulation [11] can be introduced in a modular way. Hence, the solubility and conformation of the complexes can be adjusted by external triggers.

Electrochemistry is always combined with the action at and of interfaces. This allows an electrodeposition [12–14] of preformed polymeric material onto interfaces and electrodes by modulating the polymer solubility electrochemically [15–19]. This modulation can be achieved by a counterion valency induced deposition (CVID) leaving the polymer as such electro-inactive. Anson et al. reported already in the 1980's the electrode film formation of insoluble [Fe(CN)₆]^{3−}-polycationic siloxane complexes from solutions of [Fe(CN)₆]^{4−}-polycation complexes by anodic oxidation [20,21]. Thereby, electron transfer leads to a change in the multivalent redox species' charge and consequently to a change in the interaction pattern with multiple-charged objects like metal ions [22] or strong polyelectrolytes [23–28]. It was found that such a [Fe(CN)₆]^{3−}-siloxane film was very transparent to electrons (electrochemical responses were not governed by internal film processes) [20]. Also, recent work utilized the change in solubility and the concomitant deposition for protein or polymer-based complexes by electrochemical means [29,30]. In these examples and in the examples described in this manuscript, the polymers are not redox-active, but the electroactive counterions transfer their

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To the best of our knowledge, the influence of the polymer topology on the complex formation and on the electrodeposition in particular has not been investigated so far. Hence, the architecture of the polymers is varied from linear over star-shaped polymers to crosslinked polymer particles, so-called microgels (swollen gels in the nanometer to micrometer range). In principle, the former examples can be regarded as cutouts from the microgel network at different length scales: while the linear polymers are the connectors between crosslinks, the star-shaped polymers mimic the situation around crosslinks [41]. Within this set of polymers, the molar mass increases especially when regarding the final microgels with molar masses in the 10^8 g/mol range. As the constituent monomeric cations do not provide electrodeposition under the same conditions, we found optimal conditions for electrodeposition at intermediate molar masses, as will be demonstrated in this publication (Scheme 1).

Deeper understanding of electrodeposition principles enables opportunities with regard to polymer coatings [42] upon improved control over size, shape and thickness of the polyelectrolyte-complex film. Further, such hydrogels [1,43,44] have the potential to advance the fields of medicine and polymer science as useful substrates for “smart” devices [45]. Potential applications in the biomedical field are envisioned preventing for example the inflammation caused by metallic implants by such a polymer coating loaded with antibiotics. Additionally, electrochemical detachment of the polymer coating from the implant would offer a tool to remove of the undesired biofilm at interfaces.

2.1. Reagents and Chemicals

2.2. Synthesis of PMOTAC Polyelectrolytes

The synthesis of the linear PDMAEMA₁₃₀ (with dispersity $\bar{D} = 1.1$ as seen by size exclusion chromatography), PDMAEMA₁₆₀₀ ($\bar{D} = 1.8$) [46] and star-shaped (PDMAEMA₁₇₀)_{5,6} (with apparent dispersity $\bar{D}_{app} = 1.1$; indexes assign the number-average degree of polymerization per chain or the average arm number) [47] and the poly[2-(dimethylamino)ethyl methacrylate] PDMAEMA microgel (with hydrodynamic radius $R_h = 0.20 \mu\text{m}$ in 0.1 M KCl) was described elsewhere [48]. To obtain strong polyelectrolytes

Scheme 1. Schematic Illustration of PMOTAC Polyelectrolyte Deposition onto Electrodes Depending on the Polymer Topology.

the polymers were subsequently quaternized with methyl iodide leading to PMOTAC poly{[2-(methacryloyloxy)ethyl]trimethylammonium chloride} after ion exchange (I^- to Cl^-). A more detailed synthesis description is given in the Supporting Information.

2.3. General Electrochemical Techniques

All electrochemical measurements were conducted on the CH Instruments Electrochemical Workstation Potentiostat CHI760D (Austin, Texas, USA). The experiments were performed in a conventional three-electrode setup at room temperature. For hydrodynamic voltammetry and electrochemical impedance spectroscopy experiments a platinum (rotating for hydrodynamic voltammetry, without rotation in case of impedance spectroscopy) ring disk electrode, 4 mm disk diameter and 7 mm/5 mm outer/inner ring diameter, was employed as working electrode. The counter electrode was chosen corresponding to the experiment. A spirally platinum electrode (23 cm length) was used as counter electrode for hydrodynamic voltammetry experiments and a platinum gauze electrode (35 mm $\times$ 30 mm) for electrochemical impedance spectroscopy experiments. An Ag/AgCl electrode stored in 1 M KCl served as aqueous reference electrode in both cases. All potentials in the text and figures are referenced to the Ag/AgCl couple. The working electrode was polished with 1 μ m diamond and subsequently with 0.05 μ m alumina polish, rinsed with water and dried with a stream of argon. The solutions were purged with Ar for 10 min to remove dissolved oxygen.

2.4. Rotating Ring Disk Electrode (RRDE)

Hydrodynamic voltammograms of 0.13 mM $[Fe(CN)_6]^{4-}$ in 0.1 M KCl in absence and presence of polyelectrolytes with different topologies were recorded by sweeping the disk potential in the range of 0 V–0.5 V vs. Ag/AgCl at a constant scan rate of 5 mV s $^{-1}$ and a constant ring potential (0 V) in order to obtain information about the diffusion properties and adsorption phenomena onto the electrode. In addition to the polyelectrolyte topology, the *initial charge ratio* (*icr*) between counterion to polyelectrolyte (linear, star and microgel) N^-/N^+ was varied from *icr* = 2, 1, 0.5 to 0.25 by sustaining the amount of counterion constant 0.13 mM $[Fe(CN)_6]^{4-}$ and increasing the polyelectrolyte concentration from 0.26 mM, 0.52 mM, 1.04 mM, to 2.08 mM (with respect to positively charged MOTAC unit). All solutions were prepared by use of the same stock solution 0.13 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl. The rotation rate was varied between 100–5000 rpm.

2.5. Scanning Force Microscopy (SFM)

The thickness of the deposited film at the Pt rotating disk electrode was determined using a Catalyst Nanoscope V machine (Bruker, Billerica, MA, USA) with NanoScope Analysis software (Bruker) for analysis. The SFM measurements were performed in contact mode using a DNP (0.12 N/m) cantilevers made from silicon nitride with silicon tips.

A (PMOTAC $_{170}$) $_{5.6}$ star/ferricyanide complex was deposited from a solution of 0.13 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl and 0.108 g/L (PMOTAC $_{170}$) $_{5.6}$ during the forward oxidation scan of the hydrodynamic voltammetry experiment. The surface was scratched with a sharp object and the height difference (film thickness) was determined relative to the blank electrode surface at 3 different positions in dry and in swollen state (surface was rinsed with water and water droplets were removed under a stream of air).

3. Results and discussion

PMOTAC polymers with different topologies (linear PMOTAC $_{130}$ and star-shaped (PMOTAC $_{170}$) $_{5.6}$) were synthesized by controlled radical atom transfer radical polymerization (ATRP; indexes assign the number-average degree of polymerization per chain or the average arm number). The polymerization and characterization is described elsewhere [46,47]. The microgel was prepared by precipitation polymerization from ethanol/water mixtures [48]. Subsequent quaternization of the tertiary amine function leads to highly positively charged, strong polyelectrolytes (see Fig. S1 in Supporting information, 1H -NMR spectrum, verification of successful quaternization exemplary for the DMAEMA microgel).

3.1. General Discussion of Polymer Deposition

A rotating ring-disk electrode (/hydrodynamic voltammetry) was used in order to detect an electrochemically-induced deposition of polyelectrolyte counterion complexes onto electrodes. Thereby, ferrocyanide counterions are reversibly oxidized at the disk electrode. At the same time, the charge of these multivalent hexacyanoferrates is changed leading to an altered interaction of the hexacyanoferrates with the oppositely charged polyelectrolyte and hence to a different polymer solubility. The influence on the resulting electrodeposition is studied using different polyelectrolyte architectures ranging from linear over star-shaped to internally crosslinked microgels all consisting of the same monomeric unit, namely quaternized DMAEMA (PMOTAC). In case of linear (Fig. 1C and D) and star-structured PMOTAC polymer (Fig. 1E) deposition at the electrode solution interface could be observed. Hereby, a pronounced cathodic peak in the disk currents during the reverse scan indicates reduction of the reaction product ferricyanide of the forward scan (forward scan from 0 to 0.5 V and backward scan from 0.5 to 0 V vs. Ag/AgCl). Hence, the ferricyanide $[Fe(CN)_6]^{3-}$ is stored at the disk electrode during the high overpotential part of the scan (0.25 to 0.5 V) due to its incorporation into the assembling PMOTAC/ferricyanide film instead of being swept away during the forced convection upon rotation. The oxidation of the tetravalent ferrocyanide $[Fe(CN)_6]^{4-}$ leads to the transformation of a soluble ferrocyanide/polymer complex to an insoluble ferricyanide/polymer complex (Fig. 1C–E). Although the valency is only changed from tetravalent to trivalent the influence on the solubility of the counterion-polyelectrolyte complex is tremendous. The complex formation is then accompanied by inter- and intramolecular bridging of PMOTAC by the multivalent inorganic salt and formation of insoluble crosslinked poly-complex aggregates, as described before [7]. Noteworthy, the preferential interaction of cationic polyelectrolytes with the less charged ferricyanide, which is surprising from an entropic point of view, has been observed and reported by other researchers [20,26]. Such a preferred interaction of ferricyanide with the polycation is also reflected in a moderate shift of the voltammograms to lower potentials. As the reaction and change in solubility takes place at the electrode/solution interface, the process is accompanied by the formation of a polymer-film being also “transparent” to electrons (hindered charge transport in the film would have been detected by a decreasing current during the proceeding deposition in the high overpotential region of the voltammogram). Though full film dissolution can be achieved at low overpotentials not all stored ferricyanide ions react back to ferrocyanide at the disk. But, some ferricyanides are swept away with the disassembling polymer complex toward the ring electrode. This results in another cathodic peak in the ring current (Fig. 1C–E, lower part; the ring potential is always kept at 0 V vs. Ag/AgCl).

Fig. 1. Hydrodynamic voltammograms of 0.13 mM $\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M KCl in absence (A) and presence of different cationic (poly)electrolytes: MOTAC monomer (B), linear PMOTAC₁₃₀ (C), linear PMOTAC₁₆₀₀ (D), star (PMOTAC₁₇₀)_{5,6} (E) and PMOTAC microgel (F), with a molar concentration of 0.52 mM for (B–E), with regard to MOTAC unit, $icr = 1$, at 23 °C (ring potential at 0 V vs Ag/AgCl; disk potential scanned from 0 V to 0.5 V and then reversed to 0 V with $v = 5$ mV/s, rotation rates increasing from black to blue: 100, 200, 400, 600, 1000, 2000, 3000, 4000, 5000 rpm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Influence of Molar Mass and Branching

The amount of deposited complex depends on the angular velocity ω (rotation rate f) of the rotating electrode, the polymer concentration and the actual time of deposition. With increasing rotation the limiting plateau current i_L and consequently the complex deposition increases due to an enhanced mass transport towards the electrode surface. Interestingly, the polymer deposition is prevented in case of very high molecular weight structures (microgels; Fig. 1F) and of very low molecular weight entities (monomers; Fig. 1B) as indicated by the absence of the reductive peak in both cases. The diffusion of the counterions is not affected by the presence of the monomeric unit (Fig. 1B). All polyelectrolytes instead (Fig. 1C–F) exhibit decreased limiting currents due to counterion attraction to the multiple-charged polymer. One possible explanation for the prevented film deposition in presence of the microgel is the reduced intermolecular bridging induced by ferricyanide. The bridging is caused by ion pairing and acts like an inter- and intracoloidal physical crosslinking (in addition to the intracoloidal chemical crosslinking which is required to obtain microgels during synthesis). Microgels exhibit much higher molecular weights and hydrodynamic radii compared to linear

and star-shaped polyelectrolytes. Hence, it is assumed that the counterions predominantly induce intramolecular crosslinking in case of polyelectrolyte microgels (see also results below for branched and linear high molecular weight analogues). At the same time, residual dangling chains provide probably sufficient colloidal stability. A similar system, containing microgels with a lower charge density, enabled a microgel size modulation simply by changing the counterion valency electrochemically following the same counterion switching approach [35]. These findings show that the difference in complexation behavior of the guest counterions with microgels provoke an additional internal physical crosslinking [49] of the network in case of the trivalent ferricyanide counterion, accompanied by a change in the internal osmotic pressure [50]. It is assumed that the influence on the dimensions of a highly charged system is even higher compared to a system containing only 10 mol% of charges.

Fig. 1 illustrates the mixed effect of changing the polycation architecture and the increase of the polymer molar mass. In order to assess each role individually, we used a linear PMOTAC with a molecular weight in the range of the star-shaped polymer. We see a slightly reduced i_L compared to the shorter linear PMOTAC (due to lowered diffusivity of the larger complex) but a similar cathodic

peak, indicating again pronounced film formation (Fig. 2). The most striking difference is seen in the slower film dissolution as the cathodic peaks for the PMOTAC₁₆₀₀-film dissolution are extended to more negative overpotentials (and the vast majority of ferricyanides is now reduced at the disk, seen in the only small peak in the ring currents). This can be explained by the higher molecular weight and the increased probability of polymer entanglements after deposition restricting a facile film dissolution and a “premature” ferricyanide escape.

3.3. Influence of Composition

The ratio between polyelectrolyte and counterion charges seems to be crucial for the deposition of polyelectrolytes owning a linear or star-shaped architecture. While deposition of the complexes can be observed from solutions in a stoichiometric ratio ($icr=1$, Fig. 1C and D) of counterion and polyelectrolyte charges N^-/N^+ and in less extent in supersaturated polyelectrolyte systems ($icr=2$, Figs. S5 and S7, Supporting information), no electrodeposition occurs at low initial charge ratios ($icr=0.5$ and 0.25 , Figs. S6 and S8, Supporting information). Thus, an excess of polyelectrolyte compared to inorganic salt prevents the formation of insoluble crosslinked poly-complex aggregates due to an insufficiency of bridging and physical crosslinking. Further, the stoichiometric ratio $icr=1$ is more efficient (than $icr=0.25$, 0.5 or 2) regarding the deposition onto electrodes for linear and star-shaped PMOTAC indicated by higher reductive detachment peak currents at $icr=1$ compared to $icr=2$ (Fig. 3). This strongly suggests that the charge-to-charge stoichiometry of the deposited complex (nominal charge ratio ncr between hexacyanoferrate-bound charges and polymeric charges, both being in the deposited complex) is in the range of $1.5 (=2 \cdot \frac{3}{4})$, due to valency reduction from 4 to 3) and $0.4 (=0.5 \cdot \frac{3}{4})$; see Supporting Information), most likely close to 1. This is in agreement with an expected $ncr=1$ for the ferricyanide/PMOTAC film.

3.4. Quantification and Understanding the Deposition Efficiency

Worthy to note, the ongoing deposition at the disk electrode does not reduce the ring currents as such (constant plateau ring currents at high disk overpotential) indicating that the ring detection of products coming from a more and more protruding

Fig. 2. Hydrodynamic voltammograms of $0.13 \text{ mM } [\text{Fe}(\text{CN})_6]^{4-}$ in 0.1 M KCl in presence of cationic polyelectrolyte linear PMOTAC₁₃₀ (black squares), linear PMOTAC₁₆₀₀ (dark green circles) and star-shaped (PMOTAC₁₃₀)_{5,6} (red triangles) at a constant $icr=1$, 0.52 mM with respect to positively charged MOTAC unit, $v=5 \text{ mV/s}$, rotation rate: 5000 rpm , at 23°C . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Hydrodynamic voltammograms of $0.13 \text{ mM } [\text{Fe}(\text{CN})_6]^{4-}$ in 0.1 M KCl in presence of cationic polyelectrolyte linear PMOTAC₁₃₀ (black, grey squares) and star (PMOTAC₁₇₀)_{5,6} (red triangles) at different icr ($icr=1$ and 2 ; the latter is assigned by the lighter color/open symbols), $v=5 \text{ mV/s}$, rotation rate: 5000 rpm , at 23°C . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

film surface is not influenced by the dimensions of film thicknesses and ring/disk distances used here. This allows a reliable extraction of the so-called collection efficiency $N = \frac{i_{L,R}}{i_{L,D}}$, which is defined as ratio between limiting ring and disk current (Fig. 4). It reflects the relative amount of disk product transported and detected at the ring being around 0.5 for the redox probe in absence of any polyelectrolyte. As a result of complexation and deposition N is reduced to ~ 0.3 by the presence of linear and star-shaped polyelectrolytes at $icr=1$ (stoichiometric ratio) and to ~ 0.36 at $icr=2$. These results confirm the hypothesis of stoichiometric charge ratios of counterions to polyelectrolyte being most suitable for poly-complex deposition onto electrode surfaces. In contrast, the presence of the microgel does not significantly affect the collection efficiency being ~ 0.47 in this case due to negligible deposition. These results give an estimate that approximately 40%

Fig. 4. Collection efficiency $N = i_{L,R}/i_{L,D}$ as a function of rotation rate extracted from hydrodynamic voltammograms corresponding to $0.13 \text{ mM } [\text{Fe}(\text{CN})_6]^{4-}$ in 0.1 M KCl in absence (black, open symbols) and presence of cationic PMOTAC polyelectrolytes; linear (black/grey diamonds) and star-like (red triangles) and microgel (blue square) at $icr=1$ (dark colours) and $icr=2$ (light colours), $v=5 \text{ mV/s}$, rotation rates: $100\text{--}5000 \text{ rpm}$, applied ring potential 0 V at 23°C . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the current is used for the direct deposition of the polymer complex (0.4 deposition efficiency DE_N at $icr=1$, as obtained by mere comparison of the collection efficiency N), while 60% of the ferrocyanide is converted without attachment to the electrode (reflecting the reduction of ring currents to $\sim 60\%$ after addition of linear or star-shaped polyelectrolyte). This assessment assumes negligible changes in the detectability of any disk-escaping ferricyanide at the ring electrode during addition of polyelectrolyte. Then, a compilation of the DE_N values for most samples can be found in the Supporting Information. As these values might however be upper limits, a more elaborate DE determination is desirable.

Hence, another estimation of the deposition efficiency DE can be obtained by analyzing the peak currents (and the charge transferred in the peak signals) in comparison to the total charge for the oxidation of ferrocyanide. DE gives the amount of transferred charge ending up as film-bound ferricyanides compared to non-bound ferricyanides. In other words: DE is the proportion of oxidized ferricyanides getting incorporated into the film. Thus, it measures how efficiently the current is used for film formation. More details on the DE determination procedure can be found in the Supporting Information. Dependent on the actual polymer system, a comparison of the ring and disk peak currents also shows that approximately half of the deposited ferricyanides do not get reduced at the disk upon scan reversal but escape directly into the bulk solution where a part of it is detected at the ring electrode.

More important, the analysis gives DE in dependence of the rotational speed for different polymer architectures, as shown in Fig. 5. As an important finding, the DE does not change considerably for varying rotational speed. This has implications for polymer depositions on other (non-stirred) electrodes, as the same deposition efficiency obtained by use of the RRDE can be applied to other (Pt) electrode systems. This will allow an easy estimation of the film thickness for any electrode setup, as described below.

As already discussed, deposition efficiencies are highest for icr close to 1. $DE=0$ at $icr=0.5$, while we have approximately only half of DE for $icr=2$ when comparing to $icr=1$. Further we can see substantial differences in DE for the various polymers with different molar masses and different architectures. Shorter linear polycations are found to be most effective in their deposition. A

reduced DE results when increasing the molar mass either in form of a longer linear or star-shaped PMOTAC. When comparing similar molar masses and a variance in architecture we observe the star-shaped polycations to be least effective in their deposition. This might be traced back to their more globular structure and their reduced ability to form entanglements. We speculate that the soluble, somewhat compacted (PMOTAC₁₃₀)_{5,6}/ferrocyanide and PMOTAC₁₆₀₀/ferrocyanide complexes lacks connection sites for neighboring polymer chains upon oxidation. This might be due to their reduced total surface area in contrast to the larger total surface offered by the small PMOTAC₁₃₀/ferrocyanide complexes. In contrast, the number of the charged anchoring points for ferricyanide increases with molar mass providing more and more bridging possibilities per molecule with increasing molar mass (bridging: physical crosslinking of chains by ferricyanide). Hence, monomer complexes do not deposit onto the electrode. Thus, there is an optimum molar mass (with a degree of polymerization in the range 2–1000), where deposition is most pronounced due to the best balance of bridging possibilities and bridging effectiveness (which accounts for the availability of attached ferricyanide for intermolecular crosslinking). In sum, the lacking microgel electrodeposition is in line with the observation that branching and high degrees of polymerization (>1000) are detrimental for efficient polymer deposition.

3.5. Film Thickness Estimation

This DE evaluation allows also an estimation of the deposited mass m_{dc} alongside with an approximate thickness of the films $d_{complex}$. Knowing DE and the transferred charge at the disk for the ferricyanide production $Q_{(disk\ ferrocyanide\ ox)}$ (in our example by integrating over the forward scan currents) m_{dc} can be estimated by weighing the molar masses of the single constituents and neglecting any residual monovalent counterions in the complex:

$$m_{dc} = \frac{Q_{(disk\ ferrocyanide\ ox)} \cdot DE}{F} \cdot \left(212 \frac{g}{mol} + \frac{3 \cdot 172 \frac{g}{mol}}{ncr} \right)$$

The thickness of the films $d_{complex}$ is influenced by the volume fraction of water in the complex φ , the density of a compact complex without solvent $\rho_{dry, solid\ complex}$ (here estimated as 1.5 g/cm^3) and the area of electrode A (here $\sim 0.13\text{ cm}^2$):

$$d_{complex} = \frac{m_{dc}}{\rho_{dry, solid\ complex} \cdot A \cdot (1 - \varphi)}$$

In order to confirm the validation of the derived equations the film thickness was determined experimentally for one selected system by Scanning Force Microscopy (SFM). For this purpose, the P(MOTAC₁₇₀)_{5,6} star/ferricyanide complex was deposited during the forward scan ($v=5\text{ mV/s}$) of the hydrodynamic voltammetry experiment at $\omega=5000\text{ rpm}$ onto a Pt disk and the surface was scratched with a sharp object, in order to determine the height difference relative to the blank electrode. The obtained film thickness d in swollen state amount $156\text{ nm} \pm 7\text{ nm}$ and $47\text{ nm} \pm 2\text{ nm}$ in dry state (Fig. S13, Supporting information) resulting in a swelling degree by a factor of ~ 3.3 as seen by SFM. By using the estimate for the thickness derived from the DE , we obtain a dry film thickness in the range of $0.05\text{ }\mu\text{m}$ ($\varphi=0$; $ncr=1$), which is in line with the SFM results of $0.05\text{ }\mu\text{m}$. Hence, these simple calculations can give a very reasonable estimation of the film thicknesses that can be transferred to depositions at other electrode systems. This result also indicates that the amount of entrapped monovalent co- and counterions (like Na^+ or Cl^-) is small compared to the amount of deposited hexacyanoferrate.

Further, we refer to the Supporting Information on a discussion of the concentration effect of the supporting electrolyte, showing

Fig. 5. Deposition efficiency DE in dependence of rotational speed of a rotating ring disk electrode in $0.13\text{ mM } [\text{Fe}(\text{CN})_6]^{4-}$ and 0.1 M KCl in presence of linear PMOTAC₁₃₀ (black/grey squares), linear PMOTAC₁₆₀₀ (green circles) and star-shaped (PMOTAC₁₃₀)_{5,6} (red triangles) at 23°C (the lines are a guide to the eye, lighter colors/dashed lines assign $icr=2$, while the top full lines refer to $icr=1$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Deposition efficiencies *DE* for various samples (taken from Fig. 5) and the resulting deposited masses *m* and dry film thicknesses *d* at the end of the forward scan (assuming *n*cr = 1 and $\rho_{\text{dry,solidcomplex}} = 1.5 \text{ g/cm}^3$; indices in column headings assign the rotational speed in rpm during deposition).

	<i>DE</i>	<i>m</i> ₅₀₀₀ [μg]	<i>m</i> ₁₀₀ [μg]	<i>d</i> ₅₀₀₀ [μm]	<i>d</i> ₁₀₀ [μm]
PMOTAC ₁₃₀ <i>icr</i> 1	0.30 ± 0.02	1.6	0.3	0.08	0.01
PMOTAC ₁₃₀ <i>icr</i> 2	0.16 ± 0.01	0.9	0.2	0.05	0.008
PMOTAC ₁₆₀₀ <i>icr</i> 1	0.23 ± 0.01	1.4	0.2	0.07	0.009
P(MOTAC ₁₇₀) _{5.6} <i>icr</i> 1	0.20 ± 0.02	1.1	0.2	0.05	0.009
P(MOTAC ₁₇₀) _{5.6} <i>icr</i> 2	0.11 ± 0.01	0.6	0.1	0.03	0.005

negligible deposition at high salt concentration due to electrostatic screening at 1 M NaCl (Fig. S11, Supporting information). Also low salt concentration (0.01 M) hampers electrodeposition due to the pronounced polymer attraction of both ferri- and ferrocyanide (Fig. S10, Supporting information). This leads already to a reduced solubility of the ferrocyanide/polymer complex in addition to a reduced dynamics in the ferricyanide/polymer deposits.

We summarize all deposition findings in Table 1 showing that the film thickness can be adjusted by the transferred charge and hence by the stirring speed (or the deposition time/complex concentration). In our case (at the end of the forward scan), we obtain dry film thicknesses ranging from 5 nm to almost 80 nm. When stopping the deposition during backward scan (shortly before film dissolution) film thicknesses up to 150 nm result.

Finally, a discussion on the apparent diffusional properties of the electroactive species in presence of the various polyelectrolytes (as seen by RRDE measurements and electrochemical impedance data) is to be found in the Supporting information.

4. Conclusion

Different polymer architectures were investigated on their deposition behavior onto rotating platinum electrodes upon electrochemical switching of the counterion charge. The architecture was varied from monomers over linear and star-shaped to crosslinked networks consisting of PMOTAC poly{[2-(methacryloyloxy)ethyl]trimethylammonium chloride}. The film-formation at the electrode/solution interface was induced by oxidation of the ferrocyanide counterion from solutions containing linear or star-shaped polymers. This study demonstrates that not only the polymer topology but also the molecular weight and the charge ratio between polyelectrolyte and counterion charge (*icr*) have an influence on the deposition efficiency *DE*. Thereby, an optimum molecular mass range for deposition is found exhibiting the best balance of bridging possibilities and bridging effectiveness based on intermolecular crosslinking. Further, the deposition behavior is strongly influenced by the use of branched polyelectrolyte structures. Thereby, intramolecular crosslinking is preferred compared to intermolecular crosslinking. Consequently, microgels as highly-branched polymeric particles do not adsorb significantly at the electrode surface. These results will help to develop efficient electrode coatings for future applications in e.g. sensing [51–54] and actuation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2017.02.102>.

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