

# Oxidation induced variation in polyelectrolyte multilayers prepared from sulfonated self-dopable poly(alkoxythiophene)

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Received (in Oxford, UK) 24th January 2000, Accepted 25th February 2000

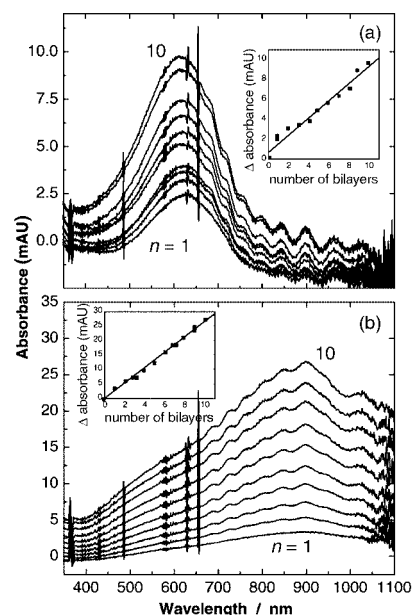
Published on the Web 17th March 2000

Polyelectrolyte multilayers have been prepared using both the neutral and oxidised forms of a poly(alkoxythiophene) derivative with pendant sulfonate groups and it is shown that the oxidation state of the polymer affects multilayer formation.

The fabrication of polyelectrolyte multilayers by consecutive adsorption of polyanions and polycations on a charged surface is a facile method for the preparation of stable multicomposite thin films.<sup>1</sup> The strongly interpenetrating layers are held together principally by electrostatic interactions between multiple ion pairs in the oppositely charged chains. Multilayers of simple polyelectrolytes have been studied in detail but electrochemically active polyelectrolytes have received considerably less attention.<sup>2,3</sup> In particular, multilayers of conducting polymers carrying pendant ionic groups have scarcely been characterised at all,<sup>4</sup> although multilayers have been prepared using oxidised conducting polymers as polycations.<sup>5</sup> Owing to their special electrical and optical properties the polyelectrolyte films containing conducting polymers can have potential applications in the fields of, *e.g.*, sensors, electrooptics and LED technology.<sup>1,6</sup>

With weak polyelectrolytes the charge density can be controlled by pH with profound effects on the multilayer formation.<sup>7</sup> Analogously, the charge density of conducting polymers can be controlled by the oxidation state. We report here the formation and preliminary characterisation of multilayers prepared from the neutral or oxidised (referring to the polymer backbone) sodium salt of poly-3-(3'-thienyloxy)propanesulfonate (P3TOPS) as polyanion and poly(allylamine hydrochloride) (PAH,  $M_w = 5\text{--}6.5 \times 10^4$ , Aldrich) or poly(diallyldimethylammonium chloride) (PDADMAC,  $M_w = 4\text{--}5 \times 10^5$ , Aldrich) as polycation. The water-soluble polythiophene P3TOPS was prepared by iron(III) chloride oxidation of the monomer† in chloroform.<sup>8</sup> The crude polymer was fractionated with a Sephadex G-50 F column using water as eluent and the highest molecular weight fraction collected.<sup>9</sup> The neutral polymer is blue with  $\lambda_{\text{max}}$  at 620 nm and the oxidised form is bluish grey. The oxidation potential of P3TOPS is *ca.* +0.2 V vs. SSCE (sodium saturated calomel electrode) and it is easily oxidised by oxygen. In solution the polymer stays in the neutral state only by addition of a strong reducing agent, *e.g.*, hydrazine or  $\text{Na}_2\text{S}_2\text{O}_4$ . Polyelectrolyte adsorption was carried out from dilute polyelectrolyte solutions (1 or 10 mM with P3TOPS or PAH and PDADMAC, respectively) for 30 min followed by washing with water ( $3 \times 1$  min). The substrates were primed with a layer of physisorbed polycation, polyethyleneimine (PEI,  $M_w = 25\,000$ , Aldrich; quartz and indium-tin oxide ITO), or chemisorbed 2-mercaptoethanesulfonic acid (MESA, Aldrich; gold). The ionic strength was set to 0.6 M with 0.2 M  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{S}_2\text{O}_4$ .

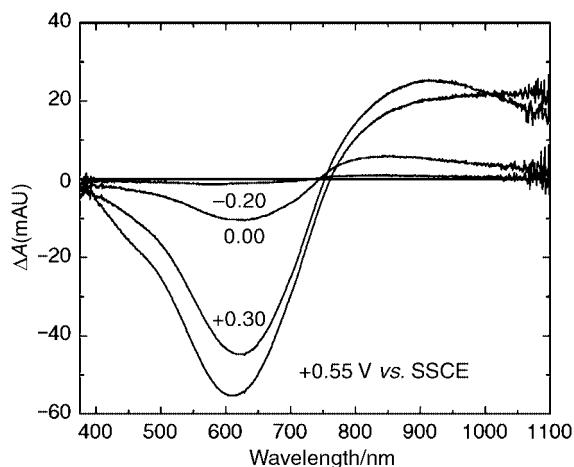
Neutral P3TOPS is a polyanion with one negative charge per monomer unit. Oxidation of the polymer introduces positive charges in the thiophene backbone and reduces the charge density. However, both forms can be used for the fabrication of



**Fig. 1** Polyelectrolyte multilayer formation on quartz. Quartz/PEI/(P3TOPS/PDADMAC)<sub>n</sub> using (a) neutral (hydrazine added) and (b) oxidised P3TOPS. Insets show the increase of absorbance at 600 and 900 nm. [Ordinate values in milliabsorbance units (mAU).]

polyelectrolyte multilayers. Fig. 1 shows the sequential build-up of P3TOPS/PAH bilayers on quartz. A linear increase of absorbance indicates a regular increase of adsorbed polymer. If the charge density of the oxidised polymer is too low multilayer formation would be hindered. However, oxidation of polythiophenes gives rise to a positive charge of *ca.* 0.25–0.4 per monomer unit, which itself is enough to render oxidised conducting polymers useful as polycations in multilayer fabrication.<sup>5</sup> The spectra of P3TOPS/PDADMAC multilayers on ITO are shown in Fig. 2. The film, which is electroactive owing to efficient interpenetration of the layers, displays behaviour similar to electrodeposited polythiophene films. As the potential is made more anodic, the  $\pi\text{--}\pi^*$  transition of the neutral form decreases, and the absorbance increases above 800 nm. At high anodic potentials the absorbance at 900 nm again decreases and a new transition forms in the NIR region above 1000 nm. This implies that these multilayers can be oxidised to the metallic state in aqueous solutions.

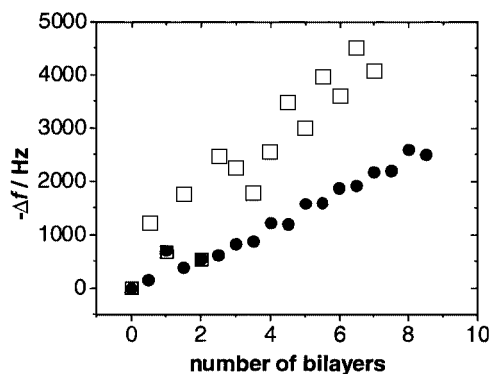
Sequential multilayer fabrication with the neutral and oxidised P3TOPS was carried out also on gold using a quartz crystal microbalance (QCM, Fig. 3). In the first case, the polyanion and polycation (PDADMAC) were adsorbed from 0.2 M  $\text{Na}_2\text{S}_2\text{O}_4$  solutions in order to keep polythiophene in the neutral state. With oxidised P3TOPS, oxygen saturated 0.2 M  $\text{Na}_2\text{SO}_4$  solutions were used. A regular build-up was observed after 2–4 bilayers, a common feature with polyelectrolyte



**Fig. 2** Difference spectra of ITO/PEI/(P3TOPS/PDADMAC)<sub>5</sub> multilayers at potentials indicated (in 0.6 M NaNO<sub>3</sub>; adsorbed using oxidised P3TOPS). Spectrum at -0.40 V vs. SSCE taken as reference.

multilayers.<sup>1,2</sup> QCM studies on polyelectrolyte layers have shown that viscoelastic properties are not important and data can be treated in a gravimetric manner.<sup>10</sup>

With oxidised P3TOPS the average mass increase per PDADMAC/P3TOPS bilayer was approximately half of that observed with neutral polymer, showing the effect of the charge density on multilayer formation. However, contrary to expectations, lower charge density results in the adsorption of less material. Lowering the charge density of weak polyelectrolytes by adjusting the pH of the adsorption solution yields thicker films because more polymer is needed to compensate the surface charge.<sup>7</sup> Closer inspection of Fig. 3 reveals a more complex behaviour with P3TOPS. Although irregular growth persists longer for the neutral (*cf.* also insets of Fig. 1; the more regular growth in that case can be attributed to the PEI underlayer) mass increase ( $\Delta f < 0$ ) or decrease ( $\Delta f > 0$ ) is observed after 3–4 bilayers upon addition of PDADMAC or



**Fig. 3** QCM frequency changes (film side in contact with water) upon multilayer formation in the Au/MESA/(PDADMAC/P3TOPS)<sub>n</sub> system. Open and filled symbols refer to neutral and oxidised P3TOPS, respectively.

neutral P3TOPS, respectively. By contrast, the adsorption of oxidised P3TOPS leads to a mass increase and the mass stays constant when PDADMAC is added. Evidently, neutral P3TOPS, with high charge density, is able to remove some of the previously adsorbed polycation whereas PDADMAC does not adhere well to the surface of oxidised P3TOPS having low surface charge density. Therefore, even though more material is deposited when neutral P3TOPS is used, more electroactive polymer is adsorbed for the oxidised material. This conclusion is supported by electrochemical experiments, which show that the film oxidation current increases more rapidly with oxidised P3TOPS as the polyanion.

In summary, we have shown for the first time that electroactive polyelectrolyte multilayers can be prepared from ionically substituted polythiophenes using both neutral and oxidised polymer as a polyanion. The oxidation state changes the charge density of the polyanion and has a marked effect on multilayer formation. This behaviour is analogous to that of weak polyelectrolytes as a function of pH.

Financial support from the Academy of Finland (Grant no. 30579) is gratefully acknowledged.

## Notes and references

† 3-(3-Bromo)propoxythiophene was synthesised from 3-methoxythiophene and 3-bromopropanol analogously as described in ref. 8. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.18 (1H, dd), 6.75 (1H, dd), 6.27 (1H, dd), 4.10 (2H, t), 3.58 (2H, t), 2.30 (2H, td). The product was refluxed with Na<sub>2</sub>SO<sub>3</sub> in acetone-water (2:1), evaporated to dryness and the crude product dissolved in ethanol. Recrystallisation from ethanol yielded white crystals of sodium 3-(3'-thienyloxy)propanesulfonate. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 7.19 (1H, dd), 6.67 (1H, dd), 6.40 (1H, dd), 4.00 (2H, t), 2.90 (2H, t), 2.03 (2H, td).

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- 9 This fraction was eluted practically at the void volume showing that the molecular weight is close to the fractionation range of the column (*ca.* 10000 for dextrans). Attempts to determine the molecular weight with analytical size-exclusion chromatography using sodium poly(styrene sulfonate) standards were not successful.
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Communication b000769m