Characterization of the First Steps in Electropolymerization by Photocurrent Spectroscopy

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By using photocurrent spectroscopy it is shown that the first traces of poly(3-methylthiophene) electropolymerized onto bare indium tin oxide (ITO) already have a long conjugation length, whereas electropolymerization onto ITO with immobilized bithiophene or bare platinum results in a stepwise chain growth of the surface-confined polymer.

Electropolymerization is a heterogeneous process taking place on the surface of a conducting substrate in contact with the monomer solution. Reactive species are generated by the electrolysis and these species initiate and/or maintain the polymerization of the monomer. At a certain stage the growing polymer chains start to adhere to the surface and film growth begins. At what stage this deposition starts is a matter of debate and a subject of this report. It seems that these very first steps play a decisive role in determining the quality of the resulting polymer film.

In principle the growth of the polymer film may start in two ways. Either the growth begins uniformly and simultaneously at every point of the surface or it is initiated at a few nucleation centres. In the former case, which corresponds to one-dimensional growth, the film can be expected to be smooth at every stage of growth and its formation can be reliably followed by optical methods based on reflection, *e.g.* ellipsometry. In the latter case, which almost always is closer to the reality, the film growth follows a combined 2D and 3D mechanism with initial separate 'islands' which finally merge forming a uniform polymer surface.[1] Due to this initiation mechanism the film is necessarily bumpy and optical reflection methods do not give reliable results. Actually there are not very many methods which allow characterization of traces of sparsely scattered material on a solid, electrically conducting surface. The method that we found most useful in this connection is photocurrent spectroscopy. In this method the sample is subjected to intense monochromated light. The excited state of the sample material undergoes further reactions giving rise to a net electron transfer through the solution–electrode interface. By varying the wavelength of light and recording the resulting electric current we get a photocurrent spectrum which in most cases corresponds closely to a conventional absorption spectrum. Photocurrent spectroscopy has been used for characterizing the semiconducting properties of polycarbazole[2] and poly(3-methylthiophene),[3] but only in the presence of rather thick films.

Poly(3-methylthiophene) is one of the most extensively studied conductive polymers and its electrochemical synthesis has been a subject for numerous studies. In spite of these studies, the very first steps of polymer formation are only poorly understood. The treatment of the electrode surface is known to have a large effect on the initial stages of polymerization in the case of platinum[4,5] and ITO[1] electrodes. However, the initial polymer deposits have not been characterized by any spectral measurement.

The electrochemical cell used in this work was similar to those described in our previous studies.[1,6] A stainless-steel auxiliary electrode, silver pseudoreference and either platinum or ITO working electrodes were used. The ITO electrodes were cleaned and chemically modified by treating with silicon tetrachloride and subsequently with 2-bithienyllithium as described previously.[1]

Polymerization of 3-methylthiophene was carried out by short galvanostatic pulses with precisely known charges in 0.1 mol dm^{-3} solutions of monomer and Bu_4NPF_6 in dry acetonitrile. To reduce the effect of photopolymerization, the solution in the cell was changed into pure electrolyte solution before the photocurrent measurement. To undope the polymer the working electrode was biased at −0.2 V. For the photocurrent spectra the electrode was illuminated by a 450 W Xe-lamp through a scanning monochromator. The light was chopped at a frequency of 25 Hz. Photocurrent was fed into a

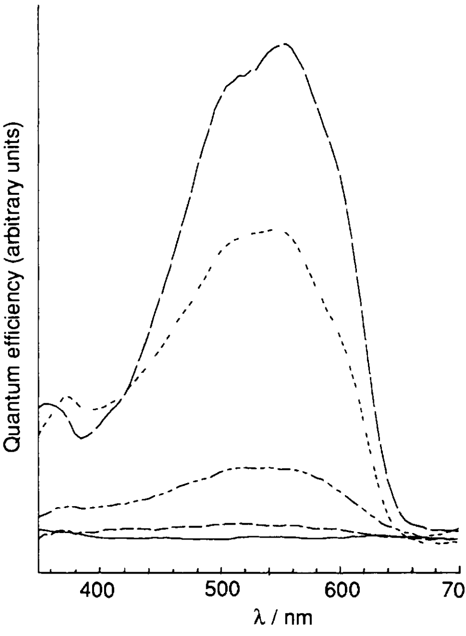

Fig. 1 Galvanostatic polymerization of 3-methylthiophene on virgin ITO. Photocurrent spectra recorded at different deposition stages (in order of increasing intensity): bare ITO, 0.1, 0.2, 0.4 and 0.6 mC cm^{-2}.

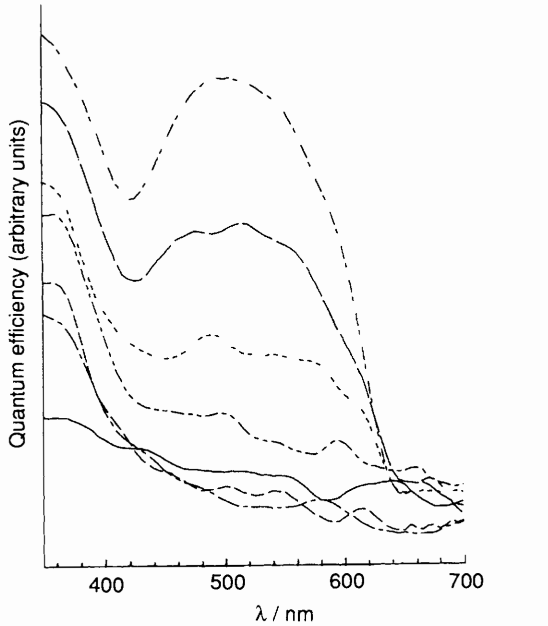

Fig. 2 Galvanostatic polymerization on bithiophene-coated ITO. Photocurrent spectra recorded at different deposition stages (in order of increasing intensity): 0.0, 0.1, 0.2, 0.4, 0.7, 1.1 and 1.6 mC cm^{-2}.

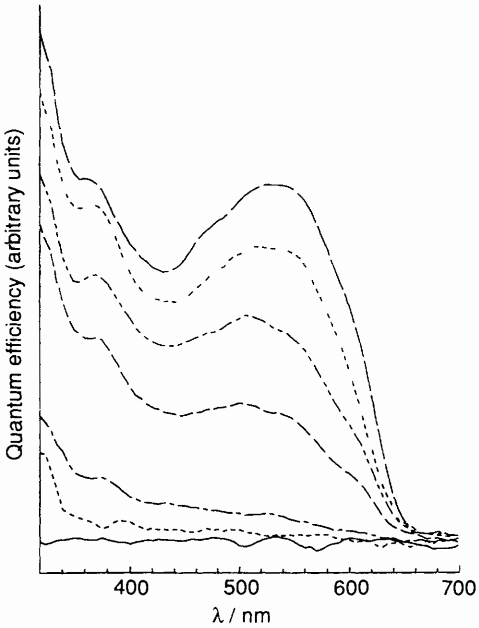

Fig. 3 Galvanostatic polymerization on platinum. Photocurrent spectra corresponding to the deposition charges of 0, 1, 2, 4, 6, 9 and 13 mC cm^{-2}.

current follower and amplified with a lock-in amplifier. The whole system was controlled and data recorded by a computer. The absorption and photocurrent spectra run from the same, relatively thick film of poly(3-methylthiophene) were in a satisfactory conformity with each other.

Polymerization charge was usually kept below 2 mC cm^{-2} and at this level the resulting polymer deposit was invisible to the unaided eye and no absorption spectra could be recorded. However, photocurrent spectra could be recorded with a rather high signal-to-noise ratio and in Fig. 1 the spectra of poly(3-methylthiophene) recorded at different polymerization charges are shown using a virgin ITO electrode as a substrate. It should be noted that the lowest polymerization charge, 0.1 mC cm^{-2}, corresponds to approximately one monolayer of 3-methylthiophene. Probably due to the stochastic nature of the initiation process, the measured intensities of the photocurrent spectra are not always reproducible from run to run, but it does not affect the conclusions in this work. What is most noteworthy in these spectra, is that (*i*) the location of the maximum does not appreciably depend on the polymerization charge, and (*ii*) the location of the maxima at *ca.* 560 nm shows that even at a very low polymerization charge the conjugation length of the polymer is very long. In fact, the extrapolated value for the infinitely long chain of polythiophene is reported to be close to 538 nm in solution,[7] using end-capped oligothiophenes as model compounds.

Chemical modification of the ITO surface by covalently bound bithiophene is known to facilitate the formation of a uniform polymer layer.[1] Fig. 2 shows how this treatment affects the photocurrent spectra at different polymerization charges. The relative absorbance at the long-wavelength region of the spectra is seen to be enhanced by the increasing polymerization charge, indicating an increasing conjugation length of the polymer chains. These spectra are reminiscent of the spectra recorded for polymerization on platinum polished with 1 μm diamond paste (Fig. 3).

There are essentially two different hypotheses on the initial stages of electropolymerization:[4] (*a*) A monomer or short oligomer is supposed to become adsorbed on the electrode surface and subsequent polymerization occurs by stepwise increase of the chain length of the adsorbed oligomer. (*b*) The oligomer molecules are first formed in the solution, and after achieving a certain stage in chain length and insolubility, the deposition onto the surface takes place. In the present work the deposition onto a virgin, untreated surface seems to follow the mechanism (*b*), because even at the lowest polymerization charges the conjugation length of the deposited material seems to be considerable and does not significantly increase at higher charges. On the other hand, the deposition onto the chemically modified surface and platinum seems to follow the mechanism (*a*), inferring from the charge-dependent photocurrent spectra.

However, in case of platinum, there is some evidence reported favouring the deposition mechanism (*b*).[4,5] This apparent contradiction could be attributed to the different surface finishes of platinum electrodes. On the other hand, the estimated critical chain lengths for deposited oligomers are very small, actually only 2 to 4 monomer units.[8] This is in accordance with the spectra shown in Fig. 3, remembering that the absorption maxima for the short oligomers in solution are *ca.* 300, 355 and 390 nm for bi-, ter- and quater-thiophene, respectively.[9] Hence equally well we may say that virgin ITO and platinum electrodes seem to both follow mechanism (*b*), the only difference being the greatly increased chain length of the critical oligomers in case of ITO. This may be due to the different affinity of the electrode surface towards thiophene species, with platinum being capable of adsorbing many organic compounds, including thiophenes.[10]

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