Electrosynthesis of Highly Conducting Poly(3-methylthiophene) Thin Films

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Poly(3-methylthiophene) thin films with conductivities in the range of 2000 S cm^{-1} have been prepared by electrochemical polymerization.

Recently, conducting polymers produced by the electropolymerization of thiophene derivatives[1] have been studied with a view to testing their application in modified electrodes and electronic devices.[2] Their synthesis and an analysis of the electropolymerization mechanism have received less attention. However, an analysis of the synthesis factors controlling the conductivity can lead to a better understanding of the polymerization mechanism, which can in turn generate further progress in the control of the polymer's properties.

The morphology and electrochemical properties of electrogenerated conducting polymers like poly(thiophene) and poly(pyrrole) depend on the thickness of the polymer films.[3] However, these observations concerned films of several micrometers thickness and they have not been correlated with modifications affecting the molecular structure of the polymer. We report here a summary of the results of the analyses of the electrochemical, spectroscopic, and electrical properties of poly(3-methylthiophene) (PMeT) as a function of the thickness of the deposited film. We show that the extent of conjugation is larger in very thin films, and that this can be applied in the preparation of highly conducting films.

The PMeT films were synthesized in a one-compartment cell containing the monomer and tetrabutylammonium hexafluorophosphate in nitrobenzene. The solutions were degassed by argon bubbling prior to electropolymerization which was performed under galvanostatic conditions, at ambient temperature, under an argon atmosphere. The anode was an indium–tin oxide transparent electrode (ITO) or a platinum plate of 8 cm^2 area; aluminium foil or ITO electrodes were used as the cathode. All potentials refer to a saturated calomel electrode (S.C.E.). After the synthesis, the films were rinsed with acetone, dried in an argon flow, and collected on adhesive tape. The thicknesses of the films were determined from the relation 20 Å/(mC/cm^2) established from thickness measurements performed on thicker films (0.75—2 μm). The optical density of the films was found to vary linearly with the deposition charge used for their preparation. This shows that the polymerization yield is independent of the deposition charge, allowing the use of the above linear relation for determining the films thicknesses. Conductivities were measured by the four probe technique on films supported on adhesive tape. The details of all these experiments will be reported elsewhere.

Table 1. Variation of the anodic peak potential and absorption maximum of PMeT as a function of film thickness.

Qs/ mC cm^{-2}	Thickness/ Å	E_{pa}[a]/ V *vs.* S.C.E.	λ_{max}[b]/ nm
2.5	50	0.500	
5	100	0.500	530
10	200	0.520	524
25	500	0.530	520
50	1000	0.570	516
100	2000	0.590	510

[a] E_{pa} = anodic peak potential = 10 mV/s in 0.1 M LiClO_4/acetonitrile.
[b] Electrochemically undoped films on ITO.

Table 1 summarizes the main electrochemical and spectroscopic data determined for PMeT films of various thicknesses on ITO. As shown by these results, the anodic peak potential (E_{pa}) shifts by ~100 mV towards less anodic values when the thickness of the films is reduced from 2000 to 100 Å. This shift of the oxidation potential towards less positive values is consistent with an increase of the mean conjugation length in the polymer.[4a,d,5b] However, taking into account the possible variation of the relative contribution of the capacitive charging currents in the overall electrochemical process, the absorption spectra of the undoped films have been recorded in order to confirm the enhancement of the mean conjugation length suggested by the E_{pa} shift. The comparison of the results listed in Table 1 shows that the decrease of the film thickness from 2000 to 100 Å produces a 20 nm bathochromic shift of the absorption maximum. This result confirms that the mean conjugation length in the polymer increases steadily as the film thickness decreases. This suggests that the number of conjugation defects occurring during the electropolymerization increases rapidly as the growth of the polymer chains proceeds. Previous work has already demonstrated the tight correlation between the mean conjugation length and the conductivity of poly(thiophenes).[4] On the basis of this correlation, one would expect ultra-thin films to be highly conductive.

In order to confirm this hypothesis, thin PMeT films have been prepared on ITO and platinum electrodes using optimized electrosynthesis conditions. Table 2 summarizes the conductivity values measured under various conditions. These results confirm that the conductivity increases with decreasing monomer concentration in agreement with our previous conclusion,[5b] and, furthermore, they show that conductivities in the 2 × 10^3 S cm^{-1} region can been obtained. Owing to practical problems related, among others, to the decrease of the stability of the doped state in very thin films when rinsed with acetone, and also to problems inherent in the manipula-

Table 2. Conductivities of PMeT films prepared under optimised electrochemical conditions.

[MeT]/ mol	[Bu_4NPF_6]/ mol	Electrode	Current density/ mA cm^{-2}	Deposition charge/ mC cm^{-2}	Thickness/ Å	Conductivity/ S cm^{-1}
0.2	0.05	ITO	20	100	2000	895
0.1	0.02	—	5	200	4000	1250
—	—	—	—	100	2000	1430
0.05	—	Pt	1.5	190	3800	1470
—	—	—		100	2000	1975

tion of very thin films (occurrence of fractures), an apparent optimum was observed in the conductivity for thicknesses ranging from 1500 to 2000 Å. However, the concomitant displacement of both the oxidation potential and of the absorption maximum observed on thinner films suggests that the conductivity of these films should be much higher. These conductivity values, which are four times higher than the ones recently reported,[5] represent, to our knowledge, the highest obtained until now for an as-grown poly(heterocycle) film.

These results, together with those obtained recently for poly(acetylene)[6] show that significant progress in the control of the structure and conductivity of conducting polymers is still possible, which is of particular interest for the future development of these materials.

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