Electrodes modified with Poly(3,4-Ethylenedioxythiophene) doped with Sulfonated Polyarylethersulfones: a combined WAXS and cyclic voltammetric study

V. Sabatini[a,b], V. Pifferi[a,b], S. Checchia[c], S. Rebeccani[a,b], H. Farina[a,b], M.A. Ortenzi[a,b] and L. Falciola[a,b]

[a] Department of Chemistry, Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italy
[b] CRC Materials&Polymers (LaMPo), Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italy
[c] ESFR- The European Synchrotron, 71 Avenue des Martyrs, Grenoble 38000, France
valentina.sabatini@unimi.it

Among Polythiophene derivates, Poly(3,4-Ethylenedioxythiophene) (PEDOT) is one of the most successful conducting polymer due to its excellent environmental stability and high electrical conductivity.
Numerous researches have been conducted on PEDOT synthesis by electrochemical and chemical polymerization of 3,4-Ethylenedioxythiophene (EDOT). Chemical approaches performed by high-concentration water-based emulsion polymerization of EDOT with 2-Naphthalenesulfonic acid as doping agent and ferric sulfate as oxidant species, produce PEDOT precipitates as dark-blue powders, which are insoluble in water [1].
In the present work, we have synthesized PEDOTs characterized by high solubility in the chosen reaction solvents (N,N-dimethylformamide, dimethylacetamide, dimethyl sulfoxide and N-methyl-2-pyrrolidone), via a high-concentration solvent-based emulsion polymerization of EDOT and ferric sulfate as doping agent.
To improve PEDOT conductive properties, the sulfonated dopants commonly used are 2-Naphthalenesulfonic acid and para-toluene sulfonic acid. Besides these species, also Sulfonated Polyarylethersulfone (SPAES), synthesized via homogeneous synthesis with different degree of sulfonation (DS) [2], can be used thanks to both the tight control over the DS and the charge separation present in SPAES structure deriving from the pre-sulfonated comonomer [3,4].
The oxidative polymerization of EDOT with SPAES was successfully performed and the resulting polymers were casted onto glassy carbon electrodes; despite the low amount of SPAES used (1% w/w respect to EDOT), it was found that PEDOT_SPAES electrochemical properties, *i.e.* voltammetric peak heights, are in general better than the ones obtained for neat SPAES and for not doped and commercial PEDOTs. Moreover, this effect is increased by SPAESs DS increases. The chemical structure of PEDOT_SPAESs was studied via wide-angle scattering (WAXS), comparing the crystalline structures of not doped and commercial PEDOTs, with the amorphous structures of PEDOT_SPAESs. To the authors' best knowledge, this is the first time that SPAES was used as PEDOT dopant and that a study, albeit preliminary, of its effect on PEDOT_SPAES structural properties was performed.

References

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