

Abstract

This thesis targets the development of conjugated polymers with improved process ability from solutions. Two types of ionic polymers are addressed: (i) conjugated metallo-supramolecular polymers (MSPs) composed of conjugated heteroaromatic unimers (building blocks) linked to chains by various metal ions giving charged main chains, and (ii) polythiophene polyelectrolytes containing ionic pendants. Processing advantages of conjugated polyelectrolytes consist in the possibility of their processing from solutions in green solvents such as alcohols or even water. The advantages of MSPs consist in the thermodynamic control of the degree of polymerization (length) of their chains in solutions by the choice of solvent and temperature. As a result, MSPs reversibly provide systems of low viscosity that can be processed from solutions more easily than high-molar-mass polymers giving highly viscous solutions.

Synthesis of appropriately designed unimer(s) is the key step of preparation of an MSP. Within this thesis, a series of novel unimers composed of linear oligothiophene type (mono-, bi-, ter- a thieno-thiophene- diyl) central blocks capped with 2,6-bis(oxazoline-2-yl)pyridine (*pybox*) or 2,6-bis(imidazole-2-yl)pyridine (*bzimpy*) end-groups have been successfully prepared, characterized and assembled with various metal ions into MSPs. It is worth noting that the cheap and commercially easy available chelidamic acid was the starting compound for the syntheses of both the above chelating end-groups (ion selectors).

The bis(*pybox*) unimers were assembled with metal ions such as Fe^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} and lanthanide ions Eu^{3+} or Tb^{3+} to give corresponding MSPs. On the other hand, MSPs derived from bis(*bzimpy*) unimers were found to show significantly lower solubility thus they were studied less in detailed using only Fe^{2+} and Zn^{2+} ion couplers. The detailed study of the MSP assembly revealed three stages of this process, same as observed for bis(*tpy*) unimers: formation of “butterfly” dimers $\text{U-Mt}^{z+}\text{-U}$ (U stands for a unimer species) at the Mt^{z+}/U mole ratios r up to ca 0.5, formation of longer MSP chains for r from above 0.5 to ca 1, and end-capping of MSP chains and their equilibrium depolymerization at r values above 1. The latter proves the constitutional-dynamic nature of the novel MSPs, which is the fastest for Zn-dynamers and the slowest for Fe-dynamers that exhibit

the presence of the metal-to-ligand charge transfer transitions. Photoluminescence properties of new *pybox*- and *bzimp*y-MSPs are also similar to those of the *tpy*-MSPs; only Zn²⁺-MSPs show high photoluminescence while the other ones exhibit quenching the luminescence with increasing content of metal ions.

Novel cationic conjugated polyelectrolytes have been prepared by modification of the parent poly[3-(6-bromohexyl)thiophene-2,5-diyl bromide]s of the low to high regioregularity, consisting in replacing the bromine side-chain-capping atoms with triethyl- or triphenyl-phosphonium bromide groups. The parent polymers were prepared by means of the Grignard metathesis polymerization and their regioregularity has been tuned by temperature regime of the polymerization process. Studies on the optical properties of these polyelectrolytes revealed their solvatochromism and possibility of tuning their luminescence through the solvent polarity. The luminescence quenching by K₄[Fe(CN)₆] and K₃[Fe(CN)₆] has been also studied. All experiments performed point to the principle influence of the main-chain regioregularity on the polymer properties except for its solubility in polar solvents.