Abstract

This Diploma Thesis presents results obtained by solution of two partial projects:

a) Preparation of monomers from renewable sources using metathesis and tandem hydrogenation catalyzed with ruthenium compounds - project solved during my Erasmus stay at the Université de Rennes 1 in France;

b) Preparation and properties of α,ω-bis(tpy)quarterthiophene oligomers carrying ionic side groups as oligomonomers for polyelectrolyte conjugated dynamers - project solved at the Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague.

Project a): Self-metathesis of 1,2-epoxyhex-5-ene (but-3-enyloxirane) and its cross-metathesis with methyl acrylate and acrylonitrile catalyzed with ruthenium compounds as well as tandem design of these metatheses and consecutive hydrogenation of their products by gaseous hydrogen have been optimized. The following influences have been studied and tuned: (i) type of the catalyst (Grubbs, Hoveyda, Zhan) and its concentration and method of dosing, (ii) concentration of reactants and additives, (iii) type of solvent, and (iv) reaction temperature. Reactions were monitored by the GC, GC and MS methods and the products were characterized by the NMR method. Methyl 6,7-epoxyheptanoate (methyl 5-oxiranyl pentanoate) obtained by the tandem cross-metathesis and hydrogenation of methyl acrylate and 1,2-epoxyhex-5-ene was quantitatively transformed by the nucleophilic oxirane ring opening into methyl esters of substituted heptanoic acids: 6,7-dihydroxy- (using H₂O, 100 °C), 6-hydroxy-7-methoxy- (CH₃ONa in methanol, 65 °C), and 6-hydroxy-7-phenylamino- (aniline, 100 °C).

Project a): Novel oligomonomers for preparation of conjugated metallo-supramolecular dynamers have been prepared and transformed into new dynamers. The optimized reaction path includes: (i) preparation of α,ω-bis(tpy)quarterthiophene carrying two 6-(p-methoxy)phenoxyhexyl side groups attached to the central oligothiophene block in positions 2 and 7, oligomonomer Q27MOF, (ii) modification of the side groups into 6-bromohexyl groups to obtain oligomonomer Q27Br, and (iii) subsequent modification of 6-bromohexyl into 6-(triethylphosphonium)hexyl side groups giving Q27P⁺. The oligomonomers have been transformed to metallo-supramolecular dynamers through the coordination of their tpy end-groups to Zn²⁺ a Fe²⁺ ions and the UV-VIS and luminescence spectral characteristics of the dynamers as well as oligomonomers have been determined. The dynamers derived from oligomonomer Q27P⁺ represent a new class of dynamers that has not been described in the literature – conjugated polyelectrolyte dynamers.