

DOCTORAL THESIS ABSTRACT

2-Oxazoline triblock copolymers with hydrophilic, lipophilic and fluorophilic blocks: from synthesis to hierarchical self-assembly

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The focus of this research was on the study of di- and triblock poly(2-oxazoline) copolymers with fluorinated blocks. The synthesis and solution properties of novel copolymers combining hydrophilic, hydrophobic (lipophilic) and fluorophilic moieties into one segmented molecule were reported.

The simple synthetic approach which provides an easy way to attach a C_nF_{2n+1} terminal chain to a poly(2-methyl-2-oxazoline)-*block*-poly(2-*n*-octyl-2-oxazoline) copolymer was described. Small-angle neutron and x-ray scattering experiments unambiguously proved the existence of polymersomes, worm-like micelles and their aggregates in aqueous solution. It was shown that increasing content of fluorine in the poly(2-oxazoline) copolymers results in a morphological transition from bilayered or multi-layered vesicles to worm-like micelles.

The synthesis of poly(2-perfluoroalkyl-2-oxazoline)s is complicated by their extremely low activity in cationic ring-opening polymerization reaction (CROP), both in the initiation and in the propagation due to strong electron-withdrawing effect of perfluoroalkyl substituent. A detailed systematic study on synthetic approaches to increase the reactivity of 2-fluoroalkyl-2-oxazolines in CROP by the insertion of methyl and ethyl hydrocarbon spacers between the 2-oxazoline ring and the trifluoromethyl group was presented. New fluorine-containing 2-alkyl-2-oxazolines were synthesized. The kinetic studies showed the gradual increase of the polymerization rate with increasing of the hydrocarbon spacer length. The 2-(3,3,3-trifluoropropyl)-2-oxazoline (CF₃EtOx) was found to have similar reactivity as non-fluorinated 2-oxazolines, which allowed the synthesis of defined triblock copolymers.

This approach was further expanded for highly fluorinated 2-oxazolines. 2-(1H,1H,2H,2H-Perfluorooctyl)-2-oxazoline was synthesized via procedure supplemented by Grignard reaction. The kinetic study proved that the length of perfluoroalkyl substituent has no effect on the reactivity of 2-oxazolines with a double methylene spacer.

A number of fluorine-containing di- and triblock copolymers with 2-methyl-2-oxazoline (hydrophilic) and 2-*n*-octyl-2-oxazoline (hydrophobic) were synthesized. The effect of the fluorinated block on the aqueous self-assembly behaviour of the copolymers was studied by dynamic light scattering, transmission cryo-electron microscopy and small-angle neutron scattering experiments.

The described fluorine containing poly-2-oxazolines represent a potential platform for future utilization as ¹⁹F magnetic resonance imaging contrast agents.

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