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Poster abstract

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Title: Theoretical Rationalization of the Cationic Ring-opening Polymerization of a Methyl Ester Functionalized 2-Oxazoline Monomer

Authors: Dietmar Hertsen,[a] Hannelore Goossens[a], Saron Catak,[a, b] Petra JM Bouten,[c, d] Maarten Vergaelen,[d] Bryn D Monnery,[c] Jan CM van Hest,[d] Richard Hoogenboom,[c] Veronique Van Speybroeck[a]

Affiliation:
[a] Center for Molecular Modeling (CMM), Ghent University, Technologiepark 903, Zwijnaarde 9052, 9000 Ghent, Belgium (Member of the QCMM Ghent-Brussels Alliance)
[b] Bogazici University, Department of Chemistry, Bebek 34342 Istanbul, Turkey
[c] Supramolecular Chemistry Group, Department of Organic Chemistry, Ghent University, Krijgslaan 281 S4, 9000 Ghent, Belgium
[d] Radboud University Nijmegen, Institute for Molecules and Materials (IMM), Heijendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

Summary (max 200 words)**:**

Poly(2-oxazoline)s are an interesting class of polymers whose physicochemical properties can easily be tuned. These pseudopeptides are readily synthesized via cationic ring-opening polymerization (CROP) of various monomers, yielding polymers with distinct properties. Because of their versatility and biocompatibility, poly(2-oxazoline)s are candidate drug-delivery systems.

The homopolymerization of 2-methoxycarbonylethyl-2-oxazoline (MestOx) was shown to be faster than that of 2-methyl-2-oxazoline (MeOx). However, the copolymerization of both monomers revealed an increased rate for MeOx, leading to rate order inversion. This remarkable behaviour was investigated by means of Density Functional Theory calculations.

MestOx residues in the polymer chain close to the reactive center stabilize the propagation transition state, explaining the faster MestOx homopolymerization and the MeOx rate increase in the copolymerization. The interactions between the MestOx residue and the monomer were characterized by Natural Bond Orbital interaction energies and Hirshfeld-I charges. The monomer nucleophilicity was increased in the pre-reactive complex due to these reactions. Furthermore, isolated MeOx monomers are more nucleophilic than MestOx monomers, supporting the inversed rate order in the copolymerization.

In conclusion, stabilization of the propagation transition state by interactions between nearby MestOx residues and the monomer, and the higher nucleophilicity of MeOx explain the experimentally observed homo- and copolymerization rate order.