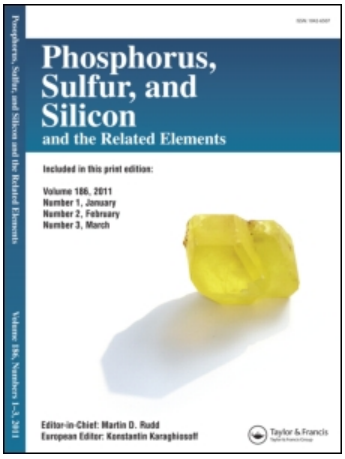

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Ring-Opening Metathesis Polymerization Approach to Phosphorus-Containing Biooligomers

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RING-OPENING METATHESIS POLYMERIZATION APPROACH TO PHOSPHORUS-CONTAINING BIOOLIGOMERS

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Naturally occurring biopolymers (peptides, oligonucleotides, and proteins) are, in theory, excellent drug candidates. However, their poor bioavailability profiles limit their use as potential therapeutic agents. In order to address this problem, the synthesis of diverse polymers consisting of *unnatural* subunits has emerged as a powerful means of constructing new scaffolds with potentially useful pharmaceutical properties. This approach has recently been applied in the synthesis of peptidosulfonamides,[1] cyclic urea scaffolds,[2] peptide nucleic acid-based (PNA) pseudopeptides,[3,4] ethoxyformacetal oligomers,[5] pyrrolin-4-one-based motifs as mimics of peptidal β-strands,[6] and peptidomimetic oligomers with a phosphodiester backbone.[7]

Ring-opening metathesis polymerization (ROMP) strategies using the Grubbs benzylidene catalyst to an array of functionalized biopolymers containing phosphorus and sulfur are discussed. The synthesis of phosphorus and sulfur containing biooligomers utilizing maleimide-based monomers has been developed. Subsequent polymerizations were carried out with various monomer:catalyst ratios and the obtained biooligomers were characterized by MALDI-TOF analysis. A strategy employing both ring-closing metathesis (RCM) reactions and ROMP reactions to derive oligomeric sulfonamides as novel peptidomimetics has also been developed. In addition, our efforts toward the synthesis of cationic, amphiphilic polymers will be presented. These phosphonium contaning polymers show an intriguing reactivity difference between the first generation and second generation Grubbs metathesis catalysts.

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