

Towards Sequence Controlled Polymer Synthesis

Subhajit Pal

In this thesis we have described new synthetic methodologies towards sequence control and telechelic polymer synthesis. Highly functional polyolefins and aramids were synthesized with an excellent microstructure control. In ROMP polymerization, a huge barrier of one-pot living heterotelechelic polymer synthesis has been overcome. We have successfully developed enyne-based prefunctionalization agents which are capable of functionalizing commercial **G3** and **G1** catalysts under very mild conditions. Methoxy, bromo, triisopropylsiloxy and substituted alkylidene were synthesized from both **G3** and **G1** with an excellent yield. Heterotelechelic polymers were obtained by initiating the polymerization with the functionalized initiator followed by functional termination.

After successful heterotelechelic polymer synthesis under mild reaction conditions, we considered the synthesis of sequence-controlled polymers. One of the simplest sequence-controlled polymers is an alternating copolymer. We have successfully addressed a new synthetic protocol for the synthesis of telechelic polymer with an excellent microstructure control under catalytic conditions. A copolymerization of an equivalent mixture of oxanorbornene derivatives and cyclooctene or cyclooctadiene with **G2** resulted in the alternating copolymer. The lower steric bulk of the synthesized copolymer backbone than the corresponding polynorbornene derivative allows efficient secondary metathesis; thus, in the presence of CTAs telechelic alternating copolymers were obtained under catalytic conditions. This unique method allows the controlled incorporation of highly functional oxanorbornene derivatives into a telechelic polymer under thermodynamic equilibration conditions.

Although a high degree of alternation was obtained in the previous polymerization protocol, it was far from a perfectly alternating copolymer synthesis. To improve the degree of alternation, bridgehead substituted 7-oxanorborneneimide derivatives (bONB) were considered due to their slower propagation kinetics compared to non-bridgehead substituted 7-oxanorbornenes. For the first time we have reported the faster reactivity of *endo*-oxanorbornene derivatives than the corresponding *exo*-oxanorbornene derivatives. Exploiting the *endo*-oxanorbornene derivatives several single addition monomers to **G3** were explored. Inability toward the homopolymerization of *endo*-, *exo*- mixture of oxanorbornene derivative gives access to strictly alternating copolymer synthesis when copolymerized with sterically less hindered cycloalkenes. A single addition monomer containing an activated acrylate was also designed for mono end-functionalization of ROMP polymer. Aliphatic thiol and alcohol end functional groups were successfully installed at the chain end of a single addition monomer capped ROMP polymer through thiol-ene click reaction.

We have also developed a living chain-growth polycondensation protocol for sequence-controlled polymer synthesis. Aromatic amino acids were chosen as monomers due to the rigid structure of polyaromatic amides and the possibilities of secondary interactions (like H-bonding, aromatic-aromatic interactions), which are beneficial for secondary and tertiary structure formation. Two chlorophosphonium iodide reagents were developed for ultra-fast in-situ acid chloride formation in the presence of an aromatic amine. In the presence of the phosphine reagent, para-aminobenzoic acids were polymerized in a living chain-growth manner from an amine initiator. Other aryl amino acids and well-defined oligomers were also polymerized in a living chain-growth fashion when monomers were added slowly to the phosphine salt and amine initiator mixture. Exceptionally mild reaction conditions allowed the synthesis of chain end-functional and backbone functional polymers. Diblock and triblock copolymers were also synthesized with narrow dispersity and good molecular weight control. Homo polymers and a diblock copolymer of Kevlar® forming poly para-phenylene terephthalamide analogous polymers were also synthesized under chain-growth conditions. Finally, conformationally stable hydrophobic and hydrophilic aromatic tubular helices were also synthesized under living chain-growth conditions. AFM and CD analysis of the synthesized polymer confirmed the helical nature of the polymers.

Jury:

Prof. Dr. Andreas F. M. Kilbinger (thesis supervisor)

Prof. Dr. Frederik R. Wurm, University of Twente (external co-examiner)

Prof. Dr. Christoph Weder, Adolphe Merkle Institute (internal co-examiner)

Prof. Dr. Fabio Zobi (president of the jury)