

Inorganic Chemistry/Polymer Chemistry: A success story

The case of coordination polymerization of isocyanates employing half-titanocene complexes

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Abstract

Transition metal complexes have been proven to promote the coordination polymerization of numerous monomers acting either as catalysts or initiators. Recent advances in both Inorganic and Polymer Chemistry have allowed the synthesis of macromolecular structures with controlled molecular characteristics, stereochemistry and complex architectures. In this specific study coordination polymerization techniques were employed using the half-titanocene complex $[(\eta^5\text{-C}_5\text{H}_5)((S)\text{-2-Bu-O})\text{TiCl}_2]$ as initiator for the synthesis of statistical and block copolymers of *n*-hexyl isocyanate, HIC, with 2-chloroethyl isocyanate, ClEtIC, 2-phenylethyl isocyanate, PEIC, and 3-(triethoxysilyl)propyl isocyanate, TESPI. In addition, statistical and block copolymers of *n*-dodecyl isocyanate and allyl isocyanate were also synthesized via the same polymerization methodology. The copolymers were characterized by NMR and IR spectroscopy, Size Exclusion Chromatography, SEC, and circular dichroism, while their thermal properties were investigated through Differential Scanning Calorimetry, DSC, and Thermogravimetric Analysis, TGA. In the case of the statistical copolymers the monomer reactivity ratios were calculated employing various graphical methods, as well as the COPOINT program, in the frame of the terminal copolymerization model. Structural parameters, such as the dyad monomer sequences and the mean sequence lengths were investigated as well. The kinetics of thermal degradation of the statistical copolymers was studied, and the activation energies of thermal decomposition were examined through the Kissinger, Ozawa-Flynn-Wall, OFW and Kissinger-Akahira-Sunose, KAS approaches. The block copolymers were synthesized by sequential addition of monomers. SEC, IR and NMR measurements confirmed the synthesis of well-defined products. The copolymers containing allyl isocyanate units were employed as scaffolds to conduct thiol-ene click reactions leading to functionalized polymers or more complex macromolecular architectures.