"Synthesis of Star-Shaped Poly(n-hexyl isocyanate) Homopolymers via Coordination Polymerization and Core-First Methodology Using Multi-Functional (Half-)titanocene Alkoxy Complexes "

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In this work, the synthesis and characterization of star-shaped poly(n-hexyl isocyanate), PHIC, homopolymers with three, four, six, and eight arms are presented. The polymers were synthesized via the core-first methodology, utilizing tri-, tetra-, hexa-, and octa-functional (half-)titanocene alkoxy complexes as coordination polymerization multifunctional initiators. These complexes served as the cores, from which the PHIC chains were grown, leading to the formation of star-shaped structures with precise arm numbers.

A significant challenge in this work was the synthesis of the multi-functional (half-)titanocene alkoxy complexes, as severe solubility issues emerged between the ligands and the primary complex [$(\eta^5\text{-}C_5H_5)TiCl_3$]. Overcoming these solubility problems between these various ligands and the primary complex required extensive optimization of the experimental parameters, making the synthesis of the initiators particularly demanding.

The resulting star-shaped PHIC homopolymers were thoroughly characterized using various techniques. Size exclusion chromatography (SEC), was employed for the study of their molecular characteristics, NMR spectroscopy to verify their star-structure as well as the composition of the (half-)titanocene alkoxy complexes, thermogravimetric analysis (TGA) in order to study their thermal degradation behavior and stability. Additionally, viscosity measurements were performed to determine the intrinsic viscosity of the polymers. This information, in combination with the weight average molecular weight of the star homopolymers from static light scattering (SLS) measurements, provided valuable data leading to the calculation of the number of branches of the star-shaped polymers.

This study demonstrates the successful application of the core-first methodology using (half-)titanocene alkoxy complexes via coordination polymerization to synthesize well-defined star-shaped PHIC homopolymers, highlighting their potential for advanced materials with tunable properties.

References:

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