Synthesis of star-shaped poly(n-hexyl isocyanate) homopolymers via coordination polymerization and core-first methodology using half-titanocene alkoxy complexes

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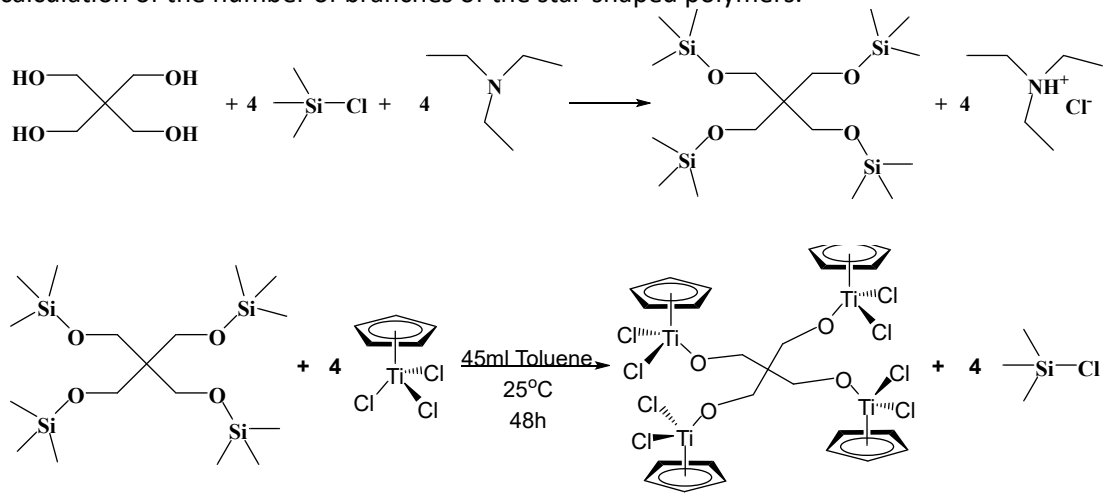
In this work, the synthesis and characterization of star-shaped poly(n-hexyl isocyanate), PHIC, homopolymers with three, four, six, and eight arms are presented. The polymers were synthesized via the core-first methodology, utilizing tri-, tetra-, hexa-, and octa-functional half-titanocene alkoxy complexes 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. The following scheme shows the synthesis of the tetra-functional half-titanocene complex employed for the preparation of the 4-arm PHIC stars. A significant challenge 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 purity of the half-titanocene alkoxy complexes. Additionally, viscosity measurements were performed to determine the intrinsic viscosity of the polymers. This information, in combination with the 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.



Scheme. Synthesis of the tetra-functional half-titanocene complex employed for the preparation of 4-arm PHIC stars

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