

Synthesis and characterization of statistical and block copolymers comprising of allyl- and dodecyl-isocyanate via titanocene-mediated coordination polymerization as scaffolds for complex macromolecular architectures.

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This study is focused on the synthesis and characterization of novel statistical and block copolymers consisting of allyl isocyanate (ALIC) and dodecyl isocyanate (DDIC) via coordination polymerization. In particular, the chiral half-titanocene complex $[C_pTiCl_2(O-(S)-2-Bu)]$ was selected as the initiator in order to induce optical activity in the synthesized polymers. The statistical copolymerizations were conducted in five distinct monomer feed ratios, with the conversion intentionally maintained at a low level to facilitate the calculation of the reactivity ratios using a variety of linear graphical methods, along with the COPOINT computational program. In addition to the P(ALIC-co-DDIC) and P(ALIC-b-DDIC) copolymers, the corresponding homopolymers PALIC and PDDIC were also synthesized and subjected to a comprehensive analysis of their thermal stability and the kinetics of thermal degradation. For this purpose, thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were employed within the framework of Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) isoconversional methods. Finally, the ALIC-based polymers were employed as scaffolds for the preparation of functional polyisocyanates via a thiol-ene click reaction with thiophenol, exploiting the presence of the double bonds at the side groups. The products of the click reaction were subjected to the same thermal analysis, which revealed that the introduction of aromatic rings into the polymer structure resulted in enhanced thermal stability.

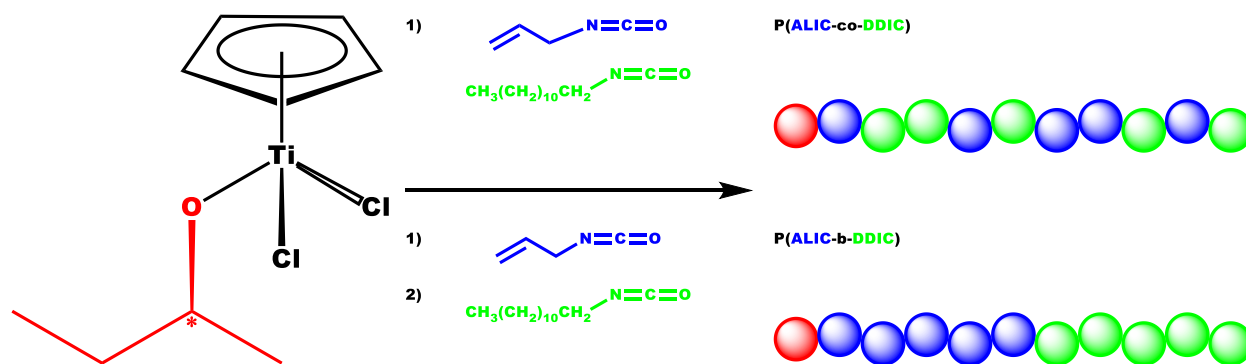


Figure 1: Synthesis of P(ALIC-co-DDIC) and P(ALIC-b-DDIC) via coordination polymerization.

References:

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- [2] I. Choinopoulos, S. Koinis, M. Pitsikalis. J. Polym. Sci. Part A: Polym. Chem. 55:6 (2017) 1102-1112.