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High Transparent Alternate Copolymer of Norbornene with Isoprene Catalyzed by Bis(phenoxy-imine) Titanium Complex

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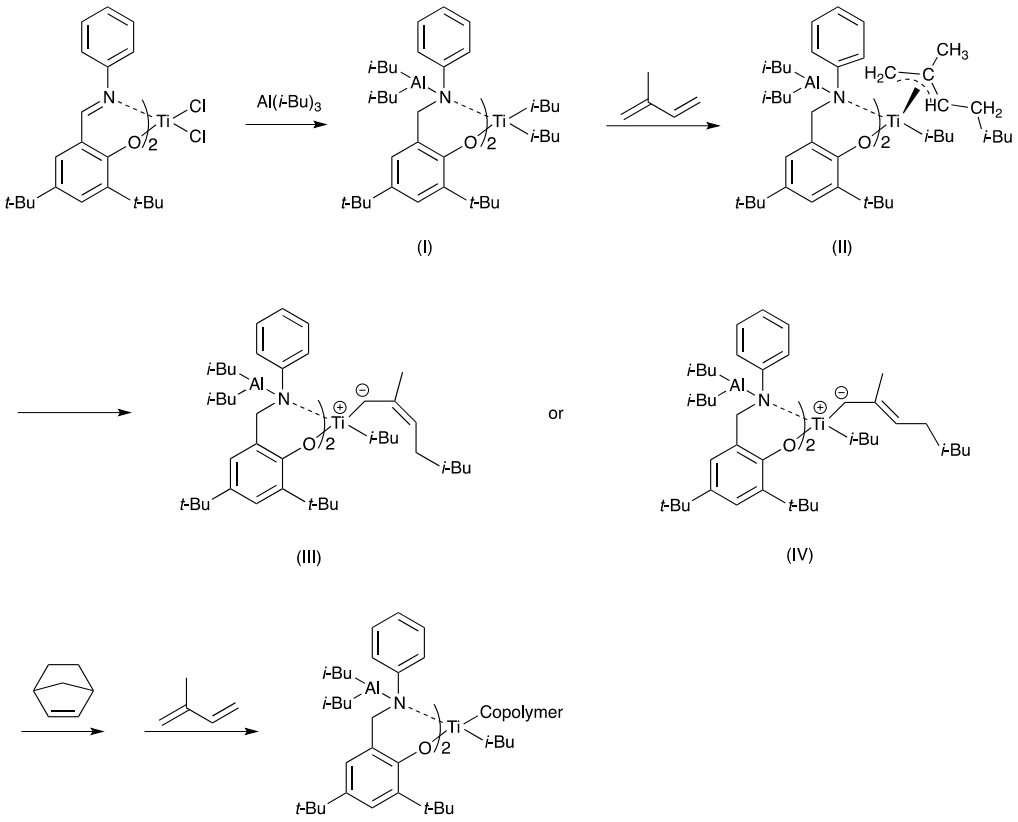

Figure S1: The plausible mechanism for the alternative copolymerization of norbornene with isoprene.

The bis(phenoxy-imine) titanium complex reacts with Al(*i*-Bu)$_3$ generated a phenoxyamine complex in Figure S1(I) as reported [1]. This amine nitrogen with an alkylaluminum group is a weak donor, and provides a weak N-Ti interaction and the phenoxyimine complex potentially possesses higher electrophilicity at the Ti center. Therefor, phenoxyamine complex (I) can not catalyze the polymerization. Normally, one of the i-Bu groups in (I) is abstracted by Lewis acid such as MAO or $Ph_3CB(C_6F_5)_4$ as an anion, and the resulting cationic Ti(IV) species was considered for the active species of coordination polymerization [1]. In this study, MAO or $Ph_3CB(C_6F_5)_4$ dose not needed for the formation of active species, thus another pathway might be considered as reported [2]. Isoprene coordinate on the central Ti atom to form the intermediate III, the insertion of isoprene to the bond between Ti center and *i*-Bu group might produce the π-allyl anion (III) or (VI) and Ti(VI) cation. In general, the copolymer chain growth from π-allyl intermediate (III) or (VI), and the steric hindrance decided insertion order of the two

monomers, leading to an alternative copolymer. The coordination model of isoprene monomer decided the cis-1,4 or trans-1,4 structure of isoprene unit.

Reference

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