High Transparent Alternate Copolymer of Norbornene with Isoprene

Catalyzed by Bis(phenoxo-imine) Titanium Complex

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

The bis(phenoxo-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. Therefore, 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