

# Polymer Chemistry

June 25-27, 2018 | Stockholm, Sweden

## Spin-dependent effects in ethylene polymerization with late-transition-metal complexes

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The general concept of spin-dependent ethylene polymerization by iron, cobalt, nickel and by chromium catalysts is developed. The role of the triplet excited state of the monomer in combination with the high spin state of the catalyst is stressed in the process of ethylene activation. The main rate-determining step in ethylene polymerization is the monomer insertion into the metal-alkyl bond; this is bond making process accompanied by bond cleavage. Catalysis of such simultaneous rearrangements can be treated by a general scheme of spin-uncoupling. The applicability of the spin-catalysis concept to the Brookhart-Gibson catalytic scheme is described by main example of the bis(imino)pyridine-Fe(II) complexes. The role of the axial-equatorial isomerization in spin-catalysis of Brookhart-Gibson type is explained in connection with the main mechanistic problem of ethylene catalytic polymerization-competition between chain propagation and  $\beta$ -hydrogen atom transfer (BHAT) termination. Considering the low-steric bulk model of the bis(imino)pyridine Fe(II) complexes (without bulky substituents in all ortho-positions of aryl rings on imino-nitrogen) the spin-orbit coupling (SOC) matrix elements are calculated at the minimum energy crossing point between triplet and singlet state during the reaction isomerization path. Calculations of SOC matrix element are performed with various approximations in order to illustrate the main qualitative spin-selection rules which govern the singlet-triplet intersystem crossing (ISC) process. Account of main prominent features of electronic orbital configurations and their abrupt change upon T $\rightarrow$ S transition in the course of isomerization made it possible to obtain reliable conclusion on competitive and spin-selective ISC process in Brookhart-Gibson catalysis. A special accent is made for clear explanation for chemists of this complicated quantum physical mechanism never used before in such polymerization. It is shown for the first time that the triplet-singlet ISC is crucial for enhancement of chain termination process via "equatorial-axial" isomerization at the alkyl-ethylene  $\pi$ -complex stage followed by  $\beta$ -hydrogen atom transfer in catalysis by Brookhart-Gibson type iron complexes. A similar analysis is applied for cyclopentadienyl complex of chromium(III) catalyst. External magnetic field effect on BHAT and chain termination yield in ethylene polymerization is predicted on the ground of strong spin selectivity in the ISC process.

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