

Abstract

A Combined Density Functional

Theory and Molecular Mechanics (QM/MM) Study of Chain Termination Catalyzed by $[(C_6H_5N=CH)C_4H_3N]_2^- RM^+$ { M = Ti, Zr } in the Presence of the Counterion, $CH_3B(C_6F_5)_3^-$

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Titanium complexes with two pyrrolide imine chelate ligands, $[(C_6H_5N=CH)C_4H_3N]_2^- TiCl_2$ { R = C₆H₅, C₆H₁₀ }, have been experimentally prepared¹ and, upon activation by cocatalysts, found to produce active polymerization catalysts. The possibility of chain termination during ethylene polymerization by such catalysts systems was considered, in a theoretical investigation using density functional theory. The system investigated was $[(C_6F_5N=CH)C_4H_3N]_2^- C_3H_7Ti-□-CH_3-B(C_6F_5)_3$. Chain termination by (i) hydrogen transfer from the propyl chain to the ethylene monomer complexed to the metal centre and (ii) transfer of □-hydrogen from the propyl chain to the metal were considered. For (i), the barrier to uptake of the monomer leading to the □ complexation, and the subsequent hydrogen transfer barrier were calculated. For (ii), the barrier to transfer of □-hydrogen from chain to metal was calculated and furthermore, the possibility of reorganization of the ionpair system was considered, for the shift of the cocatalyst, $B(C_6F_5)_3$, from the bridging CH₃ group to the extracted □hydrogen. The effect of increasing steric bulk on the ancillary ligands on the termination barriers was also investigated. A validated QM/MM model was used to represent the counterion, $B(C_6F_5)_3CH_3^-$. Solvation effects were incorporated using the Conductor Like Screening Model.

¹Yoshida, Y.; Matsui, S.; Takagi, Y; Mitani, M.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Fujita, T. *Chem. Lett.* **2000**, 1270.