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Theoretical Studies on the Insertion Reaction of Polar Olefinic Monomers Mediated by a Scandium Complex

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Abstract: This study aimed to investigate the insertion reaction of the polar monomers mediated by the cationic rare earth metal complex $[(C_5H_5)Sc(NMe_2CH_2C_6H_4-o)]^+$ utilizing a combination of density functional theory (DFT) calculations and multivariate linear regression (MLR) methods. The chain initiation step of the insertion reaction could be described by the poisoning effect and the ease of monomer insertion, which could be represented via the DFT-calculated energy difference between σ - and π -coordination complexes ($\Delta\Delta E$) and insertion energy barrier ($\Delta G^\ddagger$), respectively. The results indicate that $\Delta\Delta E$ and $\Delta G^\ddagger$ can be predicted by only several descriptors using multiple linear regression methods, with a root mean squared error (RMSE) of less than 2.5 kcal/mol. Furthermore, the qualitative analysis of the MLR models provided effective information on the key factors governing the insertion reaction chain initiation.

Keywords: rare earth metal complex; density functional theory; multivariate linear regression



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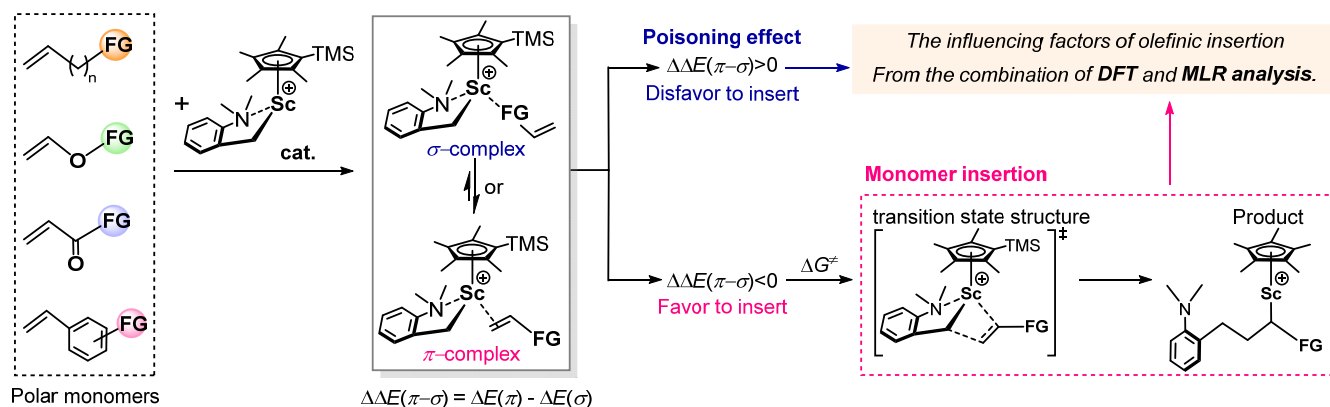
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1. Introduction

The polymers synthesized via the insertion reactions of polar monomers demonstrate excellent surface properties, solvent resistance, and adhesion [1–5]. Consequently, these reactions are critically important and have attracted significant research interest [6–14]. Research indicates that rare earth metal complexes display remarkable chain initiation and stereoselectivity in these reactions, particularly with functionalized styrene monomers, functionalized α,ω -dienes, and allyl methacrylate, among other polar monomers [15–21]. Regarding the extensively researched insertion reaction of polar monomers, it encounters specific challenges due to the simultaneous presence of C=C bonds and polar functional groups. These groups can heteroatomically coordinate with monomers, potentially poisoning the Lewis-acidic metal centers within the complexes. Currently, in the research on polar monomer insertion reaction, a significant amount of successful experimental work has been carried out. Hou et al. [22–26] demonstrated that cationic half-sandwich rare earth metal aminobenzyl complexes are highly effective in catalyzing the insertion reactions of halogenated or amino-containing styrene monomers. Cui et al. [27–31] developed constrained-geometry-configuration rare-earth metal complexes that effectively catalyze the insertion reactions of methoxystyrene monomers, ethyl vinyl ether, and other polar monomers, showing high catalytic activity and stereoselectivity. Currently, the impact of ligands on the yield, activity, and selectivity of organometallic catalysts has gradually been studied, and the selection of relevant descriptors has also been gradually introduced [32–35]. However, compared with the abundant experimental data, systematic studies on the microfactors affecting the poison effects and insertion energy barriers of various polar monomers catalyzed by rare-earth metals, incorporating DFT calculations and MLR, remain scarce [23,36–41].

Our group [42,43] has sequentially investigated both the homopolymerization of ethylene and its copolymerization with polar monomers using palladium and nickel complexes. The results suggest that the geometric parameters and electron occupancies function as molecular descriptors, effectively explaining the factors influencing the chain initiation of ethylene homopolymerization and copolymerization with polar monomers.

To expand upon our previous research, we conducted a thorough investigation into the chain initiation of insertion behavior of various polar monomers, including halogenated monomers, ether and ketone monomers, and polar styrene monomers. This analysis employed a half-sandwich scandium aminobenzyl complex to determine the factors influencing the chain initiation of polar monomer insertion (Scheme 1). The chain initiation of these polar monomers in insertion reactions is influenced by both the poisoning effect and the ease of monomer insertion. These effects can be quantified by the energy differences between π -complex and σ -complex ($\Delta\Delta E(\pi-\sigma)$) and the insertion barriers of the monomers ($\Delta G^\ddagger$), respectively. We performed DFT calculations and multiple linear regression analysis (MLR) on both $\Delta\Delta E(\pi-\sigma)$ and $\Delta G^\ddagger$ to evaluate their impacts on the chain initiation of the insertion reactions.



Scheme 1. Insertion reaction and poisoning effect mechanism of polar monomers mediated by rare-earth metal complex.

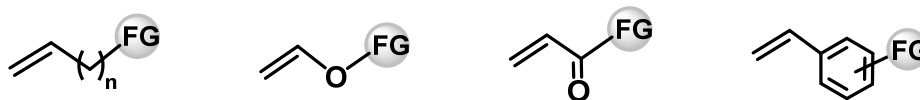
2. Results and Discussion

To systematically explore the factors influencing the chain initiation of polar monomer insertion, this study examined 45 different polar monomers, as illustrated in Figure 1. Initially, the energies of the σ -complexes and π -complexes formed by these monomers coordinating with the active species were calculated, as shown in the SI named poisoning effect.xyz. When $\Delta\Delta E(\pi-\sigma) > 0$, heteroatom coordination is favored, suggesting a potential poisoning tendency for the scandium complex. Using DFT, the coordination energies for each polar monomer were calculated. It was observed that certain polar monomers tend to form stable σ -complexes with metal centers. The lower energy of these σ -complex structures results in a larger $\Delta\Delta E(\pi-\sigma)$, signifying a strong poisoning effect from these monomers.

The poisoning abilities of the aforementioned 45 monomers were calculated, and the calculated results are shown in Table S1. The results revealed that monomers of type ester polar monomers and methylene-spaced polar monomers in groups 1–15 exhibited stronger poisoning capabilities toward the metal center, while those of type functionalized styrene monomers showed weaker poisoning abilities. To further investigate the reasons behind the poisoning effects, we developed a multivariate linear regression (MLR) model for the 15 polar monomers (1–15) that exhibited higher $\Delta\Delta E(\pi-\sigma)$ values. The structures of these monomers are illustrated in Figure S1. It was crucial to select appropriate steric and electronic descriptors to establish a linear relationship model via MLR. Initially, we considered the electronic effects of C=C bonds and heteroatoms coordinating with the metal center and calculated the NPA charge (Q_X , $Q_{C\alpha}$, $Q_{C\beta}$), NMR chemical shifts (NMR_X , $NMR_{C\alpha}$, $NMR_{C\beta}$), and the frontier orbital energies of the monomer (LUMO, HOMO)

descriptors using Gaussian 16 program. Subsequently, we addressed the steric effects arising from various substituents in polar monomers, selecting sterimol parameters using the molecular modeling pro software (B_1 , B_5 , L). B_1 and B_5 are the minimal and maximal dimensions perpendicular to the ligand length, respectively, and L is the ligand length. The bond lengths ($C_\alpha=C_\beta$, $C_\beta-R$) and bond angle ($C_\alpha-C_\beta-R$) were retrieved using Gaussian as descriptors. Consequently, 15 potentially relevant descriptors were chosen based on DFT-optimized monomer structures, as shown in Figure 2. The values of these descriptors, along with $\Delta\Delta E(\pi-\sigma)$, are compiled in Tables S1 and S2.

(a) Various types of polar monomers



(b) 45 sets polar monomers

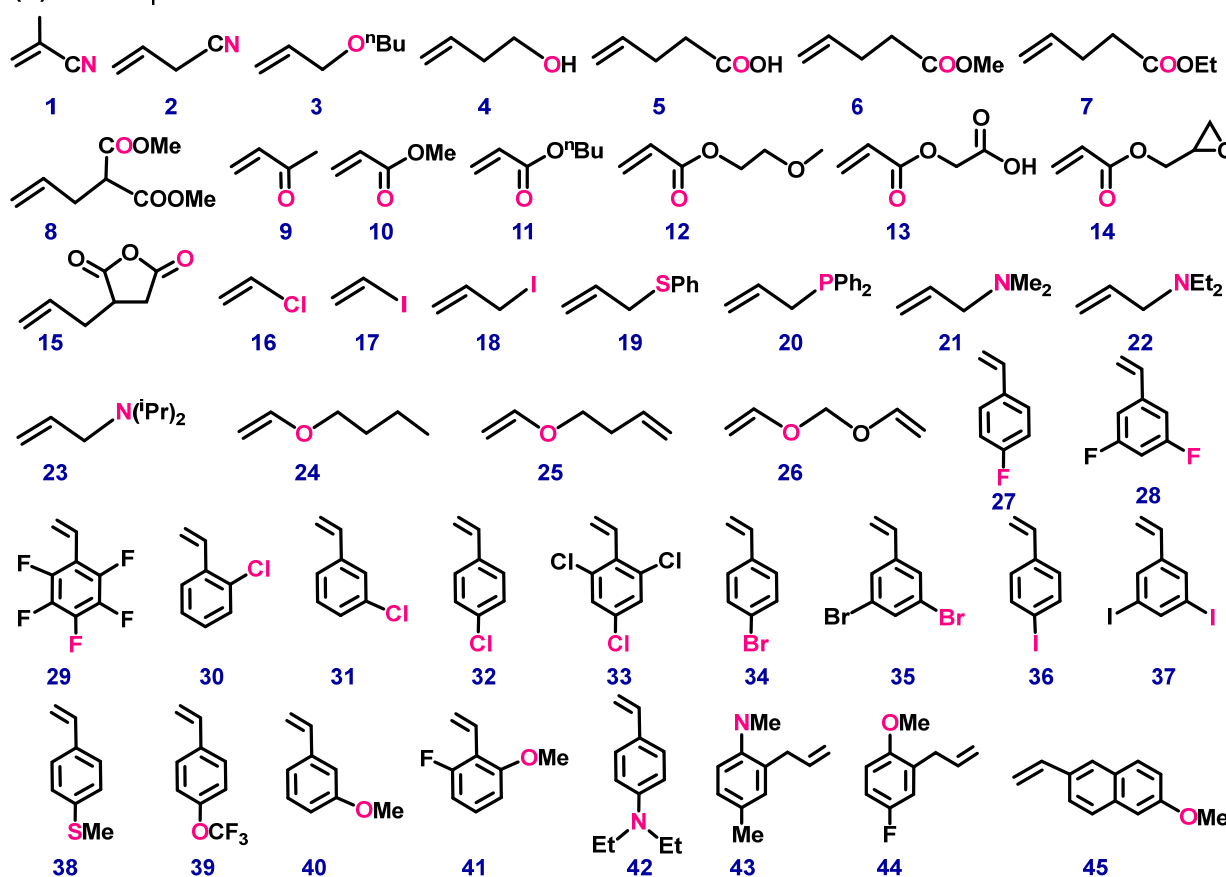


Figure 1. Several different polar monomer structures. The heteroatoms coordinated to the metal center in the polar monomer are marked in pink.

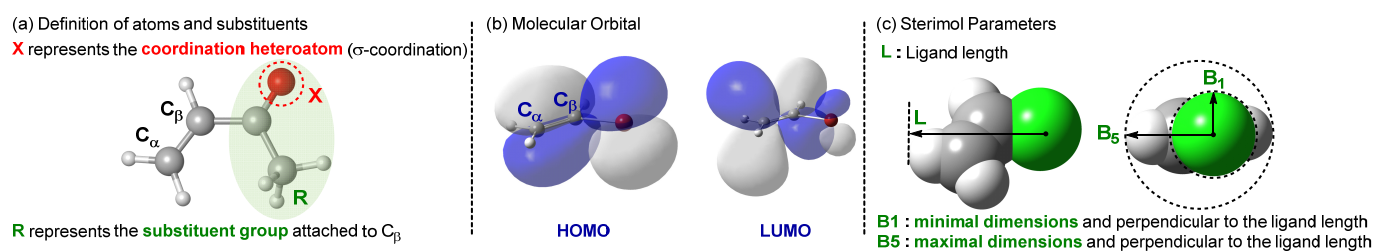


Figure 2. The definition of atoms and substituents, along with schematic representation of descriptors.

Further univariate correlation analysis was performed on data from polar monomers to examine the relationship between individual descriptors and $\Delta\Delta E(\pi-\sigma)$. The correlations were visualized using Matlab software, resulting in a correlation color map, as displayed in Figure 3. The numerical values within each colored block within the map show the Pearson correlation coefficient between the descriptors and $\Delta\Delta E(\pi-\sigma)$, as well as among the descriptors themselves. The strength of the correlation is represented by the absolute value of the correlation coefficient ($|R|$), ranging from 0 to 1, where values closer to 1 indicate stronger correlations. The last line of data specifically highlights the correlation between $\Delta\Delta E(\pi-\sigma)$ and various descriptors. The analysis identified that the three descriptors most strongly correlated with $\Delta\Delta E(\pi-\sigma)$ were $Q_{C\alpha}$ ($|R| = 0.74$), $NMR_{C\beta}$ ($|R| = 0.76$), and L ($|R| = 0.74$). Given that the maximum univariate correlation between the descriptors and $\Delta\Delta E(\pi-\sigma)$ reached only 0.76, further multivariate linear regression analyses were subsequently conducted.

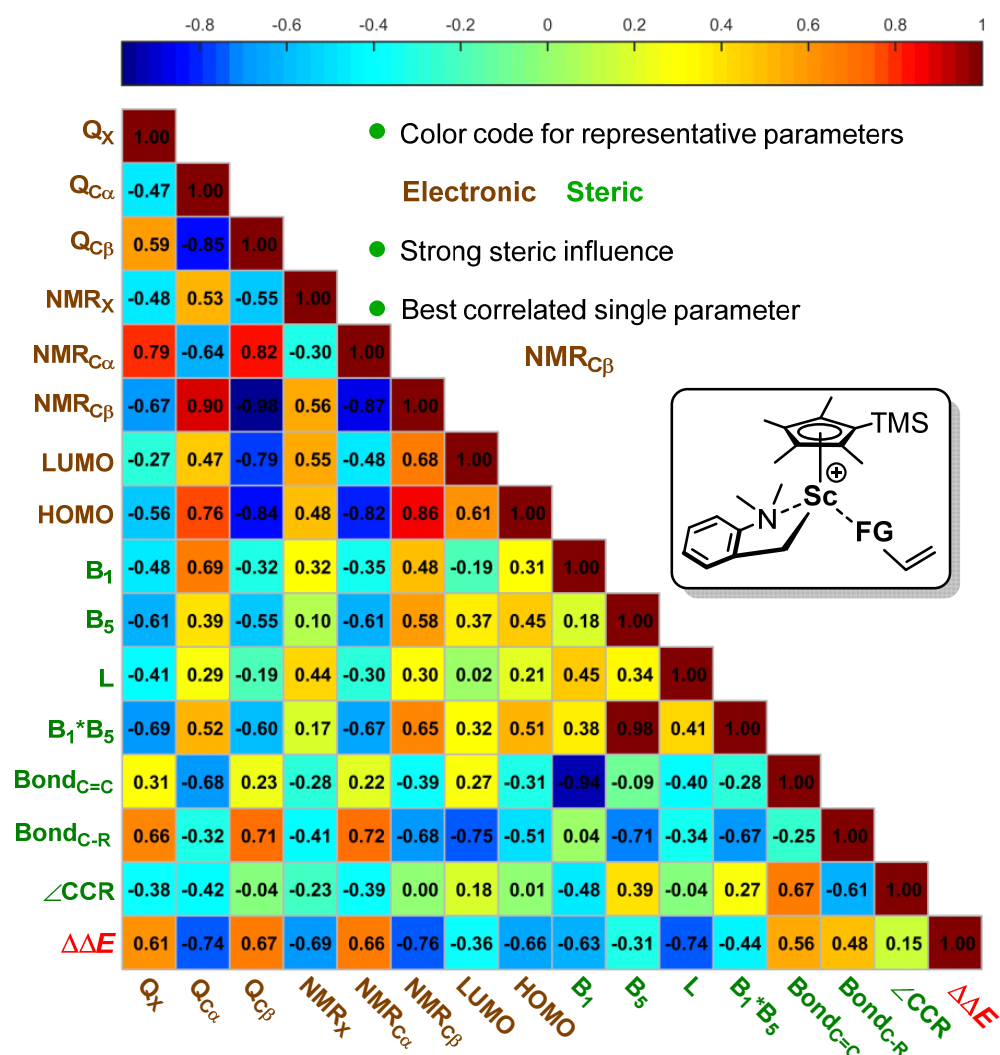


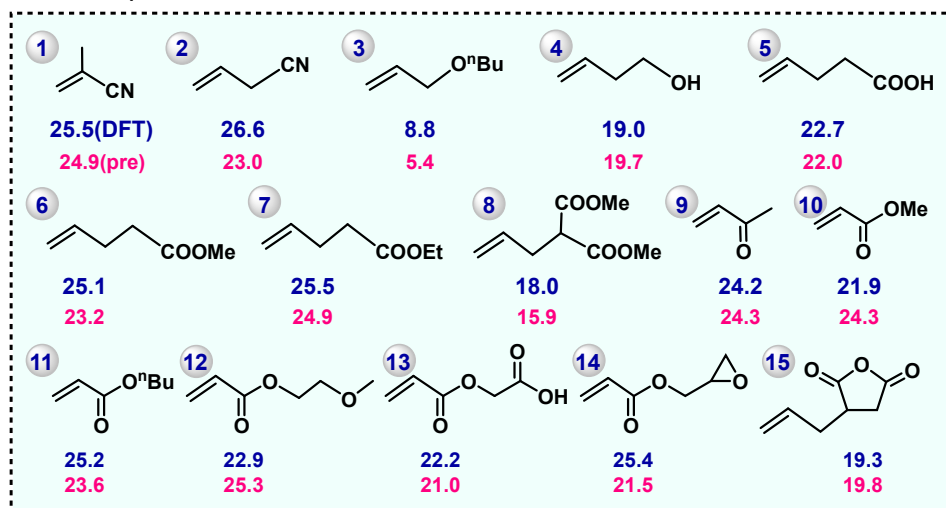
Figure 3. Correlation color map: the last line corresponds to the single-parameter correlations of the $\Delta\Delta E(\pi-\sigma)$.

Prior to model training, the values of the selected descriptors were normalized. Subsequently, descriptors were defined as independent variables and $\Delta\Delta E(\pi-\sigma)$ as the dependent variable. Stepwise regression analysis was employed to eliminate irrelevant descriptors and to construct a multivariate linear regression model, as illustrated in Figure 4. In stepwise regression analysis, the p -value is usually used to test the independent variables added at each step and to assess the significance of their coefficients. The magnitude of the p -value is

typically used to determine whether to retain the independent variable in the model. The closer the p -value is to 0, the higher the level of significance, indicating that the observed coefficient is statistically significant. According to Figure 4, it is evident that the p -values of descriptors $\text{NMR}_{\text{C}\beta}$, B_5 , and L were 0.000, 0.003, and 0.000, indicating significant influences of these three descriptors on the poisoning effect. Therefore, a multivariate linear regression model based on these variables for $\Delta\Delta E(\pi-\sigma)$ was established. The corresponding equation was constructed as follows:

$$\Delta\Delta E_{\text{pre}} = 27.9 - 21.7\text{NMR}_{\text{C}\beta} + 8.9B_5 - 13.0L \quad (1)$$

(a) 15 sets polar monomer structures



(b) $\Delta\Delta E_{\text{pre}} = 27.9 - 21.7\text{NMR}_{\text{C}\beta} + 8.9B_5 - 13.0L$

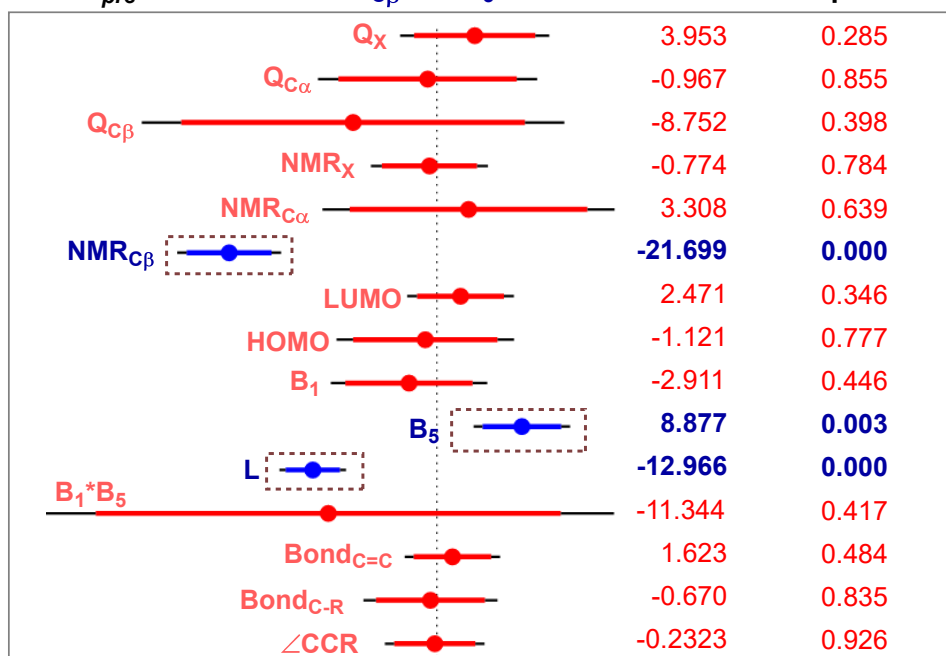


Figure 4. (a) The structures of 15 set polar monomers, along with the blue representing the calculated $\Delta\Delta E(\pi-\sigma)$ and the pink representing the predicted $\Delta\Delta E(\pi-\sigma)_{\text{pre}}$. (b) Analysis of 15 monomer structures using stepwise regression analysis of $\Delta\Delta E(\pi-\sigma)$, including coefficients and p -values. The blue horizontal lines represent the three descriptors with the highest correlation, namely $\text{NMR}_{\text{C}\beta}$, B_5 , and L .

It is important to highlight that these models utilize coefficients to reflect the significance of the descriptors. Positive and negative coefficients indicate positive and negative correlations, respectively. This result suggests that a larger $\text{NMR}_{\text{C}\beta}$ value enhances the coordination capability of the $\text{C}\beta$ atom with the metal center, favoring the formation of stable complexes and consequently resulting in a smaller $\Delta\Delta E(\pi-\sigma)$, indicating a weaker poisoning effect. Similarly, the maximum dimension perpendicular to the ligand length (B_5) shows a positive correlation, while the ligand length (L) shows a negative correlation. This result indicates that as the L increases and, simultaneously, the B_5 decreases, the coordination capacity between the heteroatom and the metal center weakens, thereby reducing the poisoning effect. Furthermore, according to the corresponding equation, the model predicted values $\Delta\Delta E(\pi-\sigma)_{\text{pre}}$ for each monomer could be obtained, as shown in Figure 4a.

To evaluate the model's fitting performance, a correlation fitting was conducted between the DFT-computed $\Delta\Delta E(\pi-\sigma)$ values and the model-predicted values, as depicted in Figure 5a. This analysis demonstrated a high coefficient of determination ($R^2 = 0.88$), indicating the model's robust performance. Additionally, with Root Mean Square Deviation (RMSE) and Mean Absolute Error (MAE) values of 1.63 kcal/mol and 1.94 kcal/mol, respectively, the model proves to be relatively stable. To further minimize the risk of overfitting, a fivefold cross-validation was performed, as illustrated in Figure 5b, resulting in an R^2 of 0.86, with RMSE = 2.50 kcal/mol and MAE = 2.11 kcal/mol, confirming that the model does not exhibit overfitting.

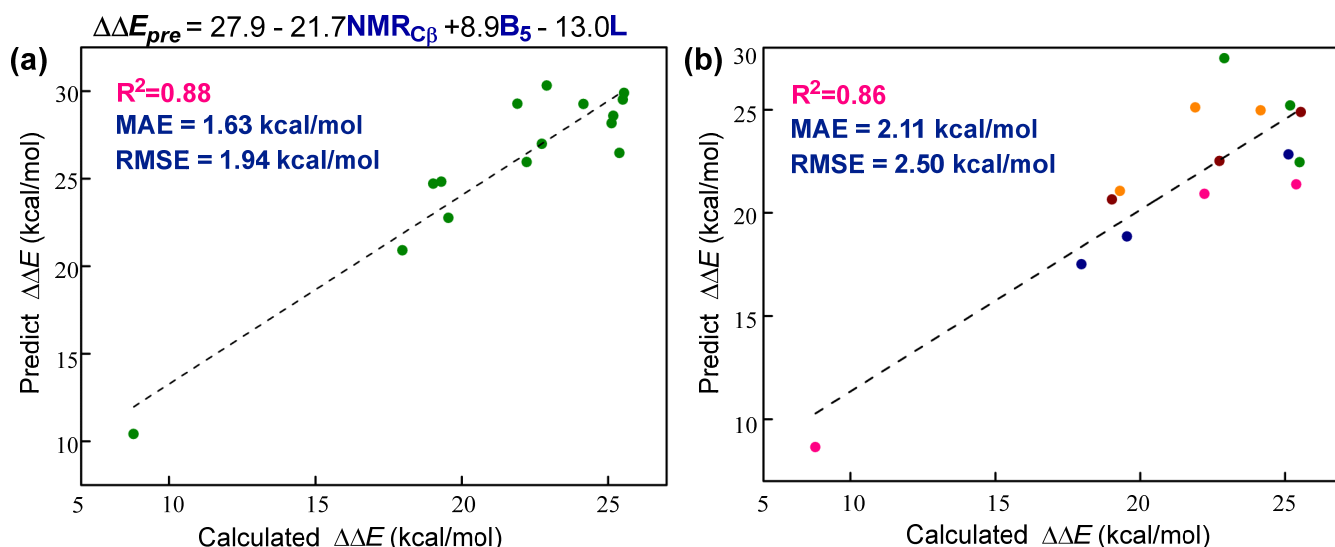


Figure 5. (a) Plot of computed vs. predicted $\Delta\Delta E(\pi-\sigma)$ using the multivariate linear regression model. (b) Linear fitting plot for fivefold cross-validation method.

To assess the extrapolation capability of the model, external data sources distinct from the initial data sets were employed for comparison and validation, as depicted in Figure 6. Five polar monomers (Figure 6a), labeled as **1'**–**5'** and not included in the initial training set, were selected for this external validation, and the parameter values for the three descriptors were compiled in Table S3. As shown in Figure 6b, the model demonstrated robust performance on these monomers, with an R^2 of 0.91, an RMSE of 1.89 kcal/mol, and an MAE of 2.22 kcal/mol, indicating strong extrapolation capabilities.

After validating the stability of our model through various means, we can conclude that the poisoning ability of polar monomers increases as their NMR and L become more negative and B_5 becomes more positive. Therefore, in future polymerization processes involving polar monomers, the poisoning capability of monomers toward metal centers can be roughly estimated by testing only these few variables.

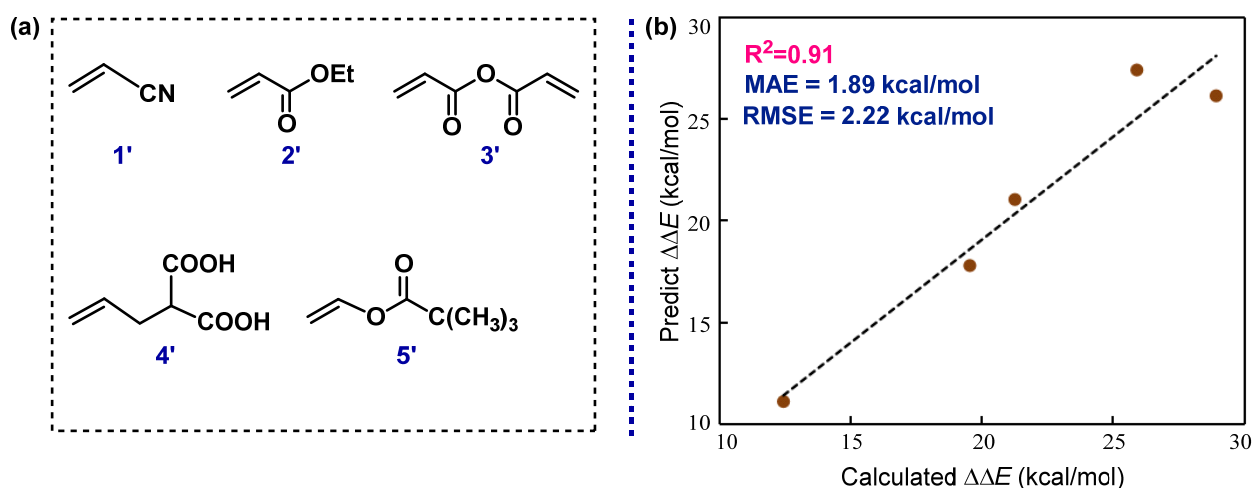


Figure 6. (a) Five polar monomers for external verification. (b) Plot of computed vs. predicted $\Delta\Delta E(\pi-\sigma)$ for external verification.

While certain polar monomers may poison the metal center in insertion reactions, other polar monomers are capable of undergoing such reactions without significant disruption. The insertion energy barriers for the remaining 30 monomers (16–45), which demonstrate a weaker poisoning effect, have been computed. The monomer coordinate structures of the four insertion paths are compiled in the SI. The structures of these monomers are depicted in Figure S2, the calculated results for the insertion barriers are shown in Table S4, and the coordinate structures are organized in the Supporting Information. DFT calculations were performed on various conformations of each coordination complex to ascertain the insertion barriers $\Delta G^\ddagger$ (1,2-*re*, 1,2-*si*, 2,1-*re*, and 2,1-*si*), with the insertion reaction mechanism illustrated in Figure 7a. A higher $\Delta G^\ddagger$ value indicates greater difficulty in initiating the insertion reaction process. For example, monomer No.16, as shown in Figure 7b, had its coordination energy, insertion barriers, and product energy calculated separately for the four insertion pathways. The computational results reveal that among these pathways, the 2,1-*si* pathway exhibits the lowest barrier, at just 8.6 kcal/mol, while the barriers for the remaining pathways are 15.0 kcal/mol, 12.3 kcal/mol, and 18.1 kcal/mol, respectively. This highlights that, from a kinetic perspective, the 2,1-*si* pathway is the most favorable for monomer insertion mediated by the active species.

Analogously, the favorable insertion behaviors of the other 29 polar monomers (17–45) were calculated using DFT, with the results listed in Tables S4 and S5.

Similarly, a stepwise regression analysis was conducted on these 30 monomers based on their $\Delta G^\ddagger$ values and the previously selected 15 descriptors through multivariate linear regression (MLR) analysis, resulting in Equation (2).

$$\Delta G^\ddagger_{pre} = 6.55 + 4.4Q_\alpha + 6.8NMR_{C_\beta} + 7.3HOMO \quad (2)$$

As depicted in Equation (2) and Figure 8a, the multivariate linear regression model identified the top three descriptors with the highest positive correlations: Q_{C_α} , NMR_{C_β} , and HOMO. The HOMO descriptor emerged as the most influential in the model, indicating that a higher HOMO energy value increases the monomer's susceptibility to electron loss. Additionally, increases in Q_{C_α} and NMR_{C_β} strengthen the coordination ability between the $C_\alpha=C_\beta$ bond and the metal center. The combined influence of these descriptors leads to a decrease in the energy of the π -complex, thereby increasing the insertion energy barrier for the monomer. Subsequent linear fitting demonstrated a robust correlation between the predicted and calculated $\Delta G^\ddagger$ values across the 30 datasets, as shown in Figure 7b, confirming a satisfactory correlation with an R^2 of 0.87, an RMSE of 0.96 kcal/mol, and an MAE of 0.80 kcal/mol.

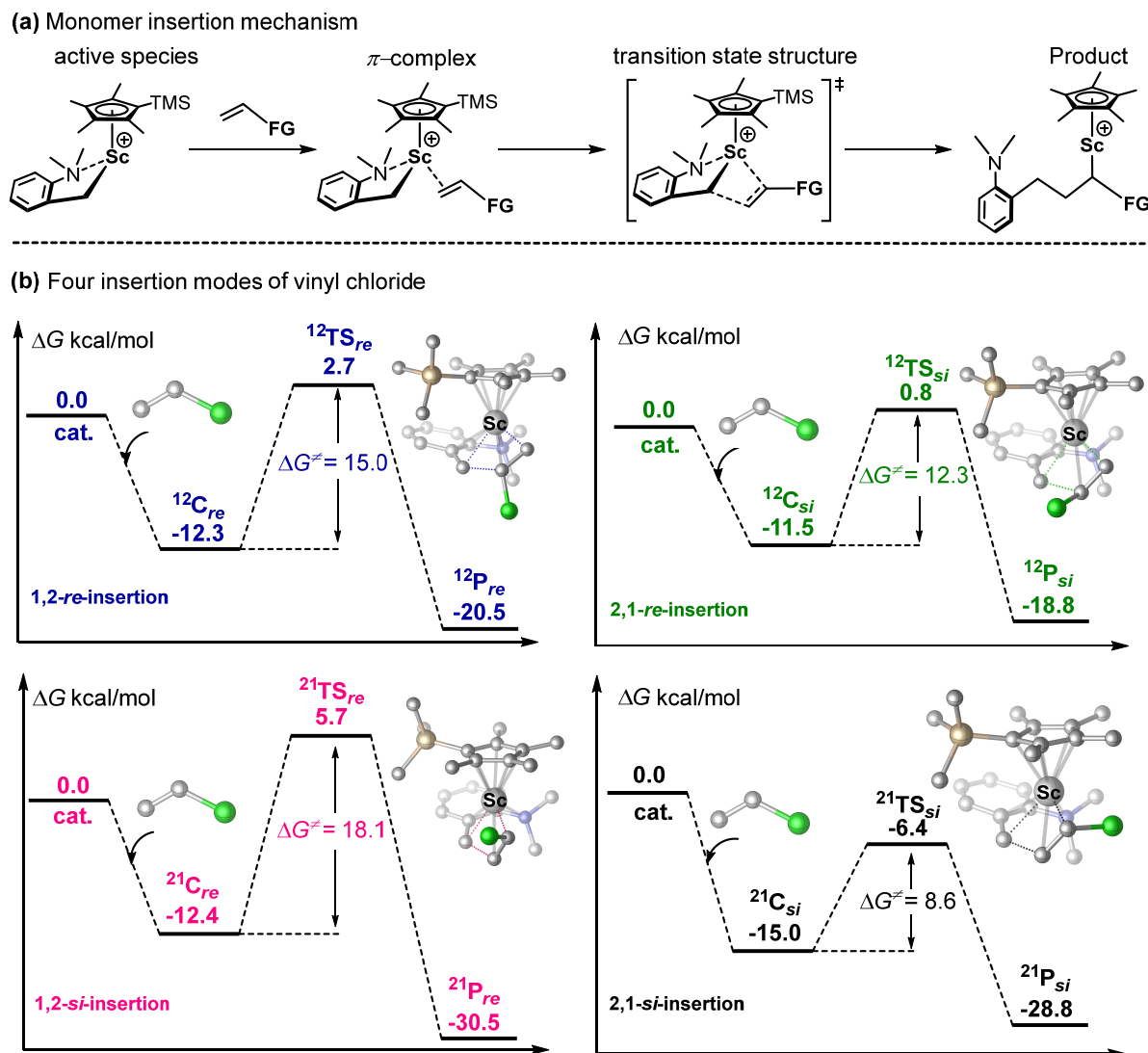


Figure 7. (a) Mechanism of the monomer insertion. (b) Computed energy profiles for rare-earth metal complex mediated various insertion manners of vinyl chloride (energies in kcal/mol).

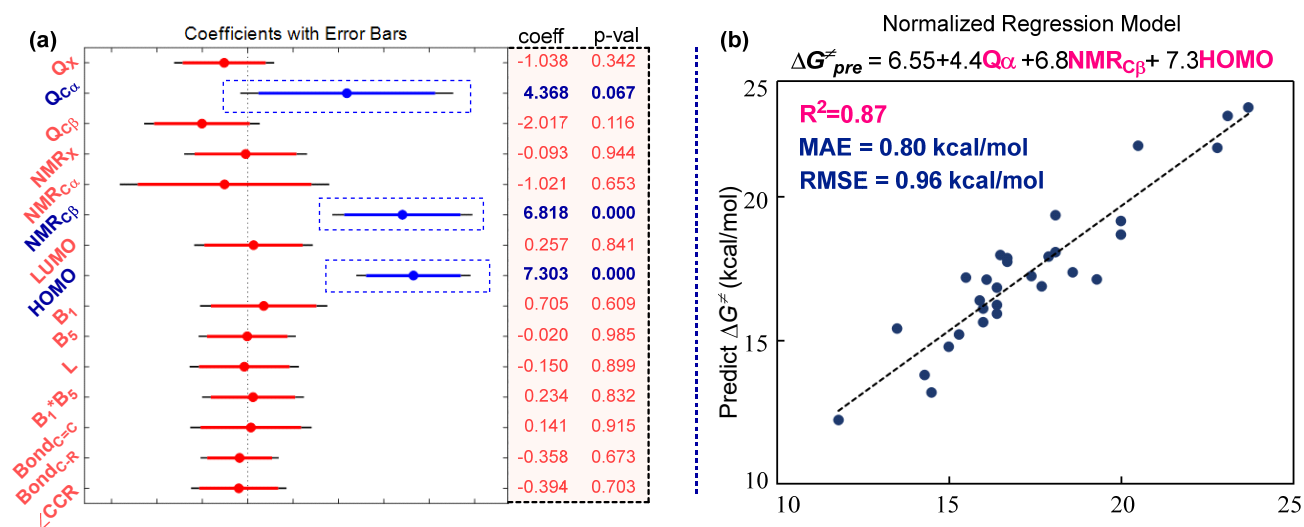


Figure 8. (a) Application of stepwise regression analysis of $\Delta G^\ddagger$. (b) Plot of computed vs. predicted $\Delta G^\ddagger$ for external verification.

We also conducted a fivefold cross-validation, as shown in Figure 9a, which resulted in an R^2 of 0.82, with an RMSE of 1.17 kcal/mol and an MAE of 0.95 kcal/mol. This indicates that the model is robust and not subject to overfitting. Furthermore, to assess the model's extrapolation capabilities, we selected an additional set of 10 monomers (6'–15'), as depicted in Figure 9b,c. The parameter values for the descriptors are summarized in Table S6. Notably, the model exhibited an impressive R^2 of 0.88, along with an RMSE of 1.36 kcal/mol and an MAE of 1.22 kcal/mol, thereby confirming its strong extrapolation ability. These theoretical analyses provide further validation for the model's rationale, reinforcing the reliability of the constructed multiple linear regression equation.

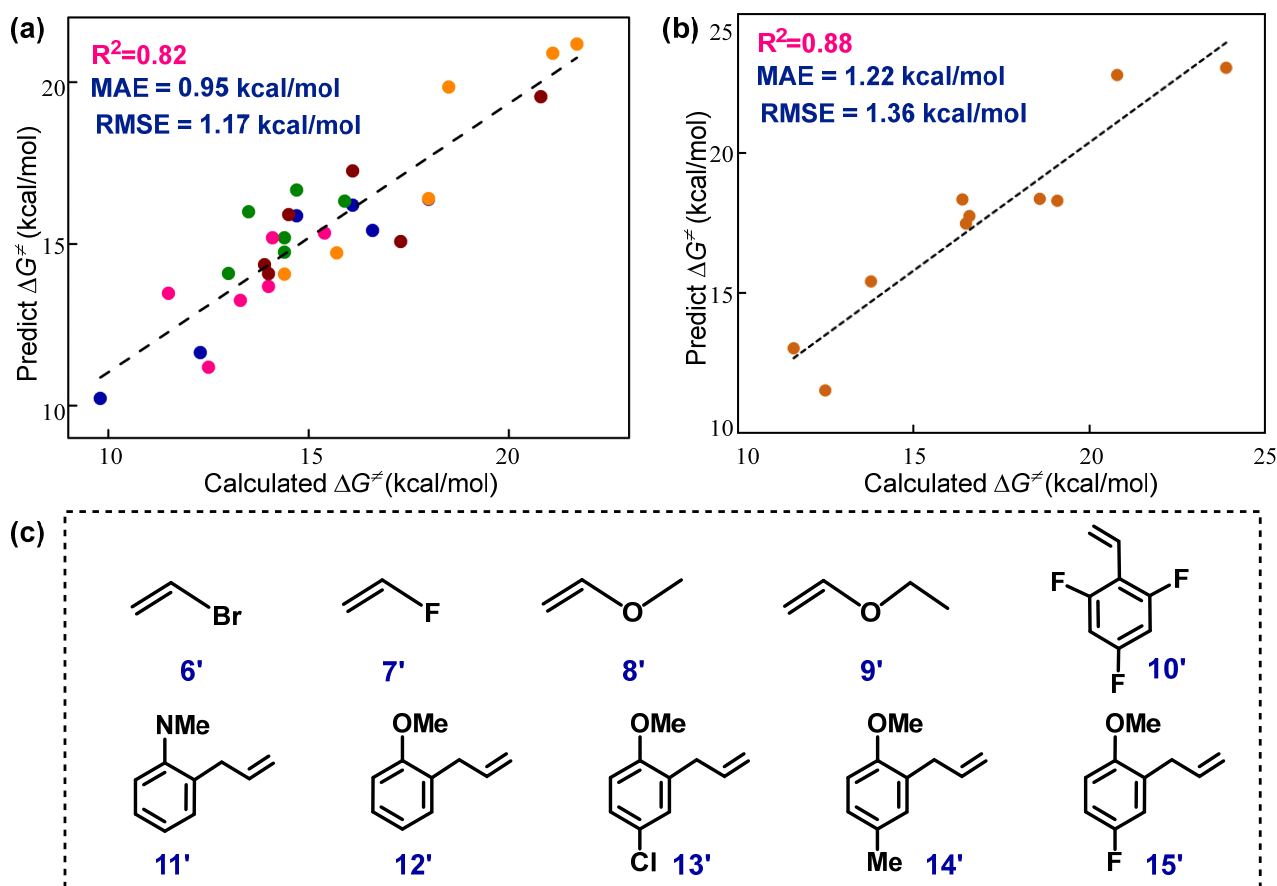


Figure 9. (a) Linear fitting plot for fivefold cross-validation method. (b) Plot of computed vs. predicted $\Delta G^\ddagger$ for external verification. (c) Ten polar monomers for external verification.

After confirming the stability of our model through a variety of methods, we can infer that the insertion energy barrier for chain initiation of polar monomers escalates as their $Q_{C\alpha}$, $NMR_{C\beta}$, and HOMO increases. Consequently, in the forthcoming insertion reaction incorporating polar monomers, the insertion energy barrier for chain initiation toward metal centers can be approximately gauged by examining these select variables.

3. Computational Details

All DFT computations were carried out utilizing the Gaussian 16 software package [44]. All geometry optimizations and frequency calculations were performed using the B3LYP functional [45–47], which includes the D3 version of Grimme's empirical dispersion correction [48,49]. The SDD basis set [50–52] was applied for Sc, and the 6-31G(d) basis set was used for nonmetal atoms. To achieve more accurate relative energies, single-point energies were calculated using the M06 functional [53] in combination with a larger basis set (SDD basis set for Sc and 6-311+G (d, p) for the remaining atoms) and the PCM model [54], which was used to account for the solvation effect of toluene. The generation of correlation color

maps and the execution of multivariate linear regression analysis were carried out using Matlab software [55]. Furthermore, sterimol parameters were computed on the basis of optimized structures by using the Molecular Modeling Pro software [56].

4. Conclusions

In summary, we employed a combined strategy of DFT calculations and multivariate linear regression (MLR) analysis to investigate the chain initiation of polar monomer insertion reaction mediated by a scandium complex. The poisoning effect and the ease of insertion of polar monomer, which is concerned with insertion reaction chain initiation, have been investigated, and the MLR models were constructed, respectively. It was found that the electronic descriptors NMR of C_β (NMR_{C_β}) and steric descriptors sterimol parameters B_5 and L play an important role in the poisoning effect. In the case of the ease of monomer insertion described by the insertion energy barrier, it was observed that electronic descriptors NPA charge of C_α (Q_{C_α}), NMR of C_β (NMR_{C_β}), and frontier orbital energy (HOMO) jointly played a role, while the impact of steric hindrance was nonsignificant. The external validation results indicate that such predictive models demonstrate a certain degree of extrapolation capability. These results demonstrated that the combination of DFT calculations and MLR analysis could serve as an effective strategy to investigate polar monomer insertion reaction systems mediated by the Sc complex. It is expected that the results will hopefully offer some useful hints for the development of a more efficient rare earth metal complex in the polymerization of polar monomers.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics12060172/s1>, Figure S1: 15 sets polar monomers for the analysis for the poisoning effect ($\Delta\Delta E$). Figure S2. 30 sets polar monomers for the analysis for the ease of monomer insertion ($\Delta G^\ddagger$). Table S1: Electronic descriptors and $\Delta\Delta E$ for 1-15 polar monomers (free energies in kcal/mol). Table S2. Steric descriptors and $\Delta\Delta E$ for 1-15 polar monomers (free energies in kcal/mol). Table S3. Descriptors and $\Delta\Delta E$ for 1'-5' polar monomers (free energies in kcal/mol). Table S4. Electronic descriptors and $\Delta G^\ddagger$ for 16-45 polar monomers (free energies in kcal/mol). Table S5. Steric descriptors and $\Delta G^\ddagger$ for 16-45 polar monomers (free energies in kcal/mol). Table S6. Descriptors and $\Delta G^\ddagger$ for 6'-15' polar monomers (free energies in kcal/mol); Optimized Cartesian coordinates of all stationary points together with their single-point energies (a.u.) in solution and the imaginary frequencies (cm^{-1}) of transition states (XYZ).

Author Contributions: Conceptualization, X.W., G.Z. and Y.L.; Methodology, X.W., G.Z. and Y.L.; Software, K.R.; Formal analysis, K.R.; Investigation, X.W.; Data curation, X.W., G.Z. and Y.L.; Writing—original draft, X.W.; Writing—review & editing, X.W., K.R., W.Z., G.Z. and Y.L.; Supervision, W.Z., G.Z. and Y.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Materials, further inquiries can be directed to the corresponding author/s.

Conflicts of Interest: The authors declare no conflict of interest.

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