

Article

Thermochemical Preference for C–C Bond Scission in an Isotactic Polypropylene Oligomer: A DFT-Based Study

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Abstract

Polypropylene (PP) waste, including microplastic debris, motivates molecular-scale studies of the intrinsic factors governing thermal degradation. In this work, the bond dissociation energies (BDEs) of C–C and C–H bonds were systematically evaluated in a finite isotactic polypropylene oligomer containing fifteen propylene repeat units, $(-C_3H_6-)^{15}$, using Density Functional Theory at the M06-2X/LANL2DZ level. Thermochemical corrections were evaluated at 873.15 K, a temperature relevant to pyrolysis studies. Within the selected oligomer model, C–C bonds exhibited lower BDE values (82.28–87.41 kcal·mol^{−1}) than C–H bonds (90.18–104.93 kcal·mol^{−1}), indicating a thermochemical preference for backbone scission. The lowest calculated BDE values were associated with specific tertiary carbon environments, including sites C24 and C28. A mixed-effects model identified bond type and carbon type as the principal factors associated with BDE variation, while principal component analysis summarized the covariation among the electronic and thermodynamic descriptors. These results provide a molecular-scale description of intrinsic scission tendencies within the selected PP oligomer and establish a basis for subsequent kinetic, catalytic, and experimental studies.

Keywords: polypropylene oligomer; bond dissociation energy; thermal degradation; pyrolysis; density functional theory; multivariate analysis

1. Introduction

The pervasive accumulation of plastic debris in marine and terrestrial ecosystems has become one of the most pressing environmental challenges of the 21st century. Among these pollutants, polypropylene (PP) is one of the most widely used commodity plastics because of its broad deployment in packaging, textiles, and automotive applications [1]. Under environmental weathering, larger plastic items progressively fragment into microplastics, commonly defined as particles smaller than 5 mm, which are now recognized as pervasive contaminants with documented ecological effects and the capacity to interact with co-occurring contaminants [2,3]. Conventional mechanical recycling remains an important strategy, but it is often limited by feedstock heterogeneity, contamination, and progressive deterioration of material properties after repeated processing. For that reason, chemical recycling—especially thermal and catalytic

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pyrolysis—has gained increasing attention as a route to recover value from plastic waste by converting it into fuels and chemical intermediates, including gasoline- and diesel-range hydrocarbons [4,5]. At the molecular level, the performance of pyrolytic conversion depends on the energetics of bond cleavage and radical evolution along the polymer chain. In polypropylene, degradation is strongly influenced by the presence of tertiary carbon sites, from which radical formation can be initiated, thereby conditioning the subsequent scission chemistry and product distribution [6,7]. In this context, computational chemistry has become an essential tool for resolving the elementary steps of plastic pyrolysis, because it enables estimation of bond dissociation energies and thermodynamic trends that are difficult to isolate experimentally [7,8]. Density Functional Theory is particularly useful for this purpose, and the M06-2X functional is frequently selected for systems dominated by main-group thermochemistry, kinetics, and non-covalent effects [9]. Combined with mechanistic modeling of polypropylene pyrolysis and modern intrinsic kinetic studies, these calculations help identify the most labile bonds and rationalize the radical pathways that ultimately control the formation of lighter hydrocarbons and liquid products during recycling [10,11].

In this study, we evaluate the intrinsic bond-dissociation trends of C–C and C–H bonds in a finite isotactic polypropylene oligomer containing fifteen propylene repeat units, $(-C_3H_6-)_n$. The selected oligomer is not intended to reproduce the full physicochemical complexity of environmental PP microplastics. Instead, it provides a computationally tractable molecular model containing terminal and internal carbon environments that can be compared systematically under a common theoretical framework. Thermochemical corrections were evaluated at 873.15 K to examine relative scission tendencies at a pyrolysis-relevant temperature. The analysis focuses on identifying comparatively labile bonds, evaluating the influence of the local carbon environment, and examining statistical associations among the calculated structural, thermodynamic, and electronic descriptors. Accordingly, the results are interpreted as model-level trends that may support subsequent mechanistic studies, rather than as direct predictions of environmental degradation rates, catalytic performance, or pyrolysis-product distributions.

2. Methodology

To examine intrinsic thermochemical trends associated with polypropylene bond dissociation, a finite isotactic oligomer containing fifteen propylene repeat units, $(-C_3H_6-)_n$, was selected as the molecular model. This oligomeric size allows terminal and internal carbon environments to be evaluated within a computationally tractable system. The model is intended to support a comparative analysis of bond lability along an idealized PP chain segment and should not be interpreted as a complete representation of an environmental microplastic particle or of bulk polypropylene. Because a systematic chain-length convergence analysis was not performed, the conclusions are restricted to relative trends obtained within the selected oligomer model [6,11–13].

2.1. Computational Framework and Electronic Structure

All electronic structure calculations were performed using the Gaussian 16 software package. The M06-2X global hybrid meta-GGA functional was employed for geometry optimizations, frequency calculations, and energy evaluations. This functional was selected because it has been developed and extensively assessed for main-group thermochemistry, thermochemical kinetics, and non-covalent interactions [9,10]. These characteristics make it suitable for examining relative bond-dissociation trends and radical stabilization effects in hydrocarbon systems.

Calculations were carried out using the LANL2DZ keyword as implemented in Gaussian 16. For the light atoms present in the C/H-only oligomer model, this implementation relies on all-electron double-zeta functions rather than on an effective-core-potential treatment of carbon and hydrogen. The selected basis should therefore be interpreted as a computationally affordable level for the systematic comparison of a large number of cleavage events within the same oligomeric framework. It is not presented as a basis-set-converged reference method [8,12].

Because a systematic functional and basis-set benchmark was not performed for the complete oligomeric dataset, the calculated bond dissociation energies are discussed primarily in terms of internally consistent relative trends. Additional calculations using larger polarized basis sets are required to quantify the residual basis-set dependence of the reported values.

2.2. Geometry Optimization and Thermodynamic Calculations

The geometry of the intact isotactic polypropylene oligomer, $(-C_3H_6-)_n$, was fully optimized without symmetry constraints. Homolytic bond cleavage events were subsequently evaluated for selected C–H and C–C bonds along the oligomeric chain. For each C–H cleavage event, the corresponding carbon-centered oligomer radical and the hydrogen atom were considered as the dissociation products. For each C–C cleavage event, the oligomer was separated into two carbon-centered radical fragments.

All radical fragments were independently optimized at the same theoretical level used for the intact oligomer. Frequency calculations were performed to verify that the optimized structures corresponded to local minima and to obtain thermochemical corrections. Only structures without imaginary frequencies were considered for the thermochemical analysis [14].

The intact oligomer was treated as a closed-shell singlet. The isolated carbon-centered radicals and the hydrogen atom were treated as open-shell doublet species. Thermochemical quantities, including enthalpy (H), entropy (S), and Gibbs free energy (G), were evaluated at 873.15 K and 1 atm. This temperature was selected as a pyrolysis-relevant reference condition. The calculations describe molecular-level thermochemical trends and do not constitute a reactor-scale simulation of an industrial pyrolysis process [8,9].

2.3. Evaluation of Bond Dissociation Energies

The homolytic bond dissociation enthalpy, hereafter denoted as BDE, was evaluated at 873.15 K using the enthalpies of the optimized reactant and dissociation products.

For each evaluated C–H bond, the BDE was calculated as:

$$BDE_i(C-H) = H(PP_i\bullet) + H(H\bullet) - H(PP-H)$$

where $H(PP_i\bullet)$ is the enthalpy of the carbon-centered oligomer radical generated by cleavage at site i , $H(H\bullet)$ is the enthalpy of the hydrogen atom, and $H(PP-H)$ is the enthalpy of the intact oligomer.

The corresponding Gibbs free energy of reaction was calculated as:

$$\Delta G_{rxn,i}(C-H) = G(PP_i\bullet) + G(H\bullet) - G(PP-H)$$

For each evaluated C–C bond, the BDE was calculated as:

$$BDE_j(C-C) = H(F_j,A\bullet) + H(F_j,B\bullet) - H(PP)$$

where $H(F_j,A\bullet)$ and $H(F_j,B\bullet)$ are the enthalpies of the two carbon-centered radical fragments generated by homolytic cleavage of C–C bond j , and $H(PP)$ is the enthalpy of the intact oligomer.

The corresponding Gibbs free energy of reaction was calculated as:

$$\Delta G_{\text{rxn},j}(\text{C}-\text{C}) = G(\text{F}_j, \text{A}\bullet) + G(\text{F}_j, \text{B}\bullet) - G(\text{PP})$$

The BDE values quantify the enthalpic cost of homolytic bond cleavage, whereas ΔG_{rxn} describes the reaction thermodynamics under the selected reference conditions. Neither quantity corresponds to an activation energy or an activation Gibbs free energy. Because transition states were not calculated, the present analysis does not provide kinetic barriers or reaction-rate constants.

2.4. Electronic Property Analysis

The frontier molecular orbitals, specifically the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were analyzed for the intact oligomer and the optimized radical fragments. The corresponding orbital energies were expressed in electronvolts (eV). The dipole moment was also extracted from each optimized structure.

Global electrophilicity (ω) was included as an electronic descriptor and was calculated from the chemical potential (μ) and global hardness (η) according to:

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$$

$$\omega = \mu^2/(2\eta)$$

These descriptors were used as comparative variables to examine electronic differences among the calculated radical fragments. Their interpretation is restricted to associations within the oligomeric dataset. They should not be considered direct predictors of reaction rates, product distributions, or process efficiency [12].

2.5. Structural and Energy Optimization of the Computational Model

The thermochemical dataset was constructed by evaluating homolytic cleavage events at selected positions along the isotactic polypropylene oligomer. The C–H dataset comprises 45 representative cleavage events, corresponding to the removal of one hydrogen atom from each carbon position along the oligomeric chain. The C–C dataset comprises 28 backbone cleavage events, each corresponding to the homolytic dissociation of a selected C–C bond and the formation of two carbon-centered radical fragments.

Each C–H cleavage event was identified using the label CH-*n*, where *n* denotes the carbon atom from which the hydrogen atom was removed. Each C–C cleavage event was identified using the label CC-*n*, where *n* denotes the evaluated C–C bond. The two radical fragments generated by each C–C cleavage event were distinguished using the suffixes A and B, as follows: CC-*n*-A and CC-*n*-B.

The complete set of optimized structures and their corresponding identifiers is provided in the Supplementary Materials. The main text retains only the representative configurations required to illustrate the structural analysis. The standardized labeling system was applied consistently in the figures, Supplementary Tables S1 and S2, and discussion.

2.6. Statistical Methods

The computational dataset comprised 73 homolytic cleavage events evaluated within the finite isotactic polypropylene oligomer. These observations included 45 representative C–H cleavage events, corresponding to the removal of one hydrogen atom from each carbon position along the oligomeric chain, and 28 C–C backbone cleavage events, each

corresponding to the homolytic dissociation of a selected C–C bond and the formation of two carbon-centered radical fragments. The bond dissociation enthalpy (BDE, kcal·mol^{−1}) was defined as the response variable.

The statistical analysis was designed to determine whether the calculated BDE values were associated with bond type, local carbon environment, and structural position along the oligomeric chain. Bond type was classified as C–H or C–C. Carbon type was classified as CH, CH₂, or CH₃ according to the local environment of the carbon atom associated with each evaluated cleavage event.

For C–H cleavage events, the structural position and carbon type were assigned according to the carbon atom from which the hydrogen atom was removed. Thus, a C–H cleavage event at carbon atom C_n was associated with position *n* and with the corresponding CH, CH₂, or CH₃ environment.

For C–C cleavage events, each dissociation configuration was identified using the notation C_n–C_{n_2}. In this notation, C_n denotes the radical fragment containing *n* carbon atoms, whereas C_{n_2} denotes the complementary radical fragment generated by the same cleavage event. The suffix “_2” is used exclusively to distinguish the second fragment of the radical pair and does not indicate its carbon count. Accordingly, the configuration C_n–C_{n_2} corresponds to cleavage of the C–C bond located between carbon atoms C_n and C_{n+1} in the intact oligomeric chain. For statistical purposes, the cleavage event was assigned to position *n*, and the local carbon environment was defined according to carbon atom C_n, which corresponds to the terminal carbon atom of the first radical fragment.

For example, the configuration C3–C3_2 corresponds to cleavage of the bond between C3 and C4. The first radical fragment contains three carbon atoms and is denoted as C3, whereas the complementary radical fragment is denoted as C3_2. In the statistical dataset, this event was assigned to position 3 and classified according to the local carbon environment of C3.

The oligomeric chain was divided into three structural regions: initial (C1–C15), middle (C16–C30), and final (C31–C45). Each cleavage event was assigned to one of these regions according to its structural position *n*. For C–C cleavage events, the regional assignment was therefore based on the value of *n* in the corresponding C_n–C_{n_2} configuration.

A mixed-effects model was fitted to account for the grouping of cleavage events associated with the same structural position. Position was included as a random-intercept term because C–H and C–C cleavage events may be associated with the same position *n* along the oligomeric chain. Bond type, carbon type, and structural region were included as fixed categorical effects. The Gibbs free energy of reaction (ΔG_{rxn}), HOMO energy, LUMO energy, global electrophilicity (ω), and dipole moment were included as continuous covariates.

The initial model was expressed as:

$$\text{BDE}_{ij} = \beta_0 + \beta_1(\text{Bond type})_{ij} + \beta_2(\text{Carbon type})_{ij} + \beta_3(\text{Structural region})_{ij} + \beta_4(\Delta G_{\text{rxn}})_{ij} + \beta_5(\text{HOMO})_{ij} + \beta_6(\text{LUMO})_{ij} + \beta_7(\omega)_{ij} + \beta_8(\text{Dipole moment})_{ij} + \beta_9(\text{Bond type} \times \text{Carbon type})_{ij} + \beta_{10}(\text{Bond type} \times \text{Structural region})_{ij} + \beta_{11}(\text{Carbon type} \times \text{Structural region})_{ij} + u_j + \varepsilon_{ij}$$

where u_j represents the random intercept associated with structural position *j* and ε_{ij} represents the residual error. The random effects and residual errors were assumed to be normally distributed with mean zero and constant variance.

The mixed-effects model was estimated using restricted maximum likelihood (REML). The statistical significance of the fixed effects was evaluated using the Kenward–Roger degrees-of-freedom approximation. The reference categories were C–H for bond type, CH₃ for carbon type, and the middle region for structural region. Model adequacy

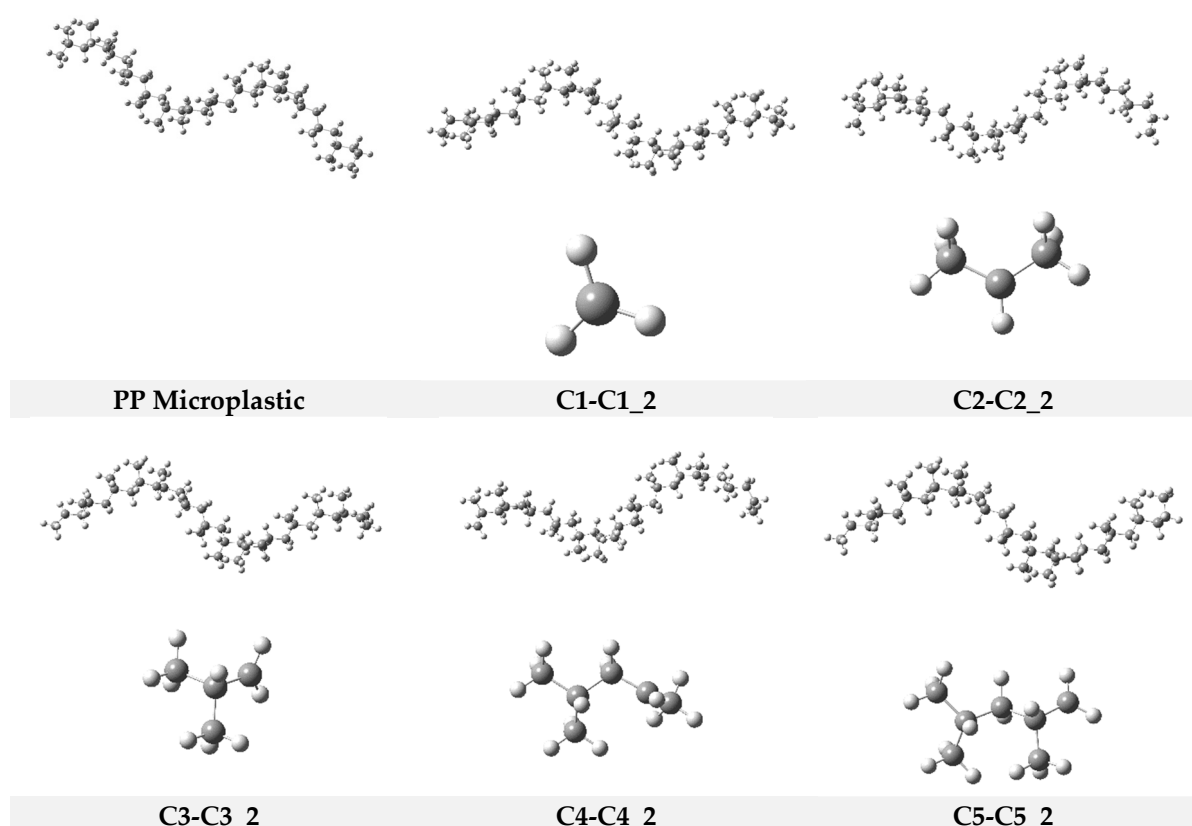
was assessed through residual diagnostics, the residual standard deviation, the variance component associated with Position, and the adjusted coefficient of determination.

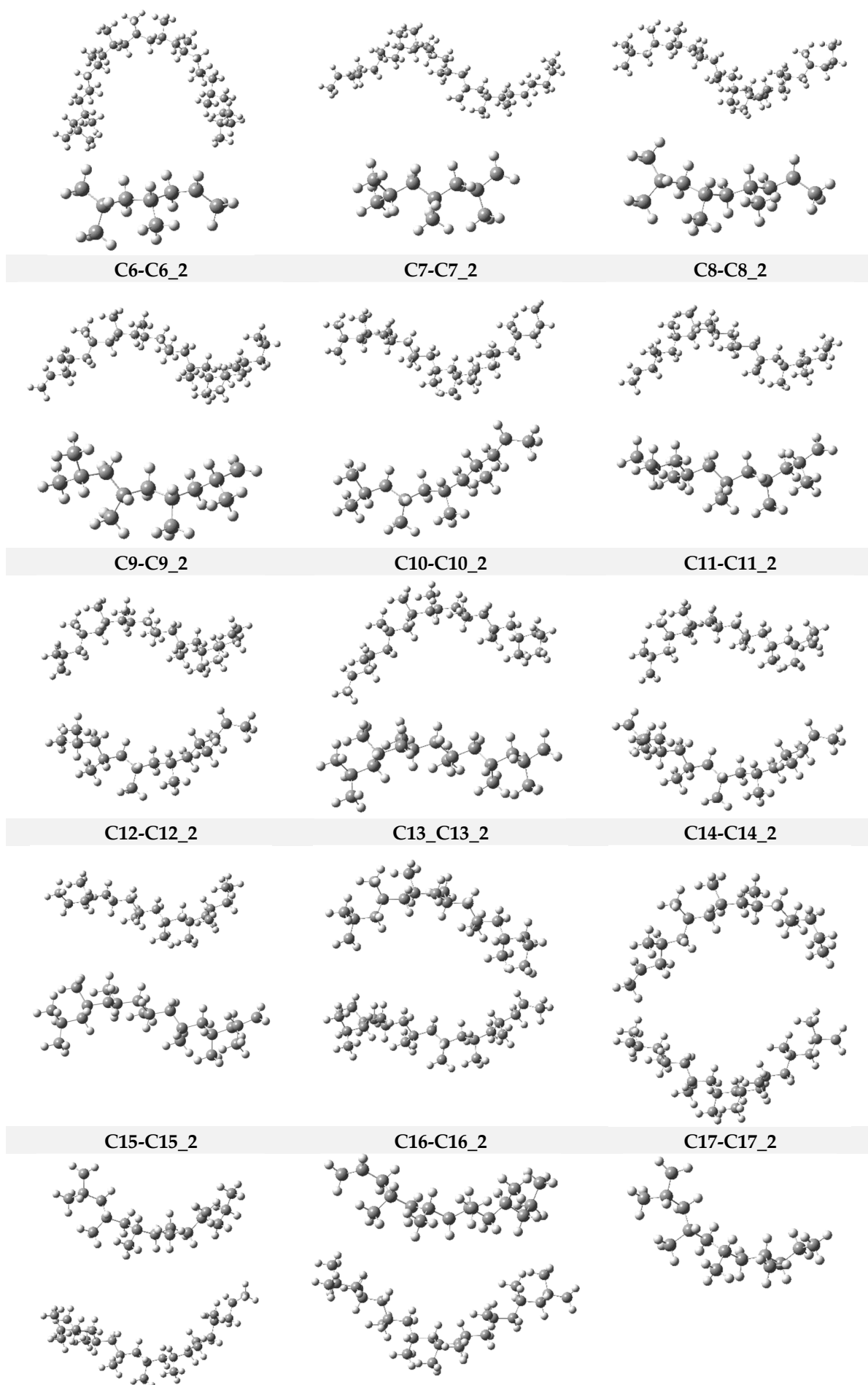
Principal component analysis (PCA) was performed as an exploratory multivariate analysis to summarize covariation among the thermodynamic and electronic descriptors. The variables included in the PCA were ΔG_{rxn} , HOMO energy, LUMO energy, dipole moment, and global electrophilicity. Because these variables were expressed in different units and scales, the PCA was based on the correlation matrix. The loadings and scores were evaluated for the retained principal components. PCA was interpreted as a descriptive tool for identifying patterns of covariation within the computational dataset and not as evidence of causal relationships.

All statistical analyses were performed using Minitab 22. Statistical significance was evaluated using a threshold of $\alpha = 0.05$.

3. DFT Results and Discussion

Figure 1 summarizes the optimized configuration of the intact isotactic polypropylene oligomer and the radical fragment pairs generated by the evaluated C–C bond cleavage events. The dissociated configurations should be interpreted as independently optimized radical products rather than as intermediates along a kinetically resolved reaction pathway. The structural relaxation observed after homolytic cleavage provides a molecular context for comparing the thermochemical susceptibility of different sites along the oligomeric chain. However, the optimized geometries alone do not establish the occurrence of subsequent hydrogen-transfer reactions, β -scission steps, or specific product-formation pathways.





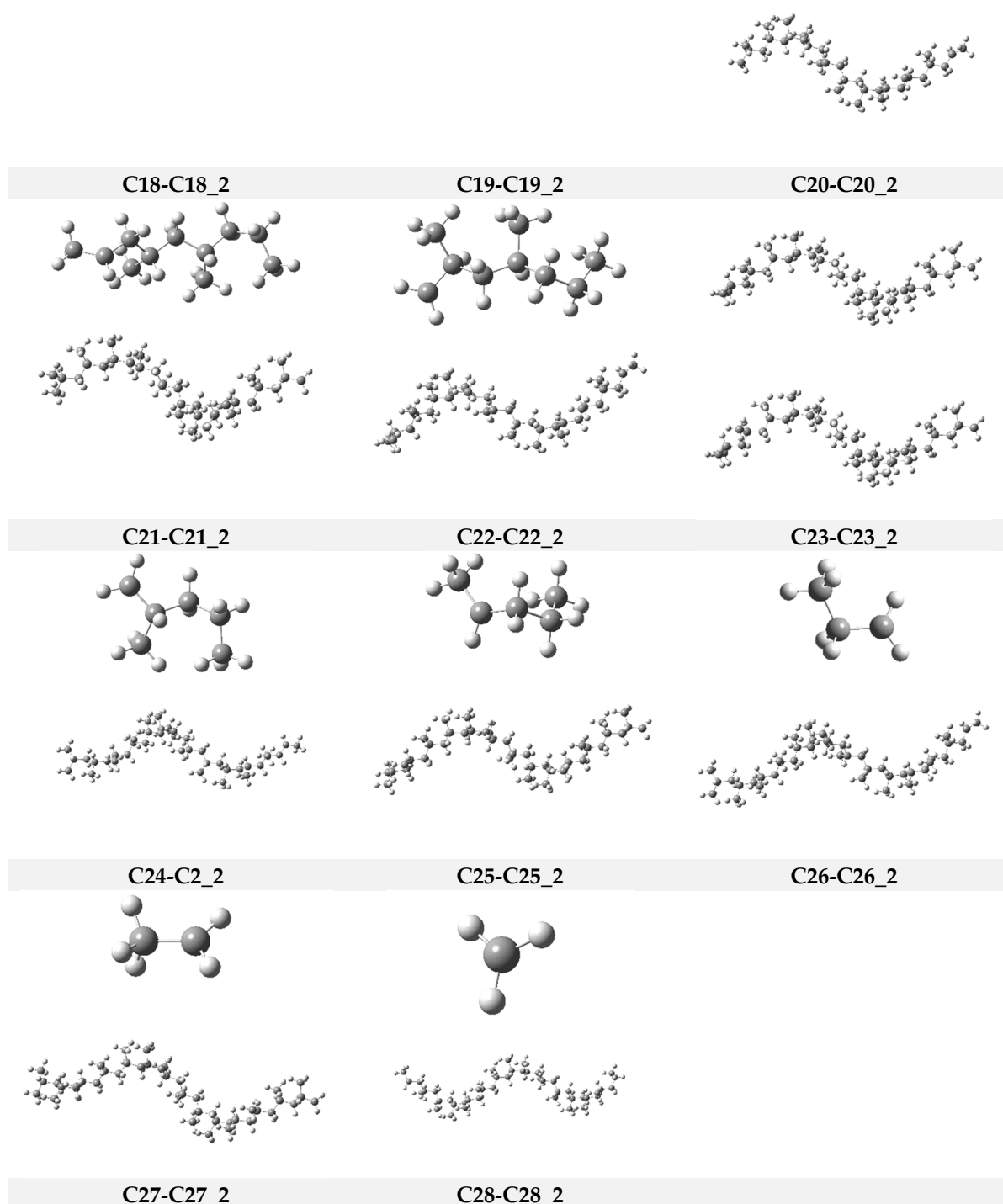


Figure 1. Optimized configurations of the intact isotactic polypropylene oligomer and the radical fragments generated by C-C bond dissociation, calculated at the M06-2X/LANL2DZ level.

3.1. Homolytic C-H Bond Cleavage in the Isotactic Polypropylene Oligomer

The C-H dataset comprises 45 representative homolytic cleavage events, corresponding to the removal of one hydrogen atom from each carbon position along the isotactic polypropylene oligomer. The calculated bond dissociation enthalpies (BDEs) range from 90.18 kcal·mol⁻¹ at C24 to 104.93 kcal·mol⁻¹ at C1 (Figure 2b and Table S1). This variation indicates that the local carbon environment influences the relative thermochemical susceptibility of the evaluated C-H bonds.

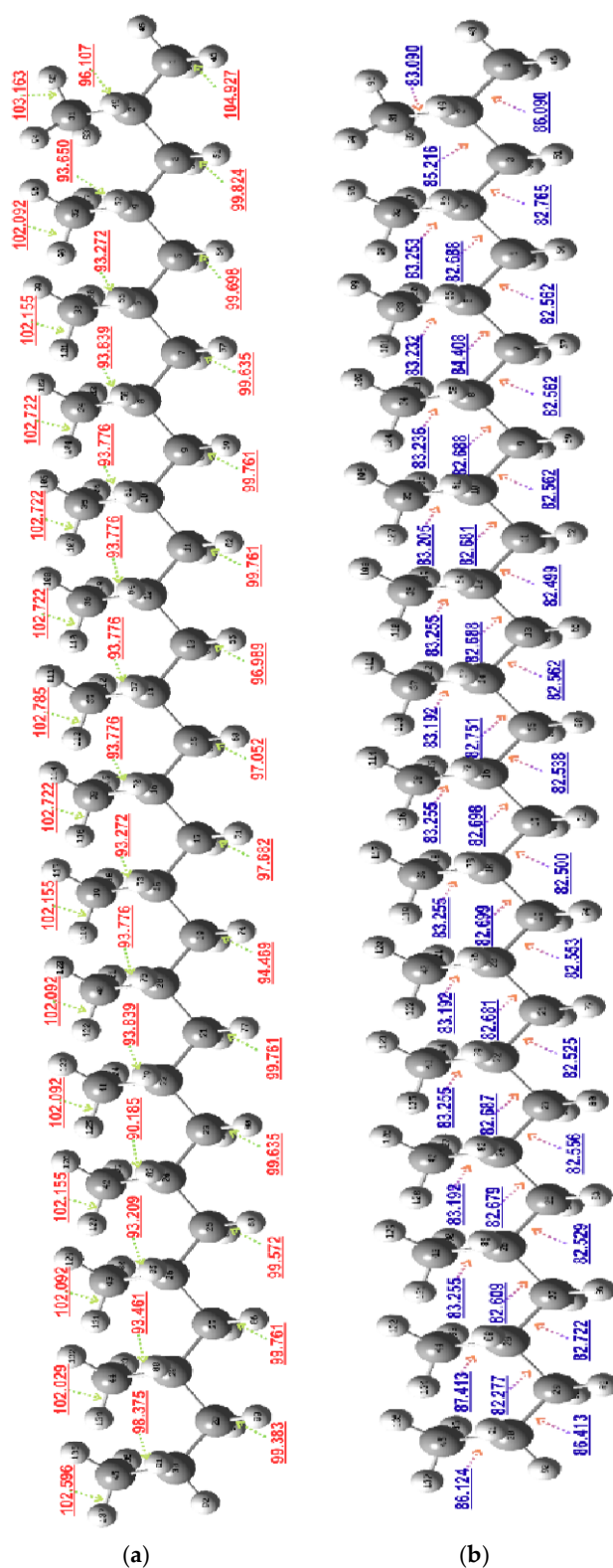


Figure 2. Three-dimensional representation of the isotactic polypropylene oligomer ($C_{45}H_{92}$) optimized at the M06-2X/LANL2DZ level, showing the calculated bond dissociation energies (BDEs, $\text{kcal}\cdot\text{mol}^{-1}$) for C–C (a) and C–H (b) cleavage events.

The thermochemical analysis was conducted at 873.15 K, a temperature relevant to experimental studies of polypropylene pyrolysis [15]. The lowest C–H BDE values were obtained for C24 (90.18 $\text{kcal}\cdot\text{mol}^{-1}$), C26 (93.21 $\text{kcal}\cdot\text{mol}^{-1}$), and C18 (93.27 $\text{kcal}\cdot\text{mol}^{-1}$). These positions correspond to tertiary methine environments within the PP oligomer.

Their comparatively lower BDE values are consistent with the relative stabilization of tertiary carbon-centered radicals through hyperconjugative interactions involving adjacent C–H and C–C σ bonds [16–18]. Previous theoretical studies on model compounds of polymeric materials have similarly shown that local structural environments influence bond-dissociation enthalpies [6].

Conversely, C1 exhibits the highest C–H BDE value within the evaluated dataset (104.93 kcal·mol^{−1}), indicating a less favorable homolytic cleavage event within the selected oligomeric model. This comparison supports the conclusion that C–H bond dissociation is not energetically uniform along the chain.

The Gibbs free energies of reaction (ΔG_{rxn}) remain positive for the evaluated C–H cleavage events at 873.15 K, indicating that isolated homolytic dissociation is endergonic under the selected reference conditions. C24 exhibits a lower ΔG_{rxn} value (55.94 kcal·mol^{−1}) than C1 (73.33 kcal·mol^{−1}). Therefore, C24 is comparatively more favorable from a thermodynamic perspective among the evaluated C–H cleavage sites. These values describe reaction thermodynamics and should not be interpreted as activation Gibbs free energies or kinetic barriers. A complete description of polypropylene pyrolysis kinetics requires consideration of the broader radical-reaction network [7,19].

The frontier-orbital descriptors also vary after radical formation (Table S1). These changes provide complementary information on differences among the optimized radical fragments. Frontier molecular orbital analysis can assist in the comparative interpretation of electronic reactivity trends [12]. However, variations in HOMO, LUMO, dipole moment, and global electrophilicity do not independently demonstrate a subsequent β -scission step, hydrogen-transfer reaction, or product-selectivity pattern.

The statistical analysis presented in Section 4 supports the relevance of the local carbon environment. After adjustment for the remaining terms included in the mixed-effects model, cleavage events associated with CH environments exhibit a coefficient of −1.766 kcal·mol^{−1} relative to the CH₃ reference category ($p < 0.001$). Taken together, the DFT and statistical results indicate that tertiary methine environments are associated with comparatively lower C–H bond-dissociation enthalpies within the selected isotactic PP oligomer.

The identification of comparatively labile C–H sites may provide a molecular basis for subsequent studies involving catalytic pyrolysis and plastic-waste valorization [7,12]. Nevertheless, the present calculations do not demonstrate catalyst performance, reaction-rate enhancement, or changes in liquid-product yield.

the evaluated sites, C24 exhibits a lower ΔG_{rxn} value than C1. These values provide a thermodynamic comparison among cleavage sites but should not be interpreted as activation Gibbs free energies or kinetic barriers.

3.2. Homolytic C–C Bond Cleavage in the Isotactic Polypropylene Oligomer

The C–C dataset comprises 28 homolytic cleavage events distributed along the oligomeric backbone. The calculated C–C BDE values range from 82.28 kcal·mol^{−1} at C28 to 87.41 kcal·mol^{−1} at C44 (Figure 2a and Table S2). These values are consistently lower than the C–H BDE range of 90.18–104.93 kcal·mol^{−1}. Within the selected oligomeric model, this difference indicates a thermochemical preference for backbone C–C scission relative to C–H dissociation. This trend is consistent with previous theoretical comparisons of bond-dissociation enthalpies in model compounds representative of polymeric materials [20,21].

The lowest C–C BDE value was obtained for C28 (82.277 kcal·mol^{−1}). Comparably low values were also calculated for C11 (82.499 kcal·mol^{−1}) and C17 (82.500 kcal·mol^{−1}), whereas C44 exhibited the highest value within the evaluated C–C dataset (87.41

kcal·mol⁻¹). The relatively narrow C–C BDE interval indicates that several backbone positions exhibit similar thermochemical susceptibility.

The distribution of the calculated C–C BDE values reveals positional variation along the selected oligomer. However, the results do not independently establish a universal mid-chain scission mechanism. Mechanistic models of polypropylene pyrolysis indicate that experimental degradation involves interconnected radical pathways and multiple secondary reactions [7,15]. Accordingly, the present BDE values should be interpreted as descriptors of relative thermochemical susceptibility rather than as a complete representation of the pyrolysis mechanism.

The statistical analysis identifies a significant association between structural region and BDE variation. Relative to the middle-region reference category, the initial region exhibits a coefficient of −0.359 kcal·mol⁻¹, whereas the final region exhibits a coefficient of +0.515 kcal·mol⁻¹. These differences are modest and specific to the selected oligomeric model. They should not be extrapolated directly to experimental reaction rates or pyrolysis-product distributions.

The corresponding ΔG_{rxn} values reported in Table S2 provide an additional thermodynamic comparison among the evaluated C–C cleavage events. As with the C–H dataset, these reaction free energies should not be interpreted as activation barriers. Explicit transition-state searches and kinetic calculations would be required to determine rate constants, competitive pathways, and the relative importance of subsequent radical reactions. Bond-dissociation enthalpies are useful molecular descriptors, but their quantitative interpretation depends on the selected computational protocol and on the broader chemical context [12,22].

The electronic descriptors of the radical fragment pairs also vary after C–C cleavage. These variations provide comparative information on the electronic characteristics of the optimized products. They do not demonstrate that the fragments will necessarily undergo a specific downstream process, such as β -scission, intermolecular hydrogen transfer, monomer recovery, or selective formation of liquid hydrocarbons. Product distributions in experimental polypropylene pyrolysis depend on reaction conditions, catalytic environments, and the broader network of primary and secondary transformations [7,15,21].

The mixed-effects model provides an independent statistical summary of the calculated trend. After adjustment for the remaining structural, thermodynamic, and electronic variables, C–C cleavage exhibits a coefficient of −5.871 kcal·mol⁻¹ relative to the C–H reference category ($p < 0.001$). This result is consistent with the lower BDE range obtained for the evaluated backbone bonds.

Overall, the DFT and statistical analyses consistently indicate that C–C backbone cleavage is thermochemically more favorable than C–H dissociation within the selected isotactic PP oligomer. This conclusion is restricted to relative bond-dissociation trends. It does not establish experimental degradation rates, catalytic selectivity, reactor operating temperatures, or pyrolysis-product yields. The calculated trends may serve as a molecular basis for subsequent kinetic, catalytic, and experimental studies [10,23].

3.3. Relationship to Experimental and Mechanistic Studies of Polypropylene Pyrolysis

The present calculations provide a thermochemical comparison of homolytic C–H and C–C cleavage events within a finite isotactic polypropylene oligomer. Although the study does not include direct experimental validation, the calculated trends can be discussed in relation to previously reported experimental and mechanistic observations.

Experimental spin-trapping studies have identified radical intermediates during the thermal degradation of polypropylene [6]. This experimental evidence supports the relevance of examining homolytic bond cleavage and radical stabilization as molecular-

level aspects of PP degradation. However, the present calculations do not reproduce the complete experimental degradation process. They evaluate isolated dissociation events and independently optimized radical products under a common theoretical framework.

Mechanistic modeling studies have shown that polypropylene pyrolysis involves an interconnected network of radical reactions leading to the formation of lower-molecular-weight products [11]. More recent studies of intrinsic polypropylene-pyrolysis kinetics have also identified multiple kinetic regimes under high-temperature conditions [12]. These findings are consistent with the need to distinguish the initial thermochemical susceptibility of a bond from the subsequent reaction network. Accordingly, the lower BDE values calculated for C–C cleavage events should be interpreted as indicators of relative backbone lability within the selected oligomer model, rather than as a complete mechanistic description of pyrolysis.

Experimental pyrolysis studies have demonstrated that product composition depends on operating conditions, including temperature, heating rate, and pressure [15]. Catalytic studies have additionally shown that catalyst composition and reaction conditions influence the distribution of liquid and gaseous products obtained from polyolefin pyrolysis [7,12]. These experimental observations reinforce the limitations of extrapolating isolated BDE values directly to product selectivity or process performance.

The present results are qualitatively consistent with the radical nature of polypropylene thermal degradation and with the relevance of backbone cleavage in molecular-weight reduction. Nevertheless, the calculated BDE and ΔG_{rxn} values do not constitute direct experimental validation of reaction rates, product yields, catalytic performance, or reactor-scale behavior. Establishing those relationships will require explicit kinetic modeling and targeted experimental studies.

The present study is intentionally restricted to an idealized finite isotactic PP oligomer and does not reproduce the full complexity of environmental microplastic particles or commercial polypropylene materials, which may exhibit broad molecular-weight distributions, amorphous and crystalline domains, structural defects, variable tacticity, additives, oxidative aging, weathering-induced functional groups, and interactions with co-occurring contaminants. The calculations do not include explicit catalysts, transition-state searches, kinetic rate constants, heat- and mass-transfer effects, or reactor-scale variables. In addition, the reported numerical values may retain residual dependence on the selected basis set because a systematic basis-set convergence analysis and a complete functional benchmark were not performed. Therefore, the calculated BDE and ΔG_{rxn} values should be interpreted as internally consistent thermochemical trends within the selected oligomeric model. The comparison with previously published experimental and mechanistic studies provides qualitative contextual support but should not be interpreted as direct experimental validation. Establishing the transferability of these trends to environmental degradation, catalytic conversion, product selectivity, and industrial pyrolysis will require further kinetic, experimental, and multiscale assessment.

4. Statistical Analysis

The structure of the mixed-effects model, including the random effect, fixed effects, number of levels, and categorical variables considered, is summarized in Table 1. The mixed-effects model was used to quantify the associations between the calculated bond dissociation enthalpies (BDEs) and the structural, thermodynamic, and electronic descriptors included in the oligomeric dataset. Bond type, carbon type, and structural region exhibited statistically significant associations with the calculated BDE values, whereas ΔG_{rxn} was the only continuous covariate showing a significant association after adjustment for the remaining model terms (Table 2). The fitted model exhibited an R^2 of 0.997 and an adjusted R^2 of 0.9946, with a residual standard deviation of 0.697 kcal·mol⁻¹

and a residual variance of $0.486 \text{ (kcal}\cdot\text{mol}^{-1})^2$ (Table 3), indicating that the model accounted for a substantial proportion of BDE variation within the evaluated computational dataset. The estimated coefficients are reported in Table 4; C–C cleavage showed a coefficient of $-5.871 \text{ kcal}\cdot\text{mol}^{-1}$ relative to the C–H reference category, while CH environments showed a coefficient of $-1.766 \text{ kcal}\cdot\text{mol}^{-1}$ relative to the CH₃ reference category, indicating comparatively lower BDE values for backbone cleavage events and tertiary carbon environments, respectively. These results should be interpreted as statistical associations within the selected isotactic polypropylene oligomer model and not as direct predictions of reactor-scale pyrolysis behavior, experimental degradation kinetics, or product selectivity.

Bond type and carbon type exhibited statistically significant associations with the calculated BDE values ($p < 0.0001$; Table 2). The coefficient associated with C–C cleavage was $-5.871 \text{ kcal}\cdot\text{mol}^{-1}$ relative to the C–H reference category (Table 4). After adjustment for the remaining terms included in the model, this result indicates that the evaluated C–C cleavage events exhibited lower BDE values than the corresponding C–H cleavage events. The coefficient associated with CH environments was $-1.766 \text{ kcal}\cdot\text{mol}^{-1}$ relative to the CH₃ reference category ($p < 0.001$), indicating comparatively lower BDE values for cleavage events involving tertiary carbon environments. This association is chemically consistent with the greater relative stabilization of tertiary carbon-centered radicals.

Structural region was also significantly associated with BDE variation ($p = 0.001$; Table 2). Relative to the middle-region reference category, the initial region exhibited a coefficient of $-0.359 \text{ kcal}\cdot\text{mol}^{-1}$ ($p = 0.013$), whereas the final region exhibited a coefficient of $+0.515 \text{ kcal}\cdot\text{mol}^{-1}$ ($p < 0.001$) (Table 4). These results indicate modest positional variation within the selected oligomeric model. However, they do not independently demonstrate a generalized mid-chain scission mechanism and should not be extrapolated directly to experimental reaction rates or pyrolysis-product distributions.

Among the continuous covariates, the Gibbs free energy of reaction (ΔG_{rxn}) was significantly associated with BDE ($p = 0.006$). This association is expected because both variables describe related thermochemical aspects of the evaluated dissociation events. HOMO energy ($p = 0.962$), LUMO energy ($p = 0.150$), global electrophilicity ($p = 0.361$), and dipole moment ($p = 0.126$) did not exhibit statistically significant independent associations with BDE after adjustment for the remaining terms included in the model (Table 2). This result does not indicate that electronic structure is chemically irrelevant. Rather, the selected global electronic descriptors did not explain additional BDE variation independently of the structural and thermochemical variables included in the fitted model.

The omnibus tests for the evaluated two-factor interactions were not statistically significant: carbon type $\times$ bond type ($p = 0.312$), carbon type $\times$ structural region ($p = 0.656$), and bond type $\times$ structural region ($p = 0.432$) (Table 2). Therefore, the principal associations observed for bond type and carbon type can be interpreted without invoking interaction-dependent effects.

Table 1. Structure of the mixed-effects model applied to the BDE values calculated for the isotactic PP oligomer.

Factor	Type of Effect	Number of Levels	Categories/Values Considered
Position	Random	45	1–45
Carbon type	Fixed	3	CH, CH ₂ , CH ₃
Bond type	Fixed	2	C–C, C–H
Structural region	Fixed	3	Initial (I), Middle (M), Final (F)

Table 2. Tests of fixed effects in the mixed-effects model applied to the calculated BDE values.

Term	GL Num	GL Den	F	<i>p</i> -Value
HOMO	1.00	69.95	0.00	0.962
LUMO	1.00	67.27	2.12	0.150
ΔG	1.00	69.64	8.02	0.006
Electrophilicity (ω)	1.00	69.05	0.84	0.361
Dipole moment	1.00	68.40	2.40	0.126
Carbon type	2.00	67.44	29.68	<0.0001
Bond type	1.00	68.88	40.03	<0.0001
Structural region (I, M, F)	2.00	37.08	7.92	0.001
Carbon type $\times$ Bond type	2.00	57.79	1.19	0.312
Carbon type $\times$ Region	4.00	32.68	0.61	0.656
Bond type $\times$ Region	2.00	37.04	0.86	0.432

The lack of statistical significance of HOMO and LUMO ($p > 0.05$) suggests that, under the evaluated conditions, global electronic descriptors are less influential than structural factors such as bond type and carbon hybridization in determining bond dissociation energies.

Table 3. Summary statistics for the mixed-effects model applied to the calculated BDE values.

Parameter	Description	Value
R ²	Coefficient of determination	0.997
Adjusted R ²	Adjusted coefficient of determination	0.9946
S	Residual standard deviation (kcal·mol ^{−1})	0.697
S ²	Residual variance [(kcal·mol ^{−1}) ²]	0.486

Table 4. Estimated coefficients of the mixed-effects model applied to the calculated BDE values.

Term	Coefficients	EE	GL	t	<i>p</i> -Value
Constant	69.722	17.998	68.86	3.87	<0.001
HOMO	4.216	89.262	69.95	0.05	0.962
LUMO	57.680	39.619	67.27	1.46	0.150
ΔG	0.144	0.051	69.64	2.83	0.006
Electrophilicity	−864.06	940.59	69.05	−0.92	0.361
Dipole moment	−1.764	1.138	68.40	−1.55	0.126
Type of carbon (CH)	−1.766	0.234	69.33	−7.53	<0.001
Type of carbon (CH ₂)	0.217	0.204	64.29	1.06	0.292
Type of bond (C-C)	−5.871	0.928	68.88	−6.33	<0.001
Final region (F)	0.515	0.130	35.99	3.96	<0.001
Initial region (I)	−0.359	0.137	39.88	−2.61	0.013
CH $\times$ C-C interaction	0.711	0.461	69.96	1.54	0.127
CH ₂ $\times$ C-C interaction	−0.210	0.185	56.47	−1.13	0.263

The PCA allows for decoupling electronic descriptors from thermodynamic ones. PC1, which explains the majority of variance, is dominated by electronic factors such as HOMO (0.540) and Electrophilicity (0.582). This suggests that the stability of the formed radical is intrinsically linked to the redistribution of electron density in the fragment. PC2, strongly influenced by Gibbs Free Energy (ΔG) (0.518), captures the thermal feasibility of the reaction at 873.15 K. The positive correlation of ΔG with BDE in the mixed model ($p = 0.006$) reinforces that, at industrial temperatures, the feasibility of rupture depends more on overcoming the thermodynamic barrier than on subtle variations in dipole moment. See Table 5.

From a green chemistry perspective, the Interval Plot clearly visualizes the reactivity threshold. The net separation between C-C (low energy) and C-H (high energy) clusters enables the proposal of “mild” or catalytic pyrolysis strategies. By focusing the process on the lower-energy bonds (~82–85 kcal/mol) identified statistically, it is possible to reduce the energy intensity of chemical recycling, thereby decreasing the carbon footprint associated with marine plastic waste treatment.

Table 5. Results of the PCA applied to the electronic and thermodynamic descriptors.

Variable	PC1	PC2	PC3	PC4	PC5
ΔG	0.307	0.518	−0.660	−0.448	−0.041
HOMO	0.540	−0.334	0.221	−0.398	0.624
LUMO	−0.498	−0.150	0.205	−0.796	−0.230
Dipole moment	−0.164	−0.715	−0.677	0.054	0.033
Electrophilicity	0.582	−0.293	0.128	−0.060	−0.745

The dominance of electronic descriptors in PC1 indicates that radical stability is primarily governed by electron density redistribution, whereas PC2 reflects the thermodynamic feasibility of bond cleavage under pyrolytic conditions.

The present study is intentionally restricted to an idealized finite isotactic PP oligomer. The model does not reproduce the full complexity of environmental microplastic particles or commercial polypropylene materials, which may exhibit broad molecular-weight distributions, amorphous and crystalline domains, structural defects, variable tacticity, additives, oxidative aging, weathering-induced functional groups, and interactions with co-occurring contaminants. In addition, the calculations do not include explicit catalysts, transition-state searches, kinetic rate constants, heat- and mass-transfer effects, or reactor-scale variables. Therefore, the calculated BDE and thermochemical trends should be interpreted as intrinsic relative tendencies within the selected oligomer model. Their relevance to environmental degradation, catalytic conversion, and industrial pyrolysis requires further kinetic, experimental, and multiscale validation.

The reported numerical values may retain residual dependence on the selected basis set because a systematic basis-set convergence analysis was not performed. In addition, the present study does not include a functional benchmark or higher-level reference calculations for representative cleavage events. The quantitative values should therefore be interpreted cautiously, while the relative trends provide the primary basis for comparison within the selected oligomeric model.

5. Conclusions

This study evaluates intrinsic bond-dissociation trends in a finite isotactic polypropylene oligomer containing fifteen propylene repeat units. Within the selected model, C–C bonds exhibit lower calculated BDE values than C–H bonds, indicating a thermochemical preference for backbone scission. The comparatively low BDE values associated with specific tertiary carbon environments also support the relevance of local radical stabilization in determining relative bond lability.

The statistical analysis identifies bond type and carbon type as the principal factors associated with BDE variation within the calculated dataset, while the multivariate analysis summarizes the relationships among the evaluated thermodynamic and electronic descriptors. These findings should be interpreted as molecular-scale trends for an idealized oligomeric system rather than as direct predictions of environmental microplastic degradation, catalytic selectivity, pyrolysis-product distribution, or industrial process performance.

Further studies should evaluate chain-length convergence, alternative computational protocols, explicit reaction kinetics, and experimental validation to establish the extent to which the observed trends can be transferred to more complex polypropylene materials and pyrolysis systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/microplastics5030135/s1>, Table S1: Thermodynamic and electronic properties calculated for homolytic cleavage of C-H bonds in PP microplastic at 873.15 K using the theoretical level M06-2X/LANL2DZ.

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