



Investigation of thermal degradation mechanism in thermoplastic polystyrene tetramer model by DFT method

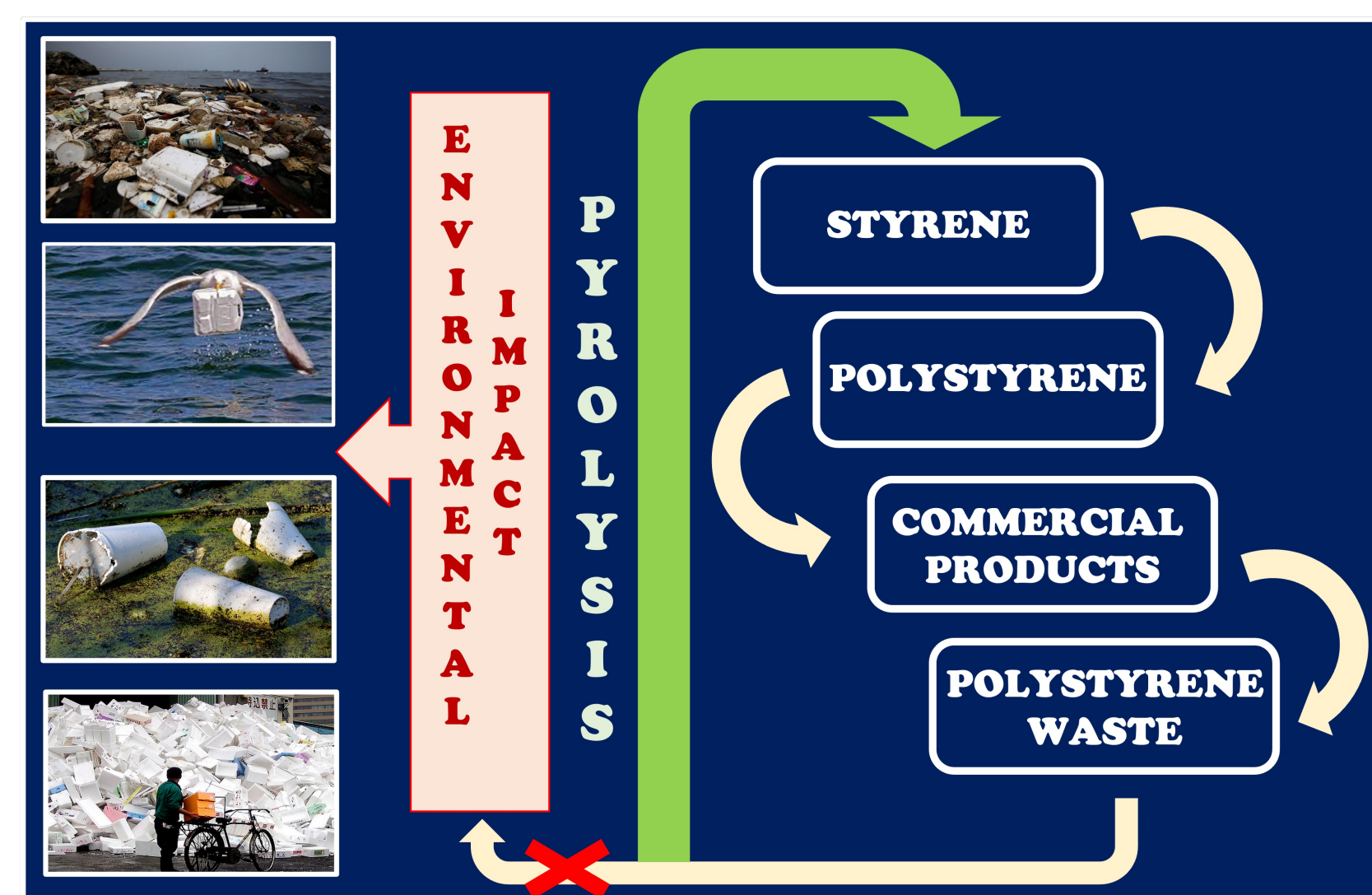
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Introduction

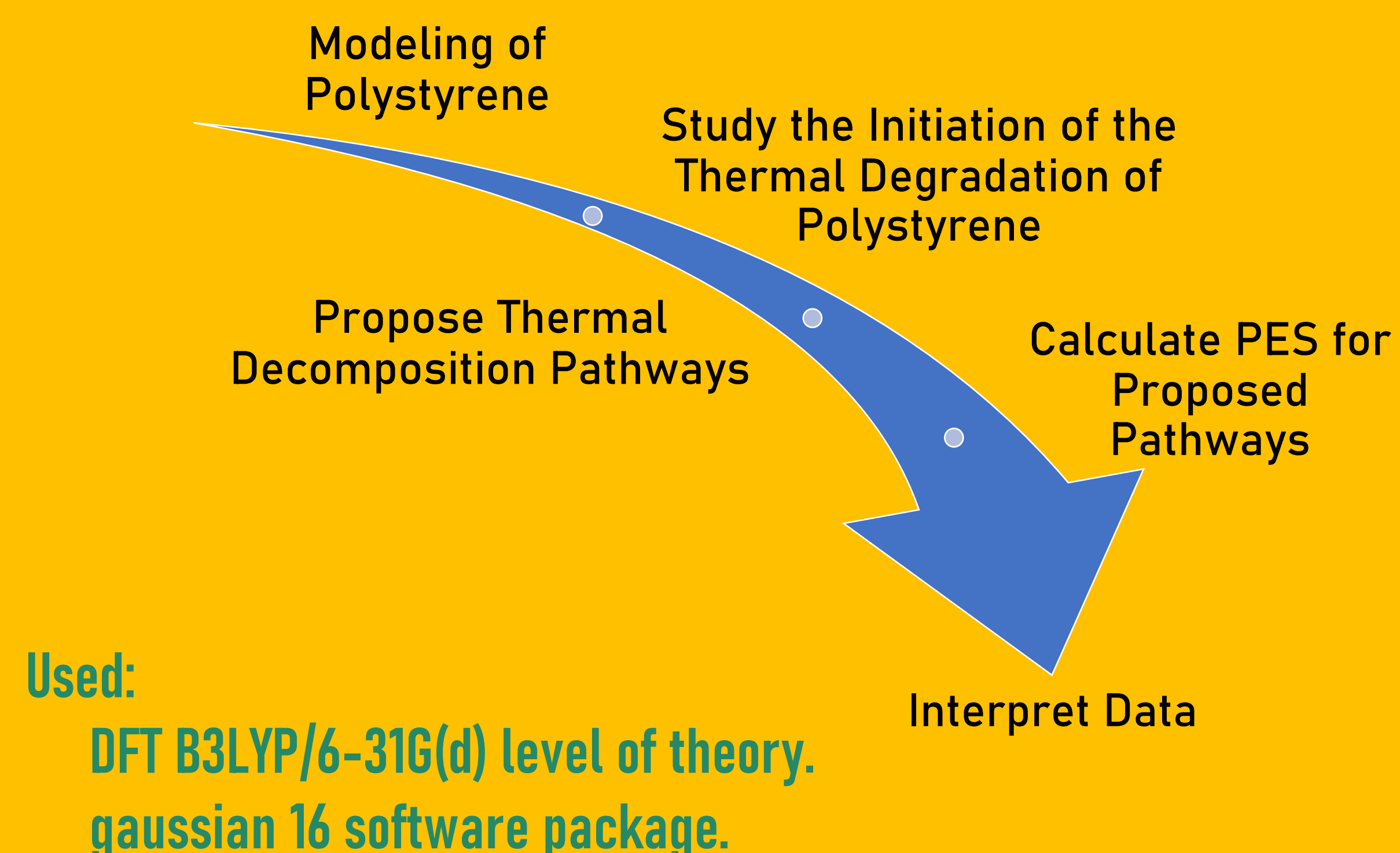


Polystyrene is one of extensively using commodity polymers as its excellent physical and mechanical properties. Even though polystyrene waste is arising in alarming rate due to its extremely slow degradation characteristics. Even for the polystyrene waste, pyrolysis is one of major solutions, it is not practically proceeding due to the lack of understanding. This research focused on studying the thermal decomposition of polystyrene model compound and ability to provide efficient and effective reaction pathways for polystyrene waste pyrolysis.

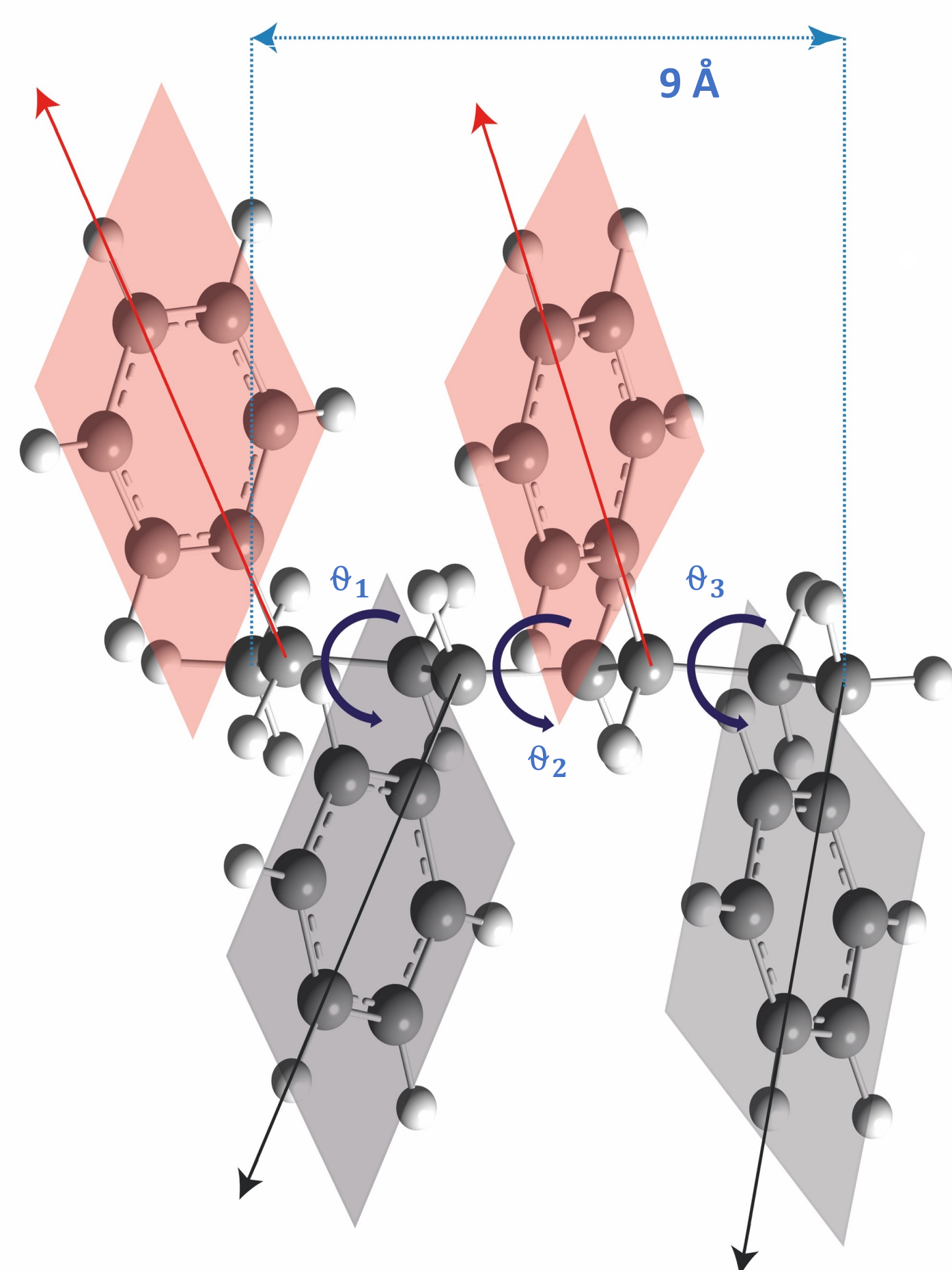
Objectives

- Long Term Objective:
 - Identify effective and productive pyrolysis pathways for polystyrene waste.
- Short Term Objectives:
 - Develop a model to study polystyrene thermal degradation.
 - Identify and study the initiation of thermal decomposition of polystyrene.
 - Propose and study feasible thermal decomposition pathways for polystyrene pyrolysis.

Methodology



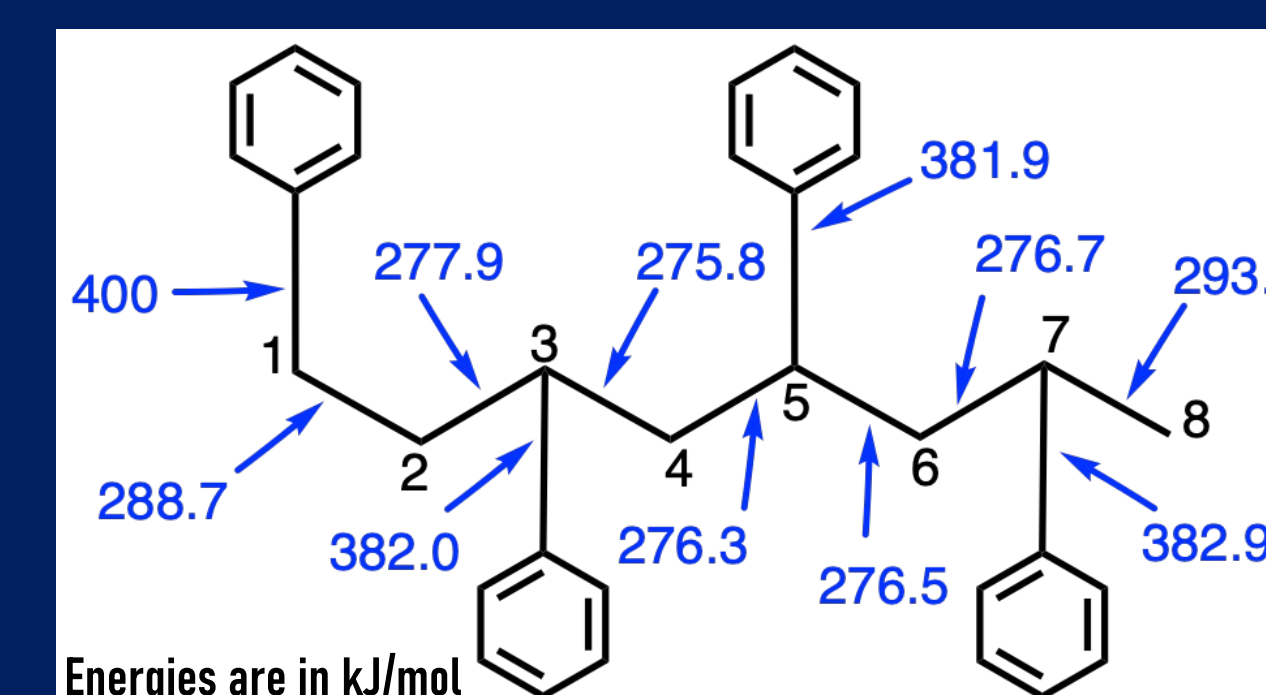
Model Development



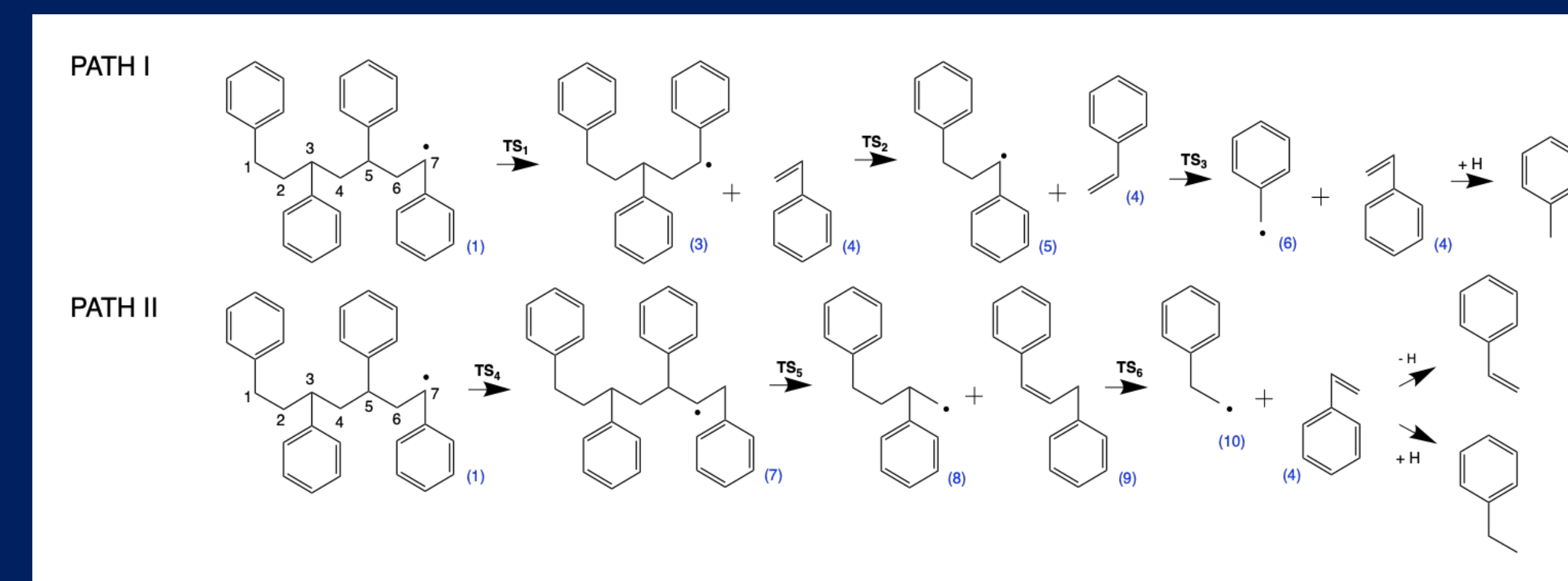
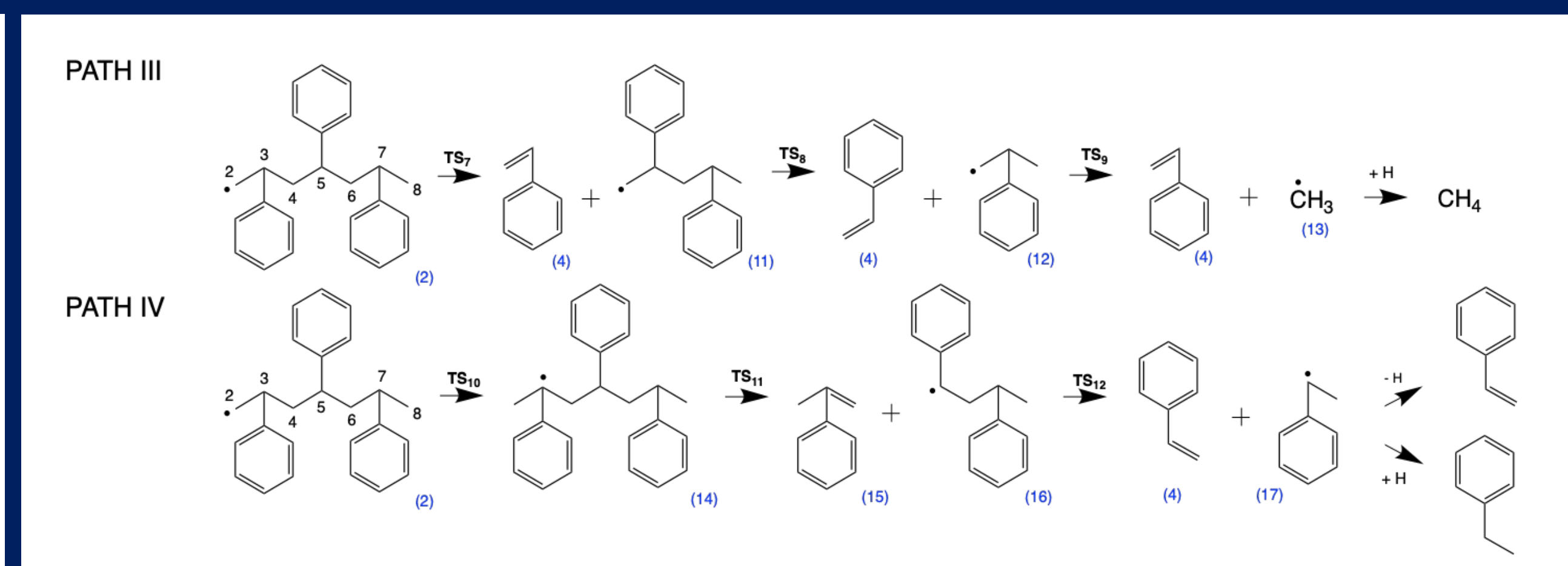
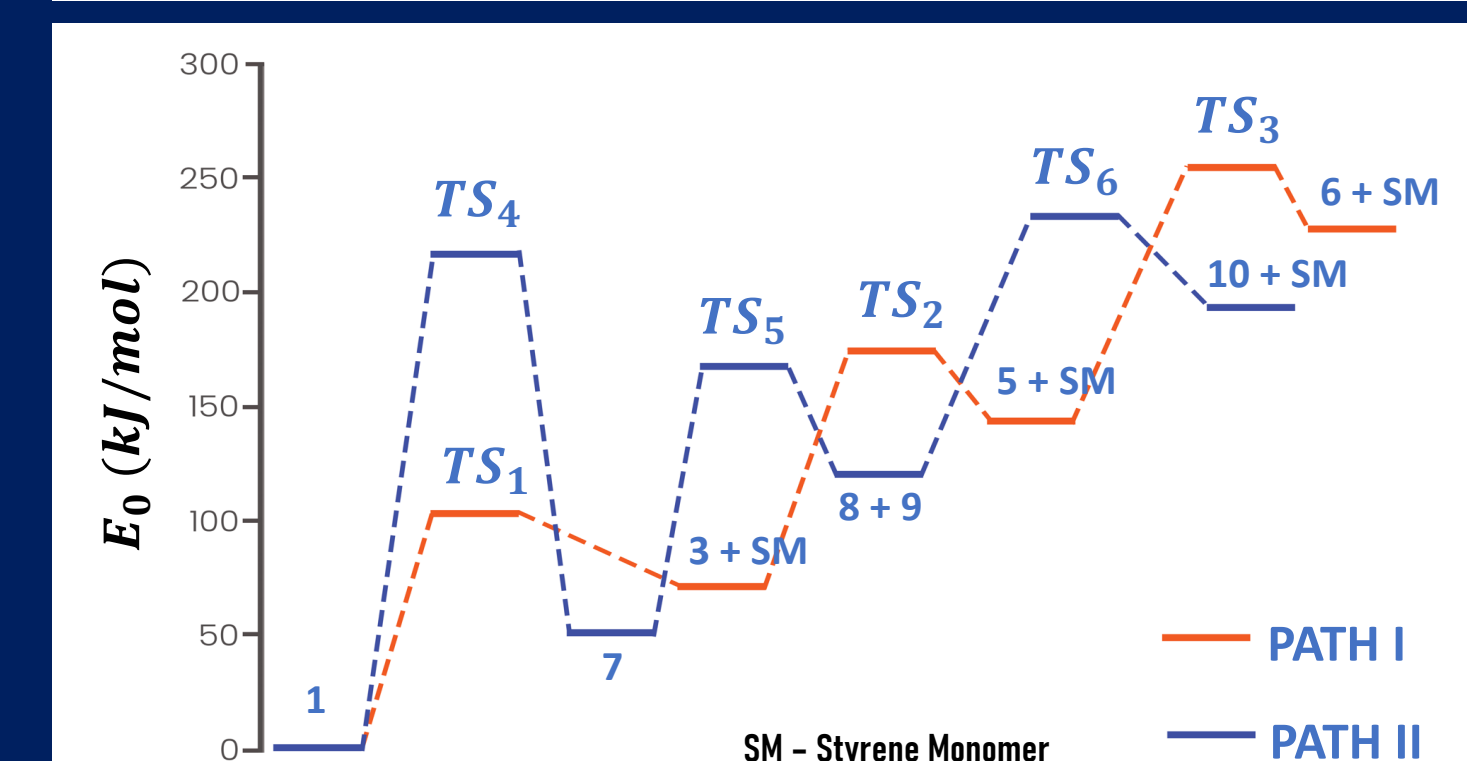
The polystyrene model compound is an oligomer that contains four repeating units, in syndiotactic nature. The model has total of 8 carbons in the backbone, and the molar mass is 418.61 g/mol.

$$\begin{aligned}\theta_1 &= 111^\circ \\ \theta_2 &= 108^\circ \\ \theta_3 &= 109^\circ\end{aligned}$$

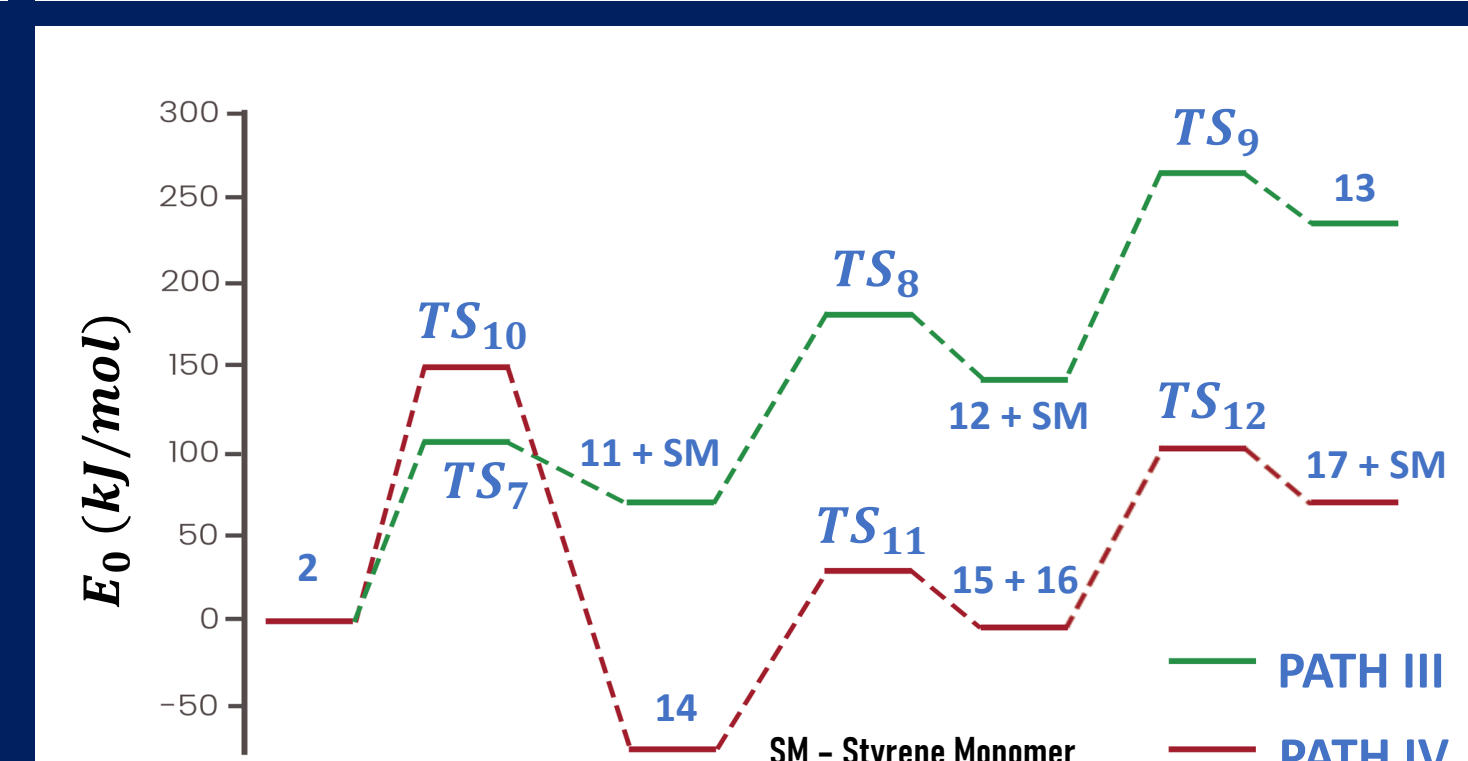
Results and Analysis



- The backbone C-C bond, C-C_{aromatic} bond, and C-H bond for polystyrene, each have computed average bond dissociation energies of 280.8 kJ/mol, 386.7 kJ/mol, and 383.4 kJ/mol, respectively.
- Terminal C-C bonds were higher than non-terminal backbone C-C bonds; this indicates the initiation of polystyrene is more likely to occur by cleavage somewhere in the middle of the backbone C-C bonds, producing large molecular weight fragments.



According to the calculated results, PATH I is kinetically favourable than PATH II. Both pathways can be considered as endothermic reactions.



PATH IV has two endothermic steps and one exothermic step while all the steps are endothermic for PATH III. PATH III is kinetically favourable than PATH IV.

All intermediates of PATH II are more stable compared to PATH I. Therefore, PATH II is thermodynamically favourable compared to PATH I.

All three intermediates are comparably stable in PATH IV compared to PATH III. Therefore, PATH IV can be identified as a thermodynamically favourable route.

Conclusions

Initiation of polystyrene is more feasible through cleavage by somewhere in between backbone C-C bonds. Rate determining step for PATH I and PATH III is step 3 whereas rate determining step for PATH II and PATH IV is step 1. The reactions in PATH I and PATH III are more effective for styrene formation in polystyrene pyrolysis.

❖ The future works will have to address on the temperature dependance behaviour of proposed PATH I and PATH III.

References

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Singh, R.K., Raju B. Time and temperature depended fuel gas generation from pyrolysis of real world municipal plastic waste. *Fuel* 174 (2016): 164-171.

Acknowledgements

Department of Chemistry, Faculty of Science, Eastern University of Sri Lanka for providing support and guidance.