Further Developments in Modeling the Thermal Decomposition of Polymers

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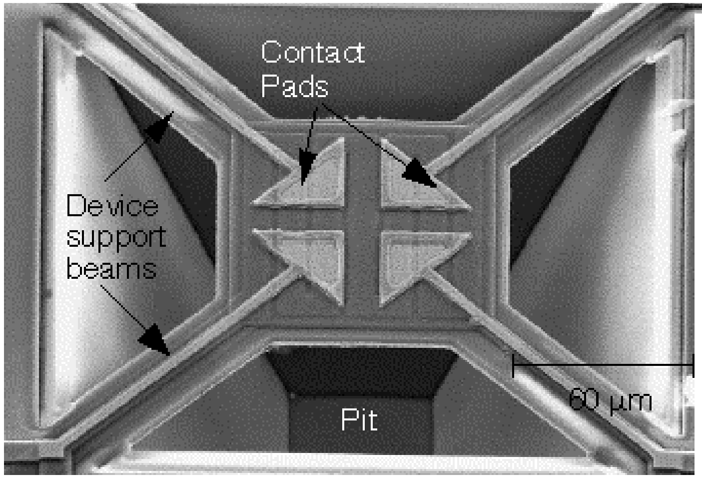
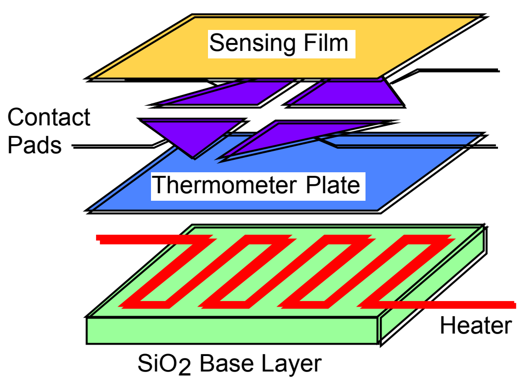
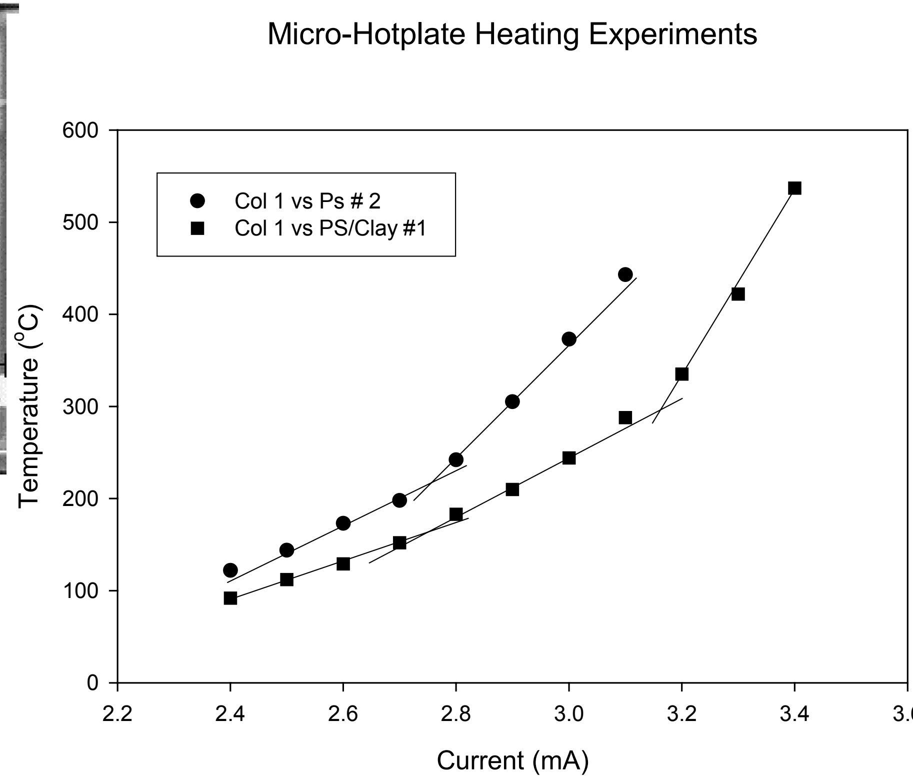
Molecular Level Understanding of Materials Flammability







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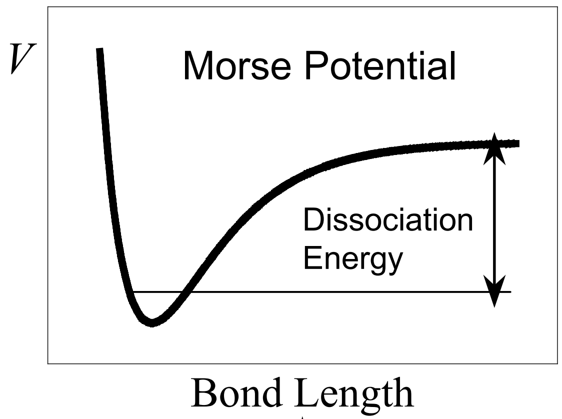
Principles of Classical Molecular Dynamics

of



The Consistent Valence Force Field:[5]

$$V = \sum^{n_{bonds}} V_{bond} + \sum^{n_{angles}} V_{angle} + \sum^{n_{torsions}} V_{torsion} + \sum^{n_{pairs}} V_{non-bond}$$

5. Dauber-Osguthorpe, P.; Roberts, V. A.; Osguthorpe, D. J.; Wolff, J.; Genest, M.; Hagler, A. T.; *Structure, Function and Genetics* 1988, 4: 31

MD Model of Thermal Degradation in Polymers

The feature that distinguishes MD_REACT from other MD codes is that it allows for the formation of new bonds from free radical fragments that are generated when bonds in the polymer break and, thereby, accounts for the chemical reactions that play a major role in the thermal degradation process.

This is achieved using the IPC protocol to send bonding information back and forth between MD_REACT and Discover.

Reactive Force Field

$$V_b = D[1 - \exp(-\alpha(r - r_e))]^2 - D$$

$$V_a = S(ij)S(jk)\,k_\theta(\theta - \theta_e)^2$$

$$V_t = S(ij)S(jk)\,S(kl)\,k_\phi[1 + \cos(n\phi - \phi_e)]$$

$$V_{nb} = \varepsilon[(\frac{r^*}{r})^{12} - 2(\frac{r^*}{r})^6] + \frac{\delta_i \delta_j}{r}$$

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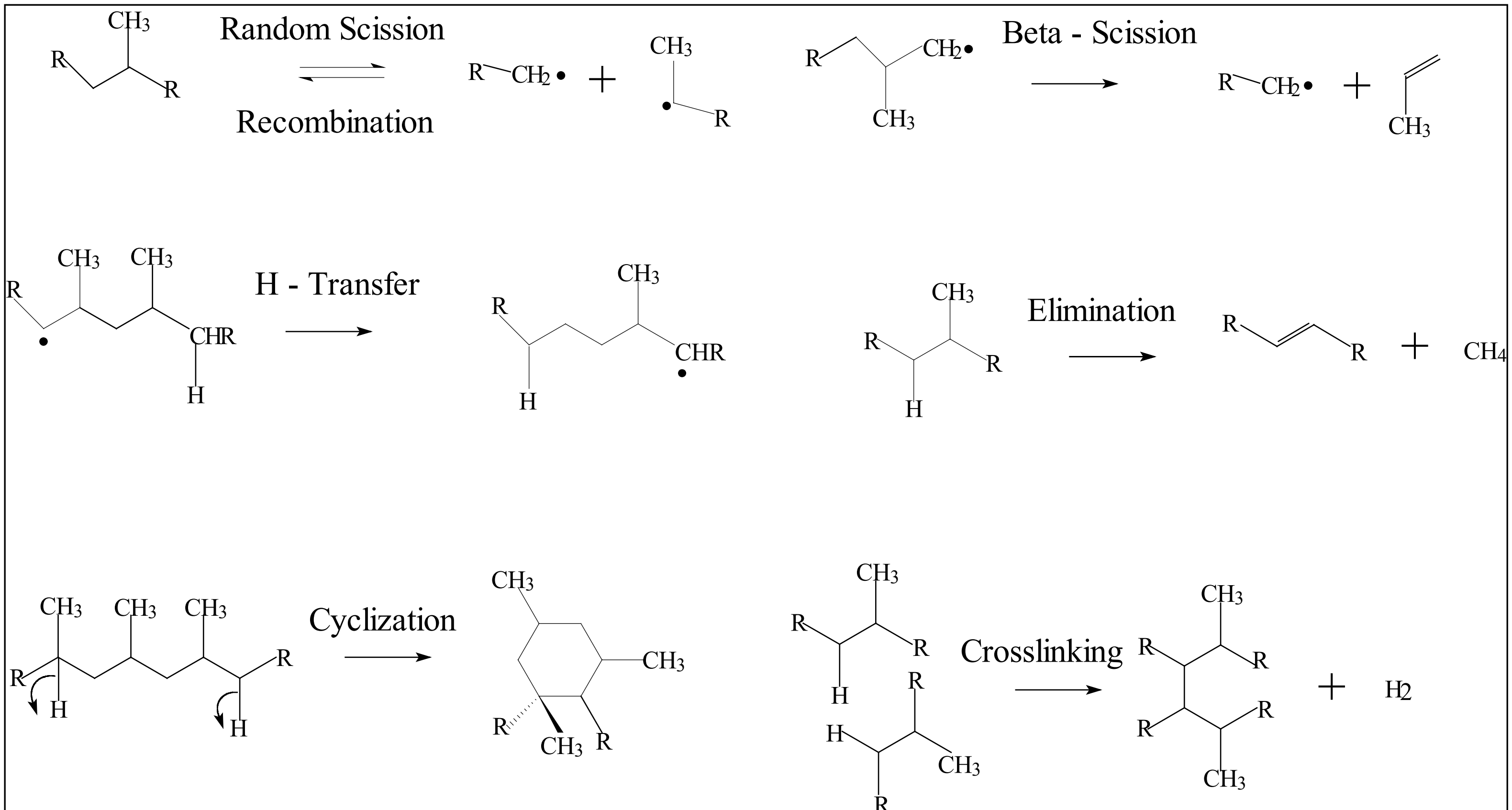
Reactive Force Field

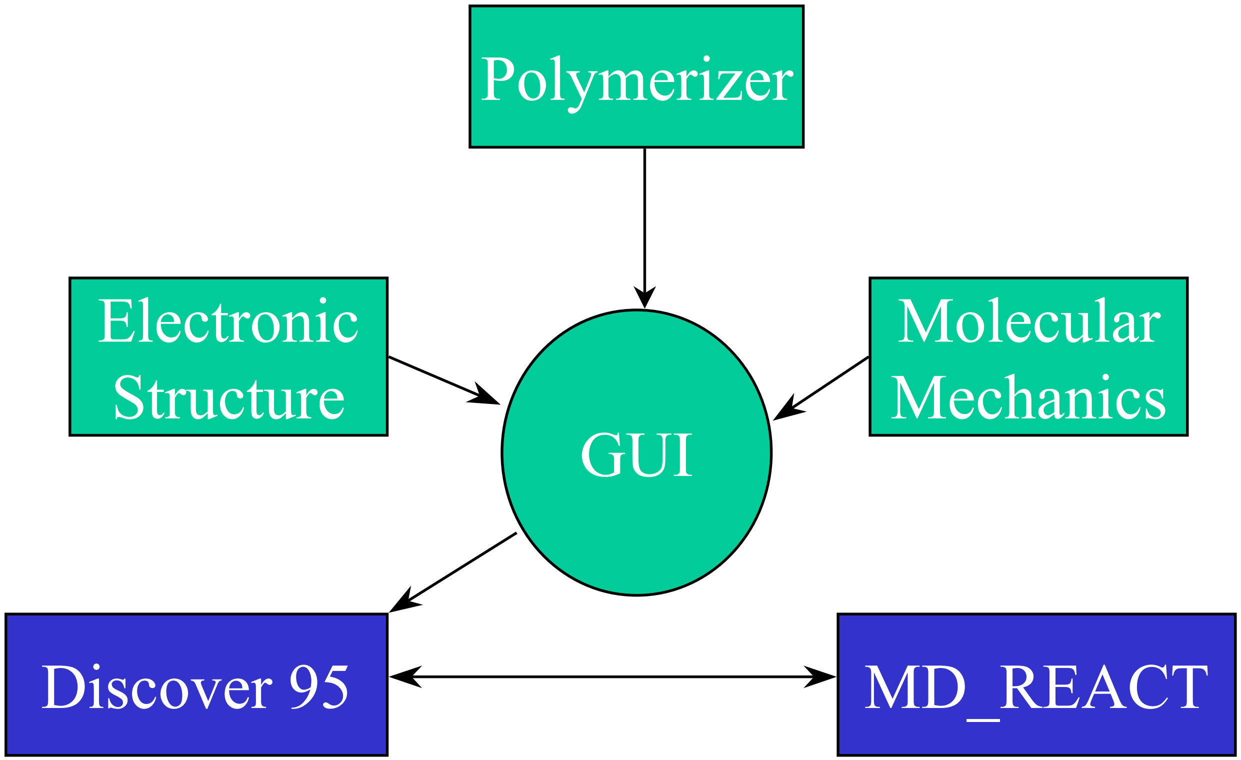
$$S(ij) = \begin{cases} 1 & r \leq r_e \\ \dfrac{-V_b(ij)}{D(ij)} & r > r_e \end{cases}$$

- The atoms participating in covalent bonds become radicals when the corresponding bond orders become less than a pre-determined value.
- The program sorts through all possible bonds between these free radicals and retains those corresponding to the lowest energy subject to the constraints imposed by atomic valence rules.

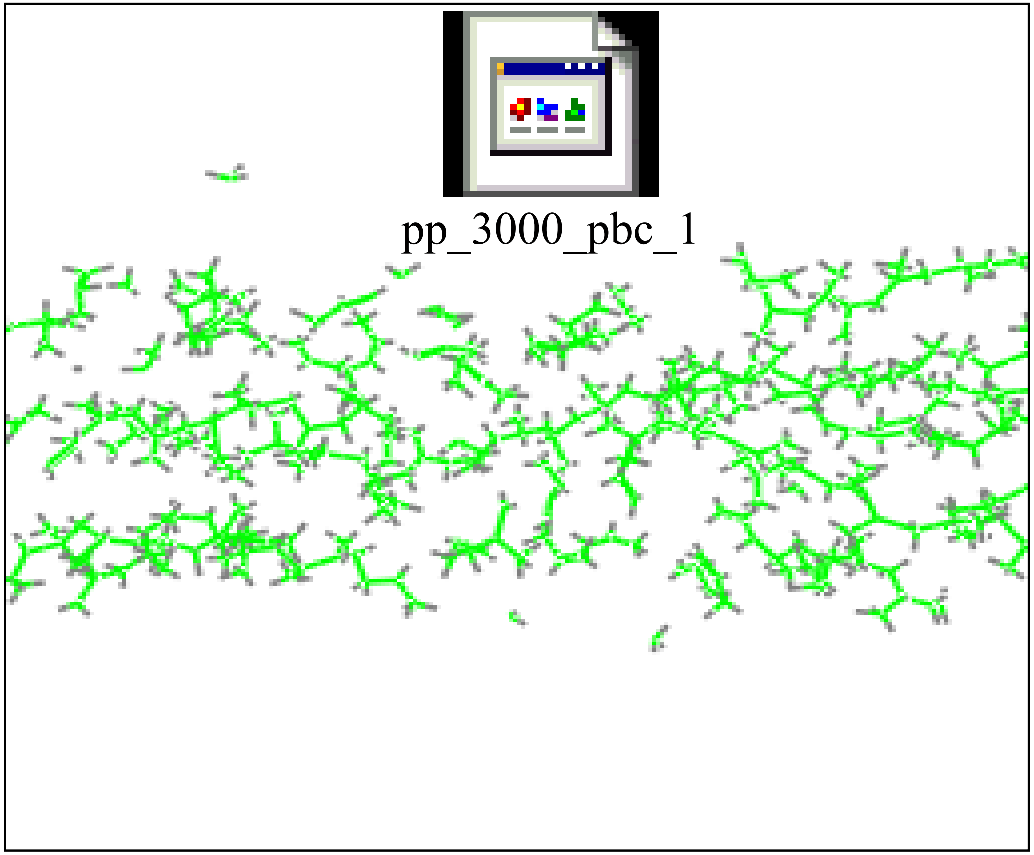
Available Reaction Channels



Interface to Discover 95



Thermal Degradation of PP



Thermal Degradation of PP

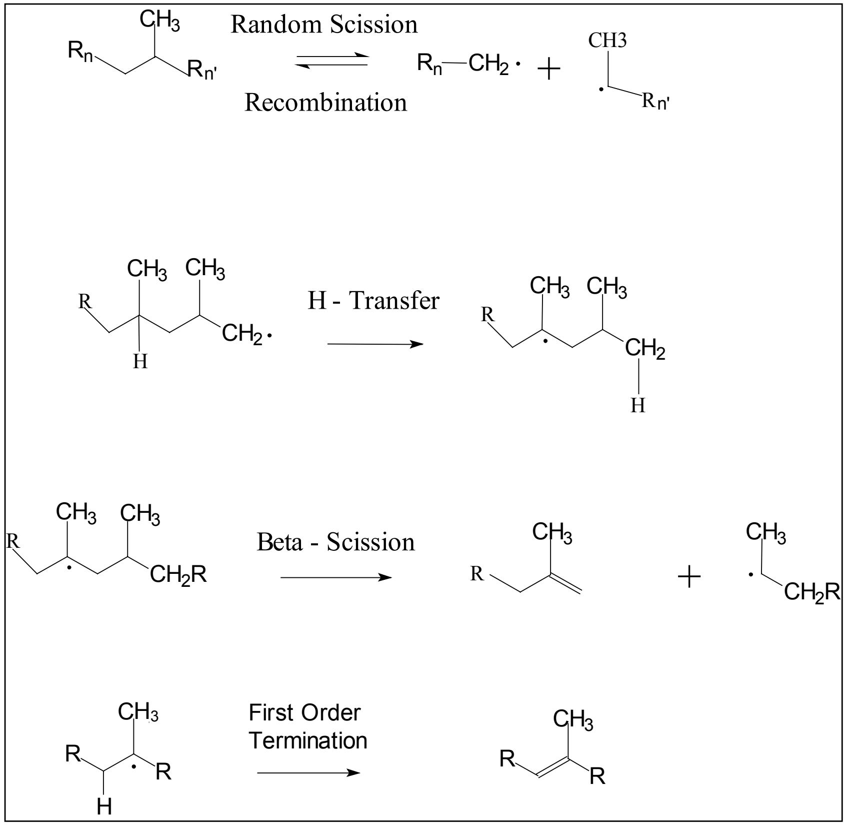


Figure 1. Major Reaction Channels in the Thermal Degradation of Polypropylene.

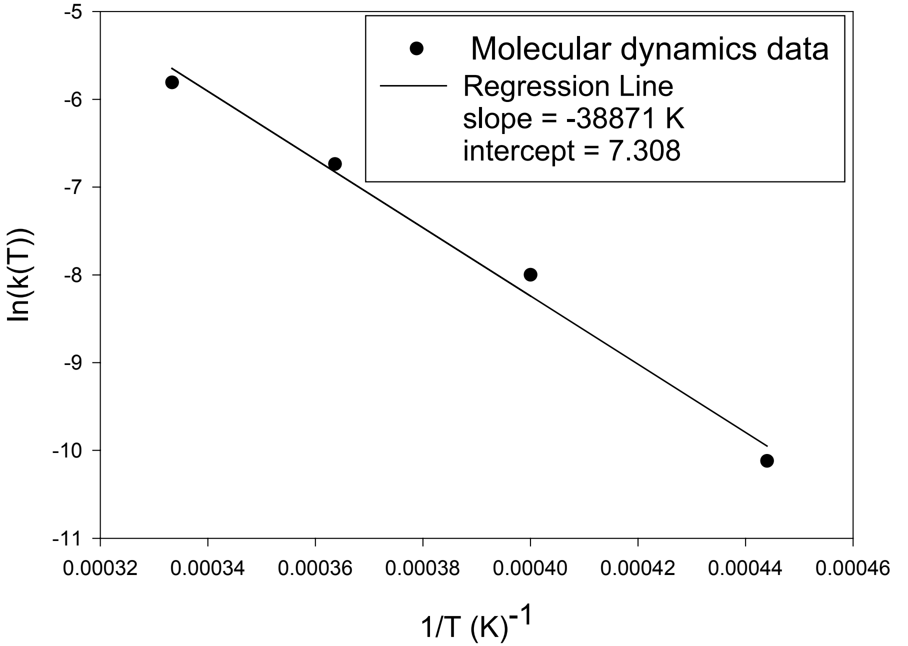
Kinetic Model

$$\frac{1}{m(t)}\frac{dm(t)}{dt} = -(2k_i(T) + [R]k_I(T))Z(T)$$

$$[R] = \frac{2k_i(T)d_0}{k_t(T)m_0}, \qquad Z(T) = \frac{k_p(T)}{(k_t(T) + k_I(T)\frac{d_0}{m_0})} \rightarrow \frac{k_p(T)}{k_I(T)\frac{d_0}{m_0}}$$

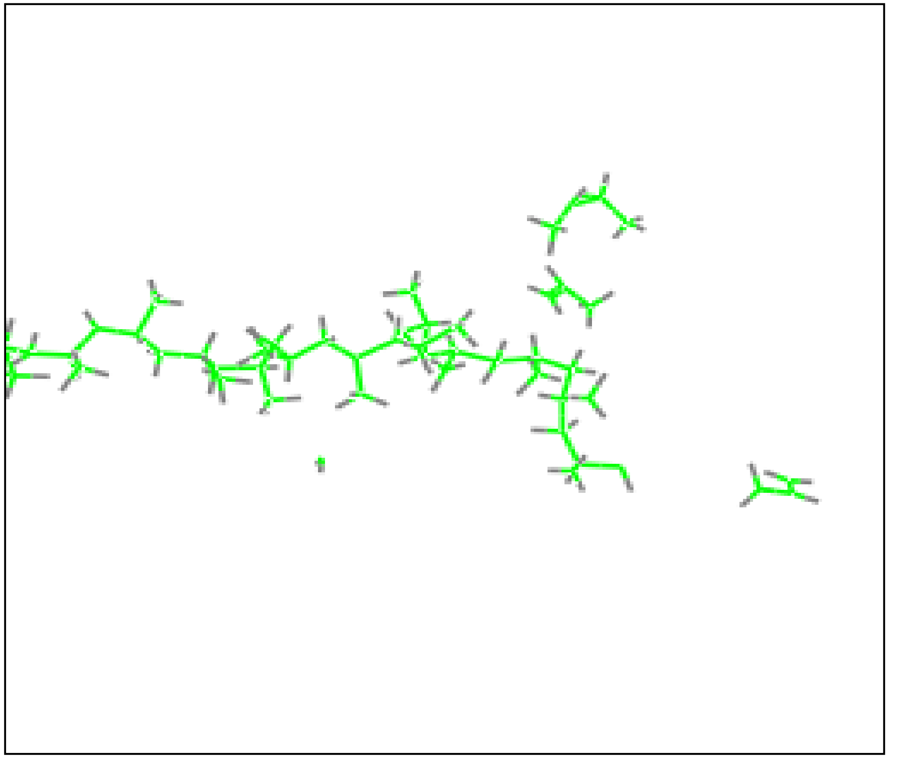
$$\frac{1}{m(t)}\frac{dm(t)}{dt} = -2k_i(T)\left[Z(T) + \frac{k_p(T)}{k_t(T)}\right]$$

Simple Kinetic Model of Thermal Degradation Random Scission

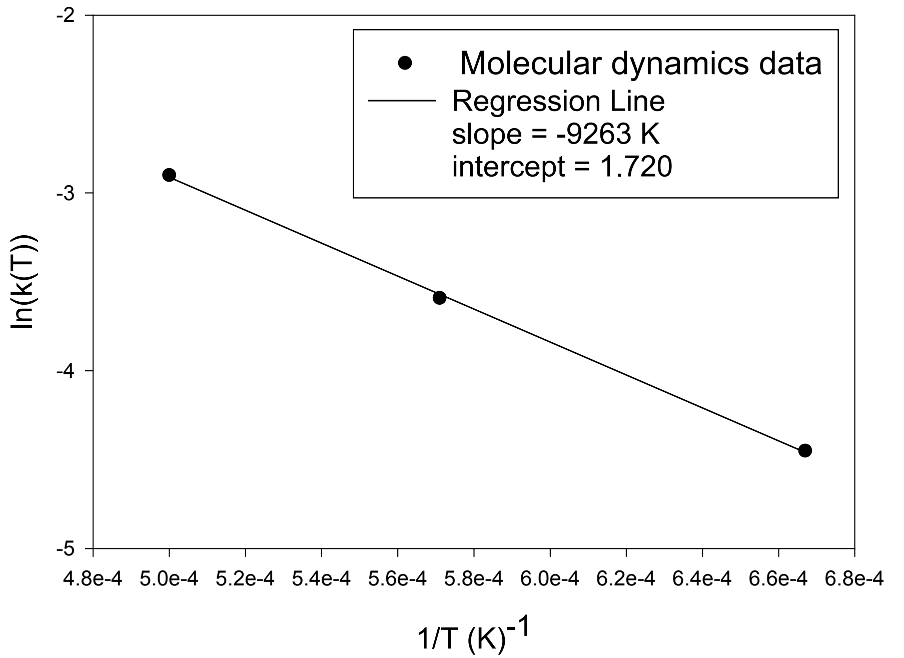


$E_a = 323$ kJ/mol $\qquad A = 1.5 \times 10^{15}\ s^{-1}$

Simple Kinetic Model of Thermal Degradation Propagation

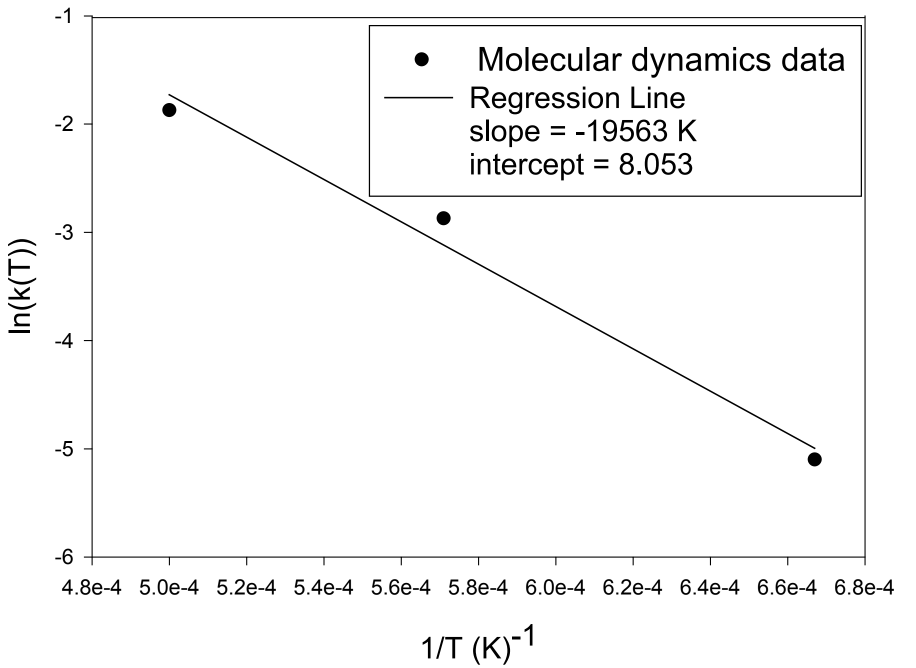


Simple Kinetic Model of Thermal Degradation Propagation



$E_a = 77$ kJ/mol $\qquad A = 5.6 \times 10^{12}\ s^{-1}$

Simple Kinetic Model of Thermal Degradation Termination



$E_a = 163$ kJ/mol $\qquad A = 3.1 \times 10^{15}\ s^{-1}$

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Simple Kinetic Model of Thermal Degradation

Rate of Mass-loss from Degrading Polypropylene

$$\frac{1}{m(t)}\frac{dm(t)}{dt} = -5.3x10^{12}\exp(-\frac{237528}{RT})$$

Experimental Values:

$E_a = 220$ kJ/mol $A = 19 \times 10^{12}\ s^{-1}$

Bockhorn *et. al.*, Journ Anal. and Appl. Pyrolysis **46**, 1998, 1

New Features of MD_REACT

- A new mechanism that allows simultaneous rupture and formation of bonds was introduced.
- Every type of chemical reaction that involves rupture and/or formation of σ and/or π bonds (with the exception of conjugated and aromatic systems) was included.
- All the chemical transformations are treated in the unified fashion based on the competition between energies of interatomic interactions. This approach results in more realistic model of reactions involving π bonds and eliminates the necessity of usage of special "effective" potentials for β- scission reactions.
- The CVFF forcefield is updated to accommodate decomposition of oxygen-containing polymers (in particular, PMMA). The new bond dissociation energies are obtained from CBS-QB3 calculations performed on model molecules.

New Algorithm of MD_REACT

The following cycle is performed at every time step:

For every covalent interaction with *BO* < *Dissociation Criterion*

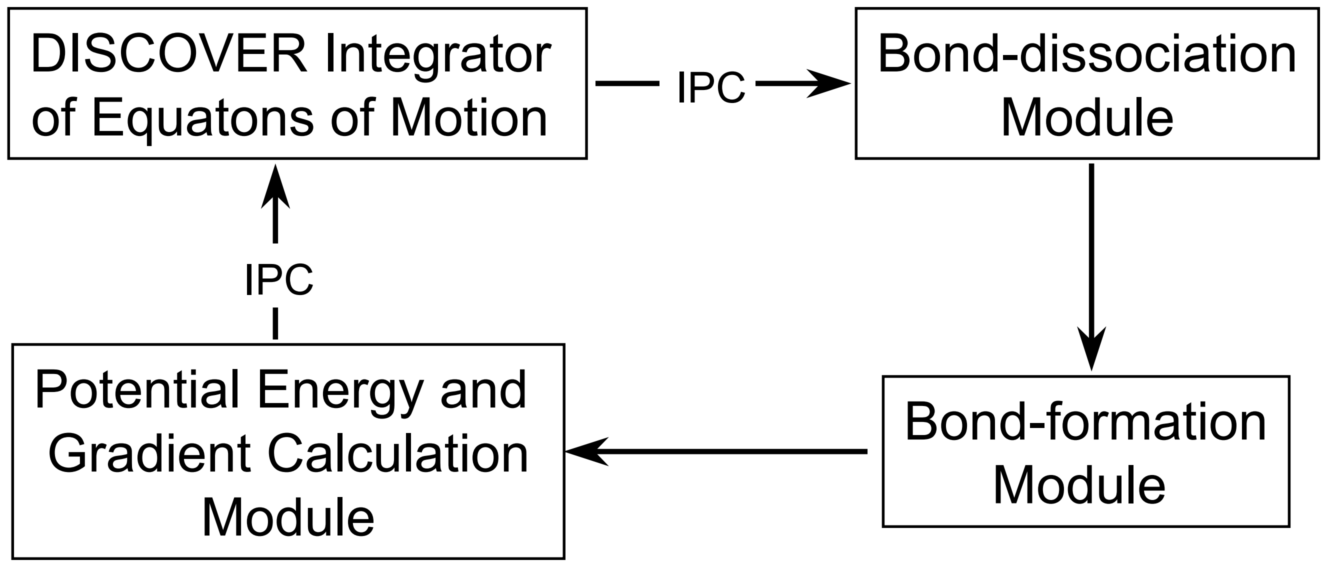
$$V_{corrected} = V_{bond} + BO \times \left[\sum^{angles} V_{angle} + \sum^{torsions} V_{torsion} \right]$$

$\uparrow$

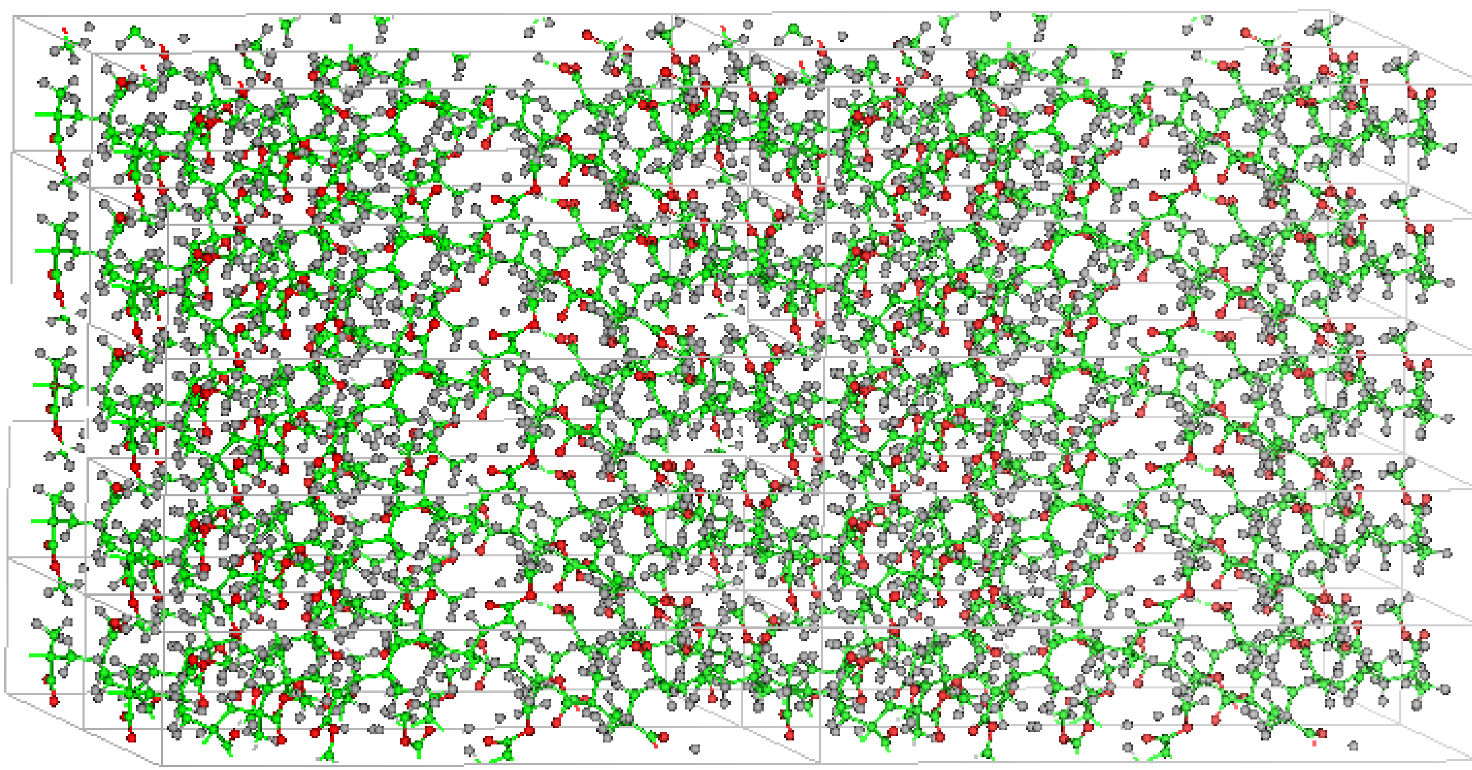
Potential Energy and Gradient Calculation Module

New Algorithm of MD_REACT

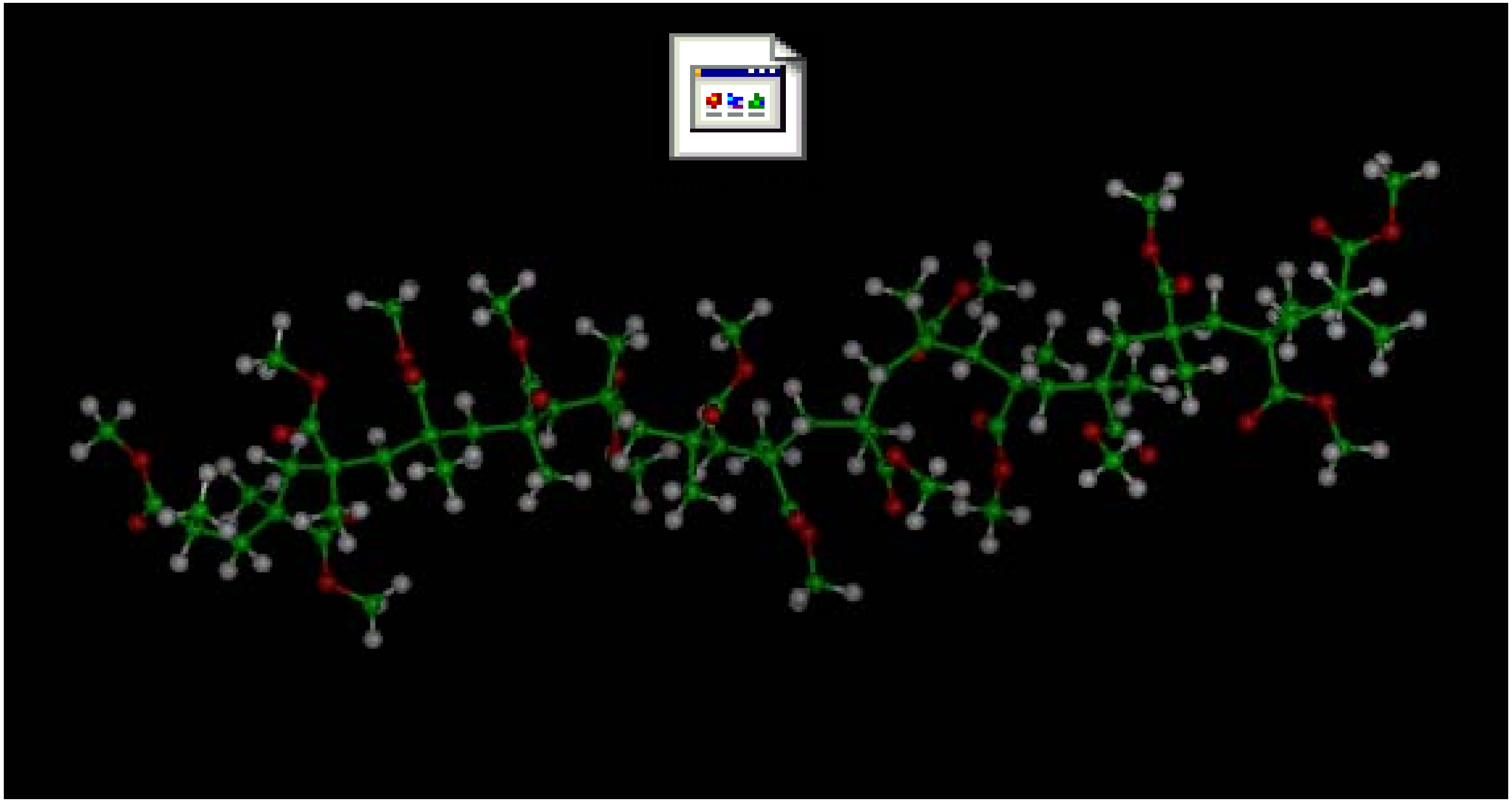
The following cycle is performed at every time step:



MD Simulations



Thermal Degradation of PMMA



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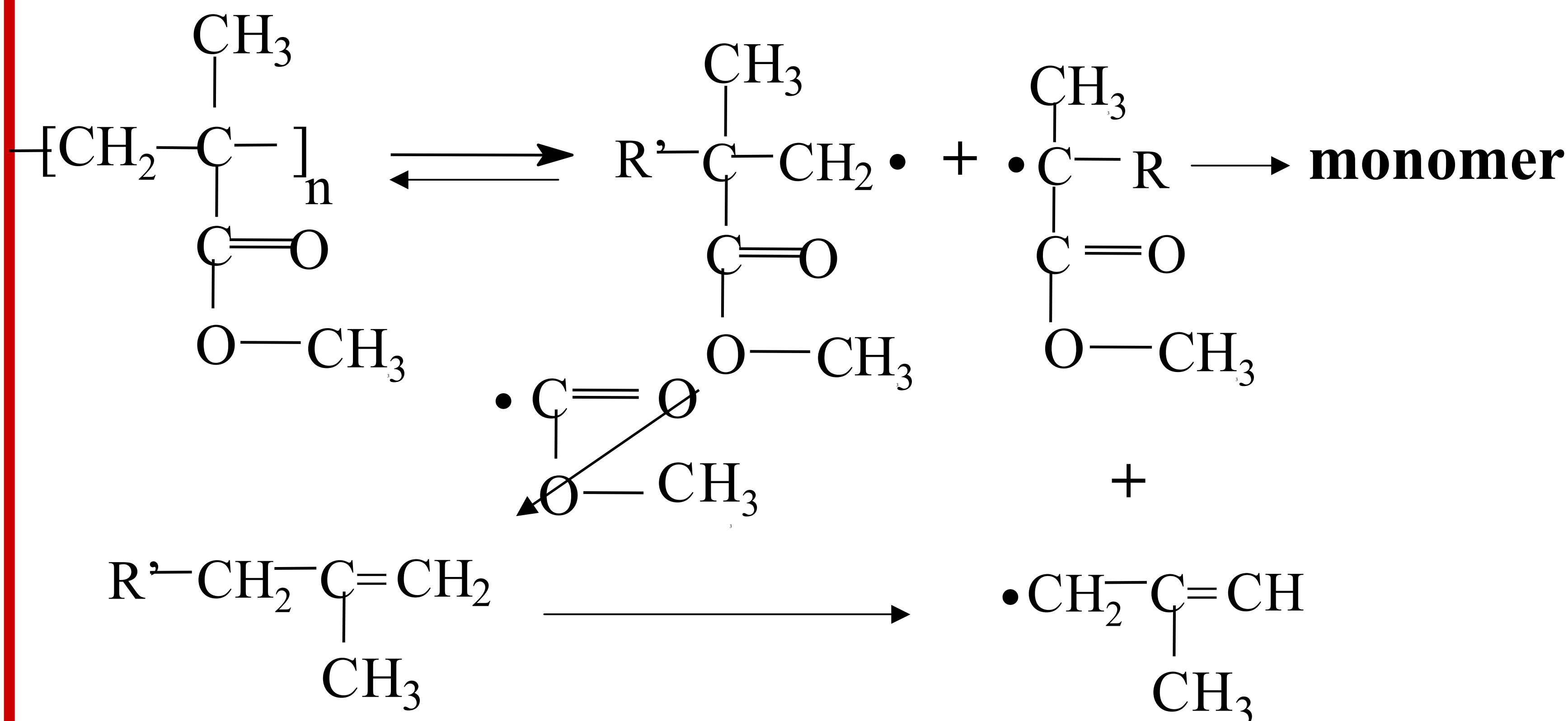
Thermal Degradation of PMMA



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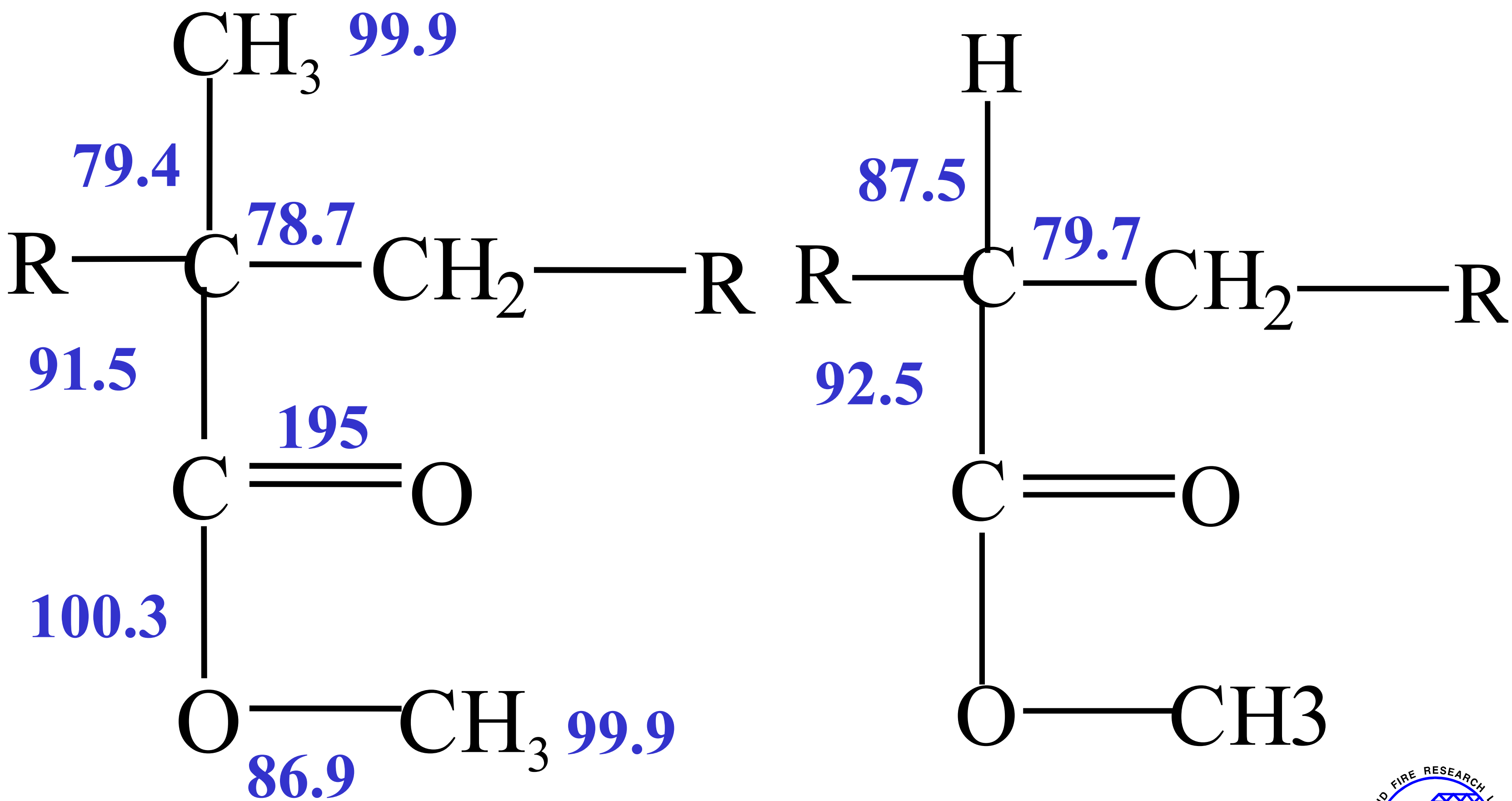
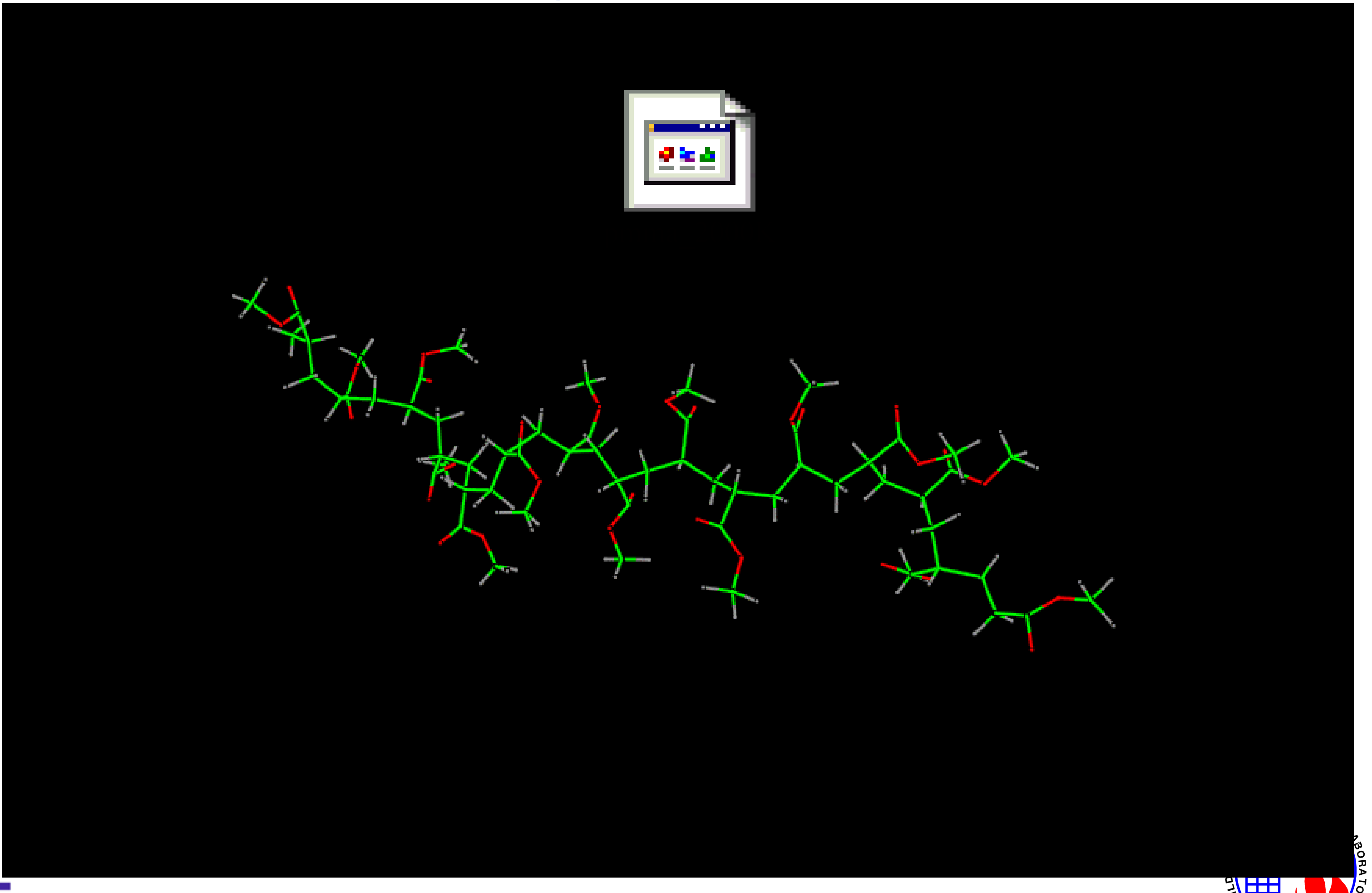
BE's in MA and MMA



Thermal Degradation of PMA



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Conclusions

- The differences in the thermal degradation chemistries of PMMA and PMA appear to be due to higher initiation temperatures required for PMA.

- Molecular modeling can be useful tool for the investigation of thermal degradation and materials flammability and the development of new and more fire resistant materials. This role will continue to expand as advances in computer technology make it possible to extend the range of applicability of molecular modeling to more complex systems.

Acknowledgements

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MOLECVIEW was written by Dr. Glenn Forney (BFRL/NIST)

Dr. Robert Bohn (ITL/NIST) performed CBS-QB3 calculations on MMA