Kinetics and Mechanisms of Elementary Reactive Processes in Polymer Pyrolysis

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<u>Notice</u>

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<p style="text-align:center">**Final Technical Progress Report**</p>

<p style="text-align:center">for the project</p>

<p style="text-align:center">**Kinetics and Mechanisms of Elementary Reactive Processes in Polymer Pyrolysis**</p>

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Abstract

Polymer backbone scission reactions were studied computationally using polyethylene macromolecules as prototypes. Classical RRKM modeling, molecular dynamics, transition state theory, and molecular mechanics were used as research tools. The results demonstrate significant effects of polymer chain length and conformation on backbone dissociation rates. The results of molecular dynamics modeling performed for single molecules in vacuum show that per-bond rates of C-C bond dissociation increase with the increasing alkane chain length. Moreover, per-bond rates of C-C bond dissociation further increase (by orders of magnitude) in the cases where the motion of polymer chain ends is restricted. Effects of macromolecular surroundings under the conditions of polymer melt on the rates of carbon-carbon bond scission reactions were observed: rate constants obtained under the condensed phase conditions are approximately an order of magnitude lower than those of single molecules in the gas phase. The condensed phase rate constants display a strong dependence on the polymer melt density, with lower density resulting in larger rate constant values. Research was started on the kinetics of the reactions of H atom transfer: chain radical isomerization and inter-chain H atom transfer. An experimental study of the initial stages of polyethylene pyrolysis was started using ^{1}H NMR and GC/MS as analytical tools applied to the condensed phase and the gas phase products, respectively.

I. Background

Combustion and flammability of plastics are important topics of practical interest directly related to fire safety. Development of new fire-safe polymeric materials requires a better understanding of the microscopic chemical processes that determine thermal stability and flammability of polymers. Detailed chemical kinetic modeling is a very promising tool for understanding and control of pyrolysis and combustion of polymers. However, at the current stage of its development, its success is hindered by the lack of fundamental knowledge of the mechanisms and kinetics of the key elementary processes involved. Combustion of polymers is, generally, a gas-phase process with gaseous fuel supplied by the decomposing solid or liquid polymer. Thus, understanding of polymer pyrolysis is key to understanding the chemistry and physics of polymer combustion and flammability.

In virtually all the existing models of polymer pyrolysis, the majority of the rate coefficients used are derived from the corresponding gas phase values of chemically similar but smaller species. These rates include those of polymer backbone scission, beta-scission of radicals, hydrogen abstraction reactions, radical isomerizations (back-biting), etc. However, use of small-molecule gas phase rate constant values under the conditions of liquid polymer melt so far has not been supported by any research. Factors specific to the polymeric chains and condensed phase may affect rates of reactions of various types.

II. Summary of objectives

Analysis of the main problems and deficiencies of kinetic modeling of polymer pyrolysis leads to the following summary of the several areas in which concentrated research is needed:

1. Development of methodology of evaluating rate constants of several types of reactions important in polymer pyrolysis: backbone scission, beta-scission of radicals, radical isomerization (back-biting), radical recombination, H-atom transfer between chains, radical recombination, and molecular chain scission.
2. Creation of a database of critically evaluated rate constant values and expressions for use in particular polymer systems.
3. Adaptation of statistical reaction rate theories such as TST or phase space theory to condensed phase applications in general and to solid and liquid polymer environments in particular.

III. Progress made

During the covered period, the research mainly concentrated on the type of reactions responsible for the initiation of polymer pyrolysis and decomposition: backbone (chain) scission. Another direction of the research performed under the current project was comparison of the performance of two

computational methods of reaction rate assessment: Transition State Theory (TST) and Molecular Dynamics. This comparison targeted the ability of TST to adequately describe the types of interactions present in long-chain molecules, first in the isolated molecules (gas phase) and then in bulk polymer melt environment. Other reaction types were also targeted: research was started on the kinetics of the reactions of H atom transfer: chain radical isomerization and inter-chain H atom transfer. The results obtained in the computational research on the rates of chain backbone scission led us to initiate an experimental study of the initial stages of polyethylene pyrolysis.

III.1. Classical RRK modeling of RMD kinetics

When reactive molecular dynamics is used as a tool of research, often, calculations are performed for a single polymer globule and influence of neighboring polymer chains is accounted for by using periodic boundary conditions. In such calculations, isothermic conditions are maintained by a procedure equivalent to fixing the overall internal energy of a globule. If the globule is considered as a single molecule, isothermic conditions thus become isoergic (constant energy).

When bond breaking (chain scission) in such a macromolecule is considered from the point of view of classical RRK theory, the results indicate that (1) temperature dependence of the effective reaction rate is not exactly Arrhenius, with negative curvature of the Arrhenius plots, and (2) the effective activation energy depends on temperature and the number of degrees of freedom in the macromolecule. The smaller is the number of degrees of freedom (N), the more pronounced is the deviation from Arrhenius behavior. In the limit of large N ($N \rightarrow \infty$) the Arrhenius limit is achieved. In practice, this limit is reached at $N = 100 - 1000$, depending on the temperature.

III.2. Potential energy surfaces of -C-C- chain scission in macromolecular globules

Potential energy surfaces (PES) of -C-C- chain scission were studied for two polymer types: polyethylene and polyisobutylene. Quantum chemical calculations using the multi-level ONIOM method were used, with density functional (DFT) calculations used at the high level and molecular mechanics (Amber force field) used at the low level. Also, MM/MM calculations were performed using modified Amber force field with incorporated Morse stretches used to describe bond breaking. Extensive PES scans were performed for polymer globules following initial structure preparation via molecular dynamics calculations. The results demonstrated significant effects of internal polymer strain and attractive dispersion forces on the PES of reactions. In particular, significant fractions of C-C bond scans yielded PES profiles with sharp potential energy drops caused by sudden rearrangements of the polymer chain on the multi-monomer scale (i.e., the scale of $5 - 50$ monomer units). Such PES profiles are illustrated in Figures $1 - 2$.

These results demonstrate the existence of a distribution of effective energy barriers for C-C backbone scission. Most C-C bonds in the backbone chain have bond strength values clustered around the C-C bond strength of an isolated prototype gas-phase molecule (e.g., *n*-octane for PE). However, a fraction of bonds has significantly lower bond strengths. It is unclear whether these potential energy drops caused by chain rearrangements will have influence on the kinetics of polymer backbone scission. On the one hand, energy released in sudden rearrangements of the polymer chain may contribute to overcoming the barrier for bond dissociation or for the subsequent beta-scission of the radical products. On the other hand, the time-scale of these chain rearrangements is not known and, if large, will likely result in dissipation of energy into degrees of freedom that do not contribute to reaction.
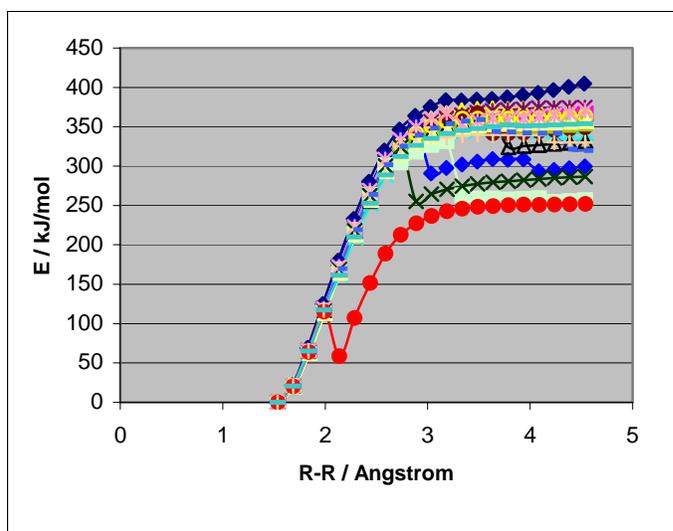
Figure 1. Results of PES scans of C-C bond scission in a 500 monomer units PE globule. Different symbols/colors represent different individual C-C bonds within the same globule. The results demonstrate the existence of a distribution of effective energy barriers for C-C backbone scission. Calculations were performed using the ONIOM(B3LYP/6-31G(d,p):Amber) method.
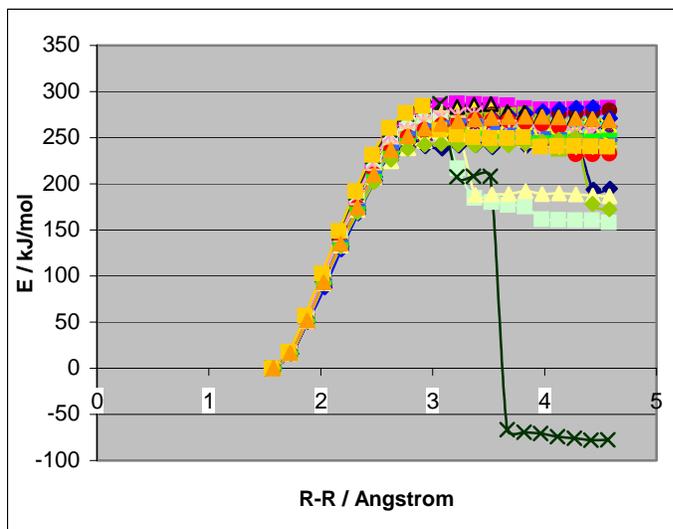
Figure 2. As in Figure 1 but for a PIB globule consisting of 300 monomer units.

III.3. Effects of Chain Length on Dissociation Rates

A systematic comparison of polyethylene chain dissociation rates obtained in TST and RMD modeling was performed. These calculations were carried out for isolated single molecules (i.e., molecules in the gas phase) . Polyethylene chains ranging in length from PE-1 to PE-1000 were studied. Here, the number corresponds to the number of monomer units in the polymer chain: PE-1 is ethane, PE-5 is decane, etc. Calculations were performed using the same representation of the potential energy surface in both the TST and the RMD modeling. Since the main purpose of the study was investigation of the hypothetical effects of chain length, rather simplistic potential energy surfaces (PES) given by the all-atom OPLS-AA force field[1] (which is very similar to that of Amber) with C-C stretch terms replaced by the Morse function were used. One feature of such force field that immediately draws attention as unrealistic is that the force constants of bending degrees of freedom do not change with elongation of adjacent bonds. Although the resultant modeling cannot thus be expected to reproduce the effects of "loose" transition states of C-C bond dissociation (e.g., refs 2 and 3, this should not affects comparison of TST and RMD based rate constants because the same PES is used in both types of modeling. Similarly, the same force field is used for all chain lengths, from PE-1 to PE-1000; thus, the observed effects of chain length are not caused by differences in the PES representation.

The variational transition state theory (VTST) calculations of the C-C dissociation rate constants were performed for decomposition of four molecules: PE-1 ($C_2H_6 \rightarrow CH_3 + CH_3$), PE-2, PE-3, and PE-5. All channels of possible C-C bond scission were analyzed for these molecules. Potential energy profiles and projected vibrational frequencies[4] were calculated along the reaction path using Gaussian 03 program package.[5] For these calculations, parameters of the Amber force field included in Gaussian 03 were modified to most closely match those of the OPLS-AA force field. Canonical variational transition state theory approach[3] was used to obtain the rate constant values. Classical (non-quantum) partition functions were used in all TST calculations to maintain compatibility with RMD modeling, which is inherently classical.

RMD calculations were performed using GROMACS program package.[6] For each polyethylene molecule, a series of 10 – 30 calculations was performed at each temperature to determine per-bond rate constants. Temperatures used in modeling ranged from 2100 to 3000 K; such high temperatures were necessary to make the RMD rates observable within the practicable range of times of molecular dynamics simulations.

Molecular dynamics modeling results demonstrate that alkane chain length has pronounced effect on the rate of backbone C-C dissociation. Significantly faster backbone scission (in terms of rate constants expressed per C-C bond, k_{CC}) was observed for longer molecules. These results are presented in Figure 3, along with the results of VTST calculations. As illustrated in Figure 4, the dependence of k_{CC} on

the chain length N in PE-N displays a fast growth at low N ($N = 1 – 5$) and saturation at larger N values ($N = 25 – 1000$). On average, MD rates of C-C bond dissociation of long-chain molecules (N > 5) are ~10 times larger than those of ethane.

Transition state theory also predicts noticeable increase in the dissociation rate constant with increasing chain length (Figures 3 and 4). Per-bond rate constants increase in the PE1 – PE-5 sequence, in approximate agreement with the MD results. VTST results for PE-1 (ethane) agree with those obtained in MD calculations: the k_{CC}(T) dependences coincide (Figure 3).

Figure 3. Per-bond rate constants k_{CC} for C-C backbone scission obtained in VTST (dotted lines) and MD (symbols and fitted solid lines) simulations. The plot shows the effect of chain length: rate constants increase with the increasing chain length; this dependence is saturated for polyethylene chains longer than PE-5. Rate constants obtained for PE-250 and PE-1000 are not shown to avoid plot congestion.
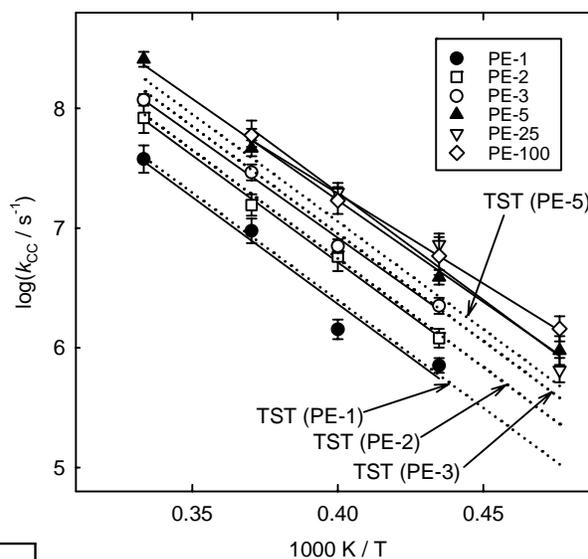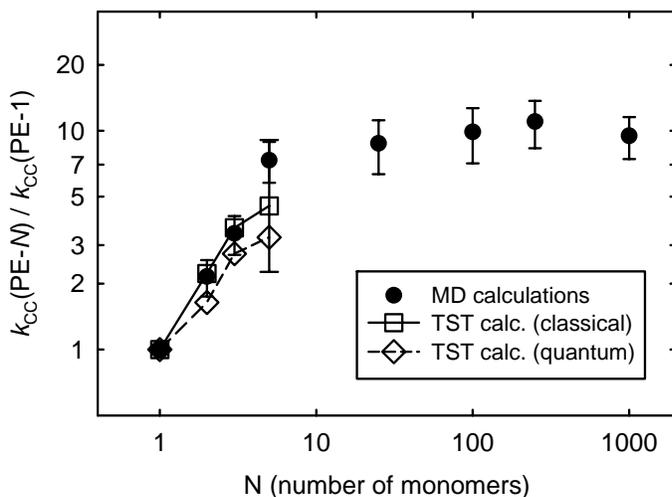
Figure 4. Dependence of the factor of acceleration of the C-C bond scission reactions (the average ratio of the per-bond rate constants obtained in simulations of PE-N decomposition to those of PE-1) on the alkane or polyethylene chain length. VTST rate constants are not calculated for N > 5 because of large uncertainties. Estimated uncertainty of classical VTST calculations is shown for PE-5 only.

III.4. Effects of Chain Conformation on Dissociation Rates

Even larger effects of reaction acceleration were found for macromolecules that were forced to remain in extended configuration by fixing the positions of the molecule ends. Three series of RMD calculations were performed for PE-250 molecules. In one of the series, the molecule was not restricted in any way and thus was free to undergo changes in configuration during molecular dynamics simulations.

In the second series, the distance between the terminal C atoms was fixed at 90% of its equilibrium value in extended PE-250 configuration. In the third series, this distance was kept at 100% of the equilibrium value. Such restrictions imposed on molecule configuration resulted in significant further increases in the per-bond rates of dissociation: by approximately a factor of 5 in the 90% extended chain case and approximately a factor of 50 in the 100% extended chain case (Figure 5). The restricted distance models bear similarity to condensed phase (polymer melt) situations where motion of polymer chains is limited by interactions with neighboring chains. In this respect, the observed effects of configurational restrictions resulting in increases in the chain dissociation rates may contribute to the rates of dissociation of polymers in their melts being larger than the reaction rates of similar (but smaller) hydrocarbons in the gas phase.

The observed increases in the per-bond rate constant with increasing chain length and with configurational restrictions imposed on the macromolecule were found to correlate with corresponding increases in average C-C bond lengths. Average C-C bond length values observed in molecular dynamics simulations were larger than the equilibrium value, even if harmonic (non-reactive) potential was used; the differences (up to 0.047 Å) increased with temperature and chain length. This correlation brings forth a hypothesis that the increases in reaction rates relative to the case of small molecules may be, at least partially, caused by the distortion of the effective potential for C-C dissociation due to chain elongation, as described by Crist et al.[7] and later by Hageman et al.[8] and Krisyuk.[9]

Figure 5. Per-bond rate constants k_{CC} for C-C backbone scission obtained in TST (dotted lines) and RMD (symbols and fitted solid lines) simulations. The plot shows the effect of restrictions imposed on chain motions: rate constants increase in the cases of chains forced to remain in 90% or 100% extended configurations.
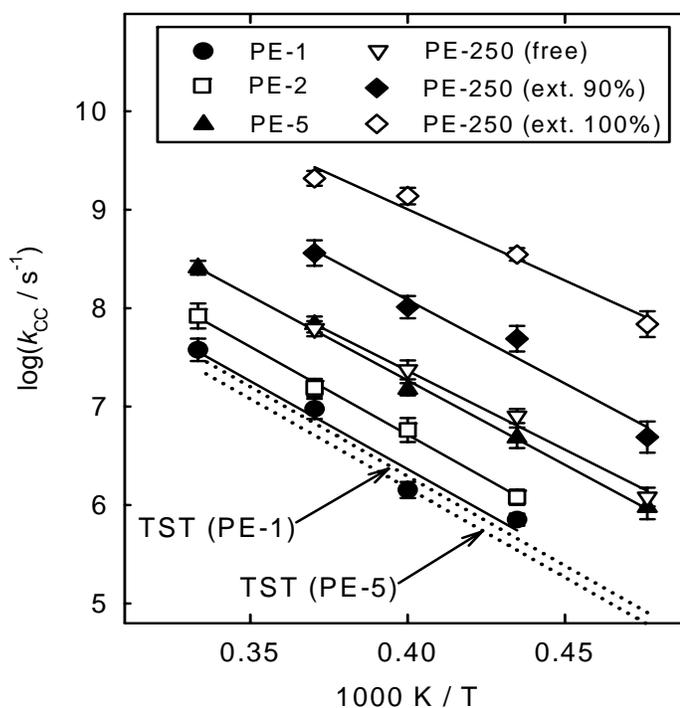
III.5. Reactions of C-C bond scission in polymer melt

Effects of macromolecular surroundings found under the conditions of polymer melt on the rates of carbon-carbon bond scission reactions were studied using computational molecular dynamics (MD). Calculations were performed using GROMACS program package with the all-atom OPLS-AA force field and Morse potential for the C-C bond stretches. Polyethylene macromolecules were used as model compounds. The results of the study demonstrate significant effects of the polymer melt surroundings on the reaction rates. Rate constants obtained under the condensed phase conditions are approximately an order of magnitude lower than those resulting from MD studies of decomposition of single molecules in the gas phase. The condensed phase rate constants display a strong dependence on the polymer melt density, with lower density resulting in larger rate constant values (Figure 6). The likely explanation of these effects lies in the activity of torsional motions of the macromolecule chains, which are impeded under the condensed phase conditions. These torsional motions and resulting centrifugal bond-stretching forces were observed to have significant effect on reaction rates in earlier gas-phase MD modeling performed in the current project.

Figure 6. Per-bond C-C dissociation rate constants obtained in molecular dynamics simulation of PE-500 decomposition.
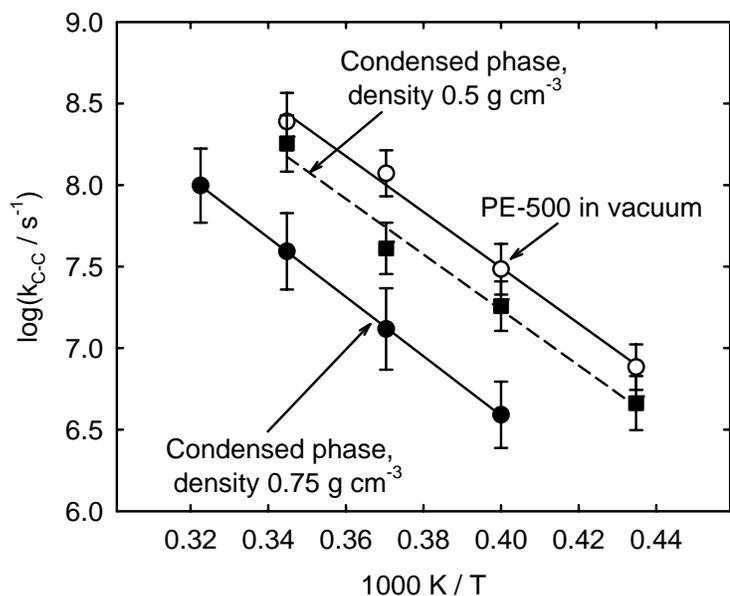
III.6.Radical isomerization and back-biting

MD simulations were performed for the reactions of radical isomerization ("back-biting"). Calculations performed for single small molecules in the gas phase result in good agreement between the rate constants obtained in MD simulations and in calculations performed using transition state theory. Modeling of the same type of reactions in long-chain molecules, both in the gas and in the condensed phase, are currently underway; these calculations will continue beyond the funding period of this grant. Reactions of H atom transfer between chains are also included in condensed phase modeling.

III.7. Experimental study of the initial stages of polyethylene pyrolysis.

The results of the computational studies of elementary reactions of polymer pyrolysis performed under this project lead us to attempt an experimental study of the initial (less that 1% conversion) stages of pyrolysis of polyethylene. These experiments are currently underway and will continue beyond the funding period of this grant.

Polyethylene samples are pyrolyzed at temperatures of 360 – 420 $^{\circ}$C under an atmosphere of nitrogen. The condensed phase is dissolved in carbon tetrachloride and analyzed using ^{1}H NMR. Application of NMR enables detection and differentiation of hydrogen atoms adjacent to double bonds in the condensed phase. The types of H atoms corresponding to different chemical shifts detected in reaction products are: R-C$\underline{\textbf{H}}$=CH$_2$, R-CH=C$\underline{\textbf{H}}_2$, R-C$\underline{\textbf{H}}$=C$\underline{\textbf{H}}$-R$_1$, R$_1$R$_2$C=C$\underline{\textbf{H}}_2$. Figure 7 displays a typical ^{1}H NMR spectrum of a sample dissolved in CCl$_4$, with the H atoms corresponding to different values of chemical shift identified. Figure 8 displays typical experimental time-dependences of the abundances of the different types of H atoms adjacent to double bonds.

The gas phase products are analyzed using GC/MS. Abundances of gas phase products are minor compared to those of double bonds in the condensed phase (~ two orders of magnitude difference). The main gas phase products observed are CH$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_4$.

Preliminary results of the experimental work are consistent with the following model of polyethylene pyrolysis:

- The rate constants of C-C bond scission are similar in values to those of gas-phase alkane decomposition (A $\cong$ 2×10^{16} s^{-1}, Ea $\cong$ 366 kJ mol^{-1}).
- Radical recombination rate constant is very low due to diffusional constraints: k $\cong$ 10^{-14}-10^{-13} cm^3 molecule^{-1} s^{-1}.
- Among radical reactions, H atom transfer dominates over beta-scission by approximately two orders of magnitude.
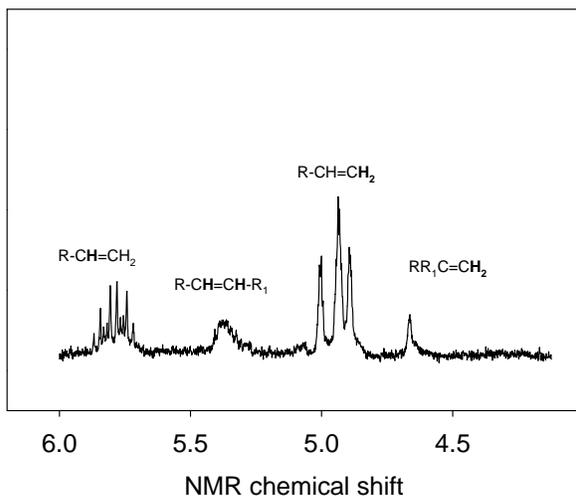
Figure 7. A typical ^{1}H NMR spectrum of a sample of the products of partial pyrolysis of polyethylene dissolved in CCl$_4$, with the H atoms corresponding to different values of chemical shift identified.
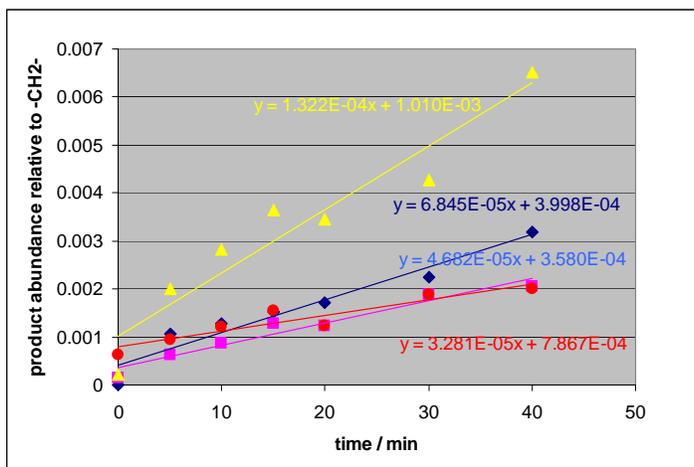
Figure 8. Typical time dependences of the abundances of the different types of H atoms adjacent to double bonds obtained in NMR analysis. Low-density polyethylene pyrolyzed at 411 $^{\circ}$C. Triangles: R-CH=C$\underline{\text{H}}_2$. Diamonds: R-C$\underline{\text{H}}$=CH$_2$. Squares: R-C$\underline{\text{H}}$=C$\underline{\text{H}}$-R$_1$. Circles: R$_1$R$_2$C=C$\underline{\text{H}}_2$.

IV. Significant findings

This section summarizes the findings described in the previous part of the report.

1. Effects of internal polymer strain and attractive dispersion forces on the potential energy surfaces of bond scission reactions.

2. Significant effects of alkane chain length on backbone dissociation rates. Per-bond rates of C-C bond dissociation increase with the increasing chain length.

3. Significant effects of polymer chain conformation on backbone dissociation rates. Per-bond rates of C-C bond dissociation increase (by orders of magnitude) in the cases where the motion of polymer chain ends is restricted.

4. Significant effects of polymer melt density on backbone dissociation rates. Per-bond rates of C-C bond dissociation are lower in the liquid phase compared to the gas phase by an order of magnitude. Lower polymer melt density results in larger rates for C-C bond dissociation.

5. Preliminary results of an experimental (ongoing) study of the initial stages of polyethylene pyrolysis can be described with a simple steady-state model consisting of several reactions and using rate constants obtained by analogy with the gas-phase kinetics of small molecules with the exception of a much slower radical recombination rate.

V. References

1. Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids . *J. Am. Chem. Soc.* **1996**, *118*, 11225-11236.

2. Benson, S. W. *Thermochemical Kinetics, 2nd Ed.*; John Wiley and Sons: New York, 1976.

3. Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell: Oxford, 1990.

4. Miller, H. W.; Handy, N. C.; Adams, J. E. Reaction path Hamiltonian for polyatomic molecules. *J.*

Chem. Phys. **1980**, *72*, 99-112.

5. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02* Gaussian, Inc.: Wallingford,CT, 2004.

6. Lindahl, E.; Hess, B.; van der Spoel, D. GROMACS 3.0: A package for molecular simulation and trajectory analysis. *J. Mol. Mod.* **2001**, *7*, 306-317.

7. Crist, B.; Oddershede, J.; Sabin, J. R.; Perram, J. W.; Ratner, M. A. Polymer Fracture - A Simple-Model for Chain Scission. *Journal of Polymer Science. Part B-Polymer Physics* **1984**, *22*, 881-897.

8. Hageman, J. C. L.; de Wijs, G. A.; de Groot, R. A.; Meier, R. J. Bond scission in a perfect polyethylene chain and the consequences for the ultimate strength. *Macromolecules* **2000**, *33*, 9098-9108.

9. Krisyuk, B. E. Reactivity of stressed molecules: calculation of the effect of chain deformation on scission for macromolecules and middle macroradicals. *J. Molec. Struc.-Theochem* **2004**, *677*, 77-83.

VI. Student participation

One CUA graduate student (Mr. Kostyantin Popov) participated in this research. Mr. Popov joined the CUA graduate program in Fall 2005.

VII. Publications

1. Vadim D. Knyazev. *Effects of Chain Length on the Rates of C-C Bond Dissociation in Linear Alkanes and Polyethylene.* J. Phys. Chem. A, 111, 3875 - 3883 (2007).

2. Marc R. Nyden, Stanislav I. Stoliarov, Vadim D. Knyazev. *Modeling the Thermal Decomposition of Large Molecules and Nanostructures*, in Multiscale Simulation Methods for Nanomaterials, Richard B. Ross, Sanat Mohanty, Editors, Wiley, 2008, pp 219-244. ISBN: 9780470105283

3. Konstantin V. Popov and Vadim D. Knyazev. *Molecular Dynamics Study of C-C Bond Dissociation in Linear Alkanes and Polyethylene: Effects of Condensed Phase*. Manuscript in preparation. Preliminary report was published as part of the proceedings of the Eastern State Fall Technical Meeting "Chemical & Physical Processes in Combustion," University of Virginia, Charlottesville, October 21-25, 2007, paper A-07.