Initial Stages of Pyrolysis of Polyethylene

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Combustion and flammability of plastics are important topics of practical interest directly related to fire safety and recycling of polymeric materials; pyrolysis of the solid is the initial step of its combustion. One of the main ways to study such complicated processes is through detailed mechanistic modeling, in which the process is represented by a set of many elementary chemical reactions. Mechanistic modeling of combustion of plastics, however, is considerably hindered by the lack of kinetic data necessary for the modeling. In virtually all existing models of polymer pyrolysis the majority of kinetic data used are derived from the corresponding gas phase values of smaller species due to the difficulty of experimental measurement of rate constants in a polymer melt. The use of gas phase rate constants is, generally, not justified without an experimental support for the values used.

In the first part of the work the influence of condensed phase on the rate of scission of a carbon-carbon bond (i.e., the chemical reaction that initiates the processes of pyrolysis and combustion) in polyethylene (PE) was studied using the method of Reactive Molecular Dynamics
A method based on the use of a two-step kinetic mechanism was developed to decouple the cage effect from the kinetics of the reaction under study. It was observed that under the conditions of condensed phase the rate constant of C-C bond scission in PE decreased by an order of magnitude compared to that obtained in vacuum. It was also shown that, unlike in vacuum, under the conditions of polymer melt the rate constant does not demonstrate any dependence on the length of the polymer chain.

In the second part of the current work the kinetics of liquid phase and gas phase products of PE pyrolysis was studied experimentally using the methods of Gas Chromatography and Nuclear Magnetic Resonance spectroscopy. Based on the assumption of applicability of gas phase kinetic data for C-C scission reaction (supported by the results of the RMD study conducted in first part of the work) and β-scission reaction under the conditions of polymer melt, rate constants of hydrogen transfer, radical addition to double bonds, and radical recombination were determined via kinetic modeling of the experimental results. The obtained values of the rate constants were found to be in reasonable agreement with the constants of similar reactions of smaller molecules in the gas phase.
This dissertation by Konstantin V. Popov fulfills the dissertation requirement for the doctoral degree in physics approved by Vadim D. Knyazev, Ph.D., as Director, and by Ian L. Pegg, Ph.D., Irene R. Slagle, Ph.D., and Stanislav I. Stoliarov, Ph.D. as Readers.

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1 LITERATURE REVIEW

1.1 EXPERIMENTAL STUDIES OF POLYETHYLENE PYROLYSIS AND ITS MECHANISTIC MODELING

The first attempts to study the pyrolysis of polymers were made in the first half of the 20th century. In 1940 Montroll and Simha (1) developed a theory of depolymerization of long chain molecules on a statistical basis assuming that all bonds are equally likely to be degraded. The authors derived expressions for the distribution of molecular sizes in the depolymerized system as a function of the initial chain length.

In 1949 Jellinek (2) studied the pyrolysis of polystyrene and polyethylene in vacuum at a constant temperature in the range 340-400°C via the thermogravimetric analysis method (TGA). The main object of the study was to ascertain the activation energies of the processes. The author found that the thermogravimetric curves reflecting the dependence of the sample’s weight loss on time are linear over a considerable time range, showing some slowdown in the later stages due to the sample’s exhaustion. It was also observed that polyethylene is more heat resistant than polystyrene and poly-α-methylstylene, an effect that was expected because of the weakening action of phenyl and methyl groups on the C-C bonds in the chain. Based on the fact that even after the weight loss of a polyethylene (PE) sample reaches 40%, the residue still consists of the polymer, the author concluded that PE does not depolymerize during pyrolysis via random breaking of carbon-carbon bonds, in a fashion proposed earlier by Montroll and Simha (1).
However, the author found that the mechanism developed in the same article for polystyrene in which the molecules of the monomer break off from the chain one after another to be also incompatible with the experimental results for PE. Further, Jellinek suggested a mechanism in which, once the first or the last monomer unit gets broken off the chain, the chain falls apart completely by loosing monomer units in rapid succession. He described the kinetics of this mechanism with the following equation:

\[- \frac{dg}{dt} = kg, \quad \text{(Eq. 1.1)}\]

where \( g \) is the number of chain ends in the sample and \( k \) is the rate constant. The solution of this equation is

\[ g = g_0 e^{-kt} \quad \text{(Eq. 1.2)} \]

with \( g_0 \) denoting the initial number of chain ends. If \( P_0 \) represents the initial average chain length, the number of monomer molecules, \( n_{\text{mon}} \), can be determined from

\[ \ln \left( 1 - \frac{n_{\text{mon}}}{P_0} \right) = -kt. \quad \text{(Eq. 1.3)} \]

The proposed mechanism was found to describe the experimentally obtained weight loss curves well. The author, however, admitted that viscosity measurements would be necessary to evaluate the correctness of the mechanism.

In 1949, Oakes and Richards (3) experimentally studied the process of the thermal degradation of polyethylene (PE) by heating the polymer both in vacuum and in the atmosphere of nitrogen at atmospheric pressure. The authors estimated the average molecular weights of
pyrolyzed samples from the intrinsic viscosities of the samples. The viscosities of the samples dissolved in tetralin were measured at 75°C. The chemical structure of the pyrolyzed samples (particularly, the abundances of double bonds) was studied using a modification of the Wijs iodine method (4), quantitative hydrogenation in decalin solution in the presence of Adams’s platinum oxide (5), and infra-red absorption spectroscopy. The pyrolysis experiments were conducted over the temperature range 295°C to 360°C for a duration of up to 40 hours.

The authors discovered that in the absence of oxygen, PE is stable at temperatures up to 290°C, but at higher temperatures its molecular weight starts decreasing. The products of mild degradation are plastics similar to the original PE or hard waxes. More extensive degradation produces semi-solid pastes or liquid products, but gaseous products are not yielded in any considerable quantities below 370°C. At the temperatures when gaseous products are produced in appreciable amounts, however, the monomer (ethylene) constitutes only a small fraction of them, unlike in the case of pyrolysis of such polymers as polystyrene, where the monomer is produced in very large amounts (2).

Based on the changes in the average molecular weight, the authors expressed the amount of degradation in terms of the number Q of broken polymer carbon-carbon links:

\[ Q = N_A \left( \frac{1}{M_t} - \frac{1}{M_0} \right), \tag{Eq. 1.4} \]

where \( M_0 \) and \( M_t \) are respectively the initial and the final average molecular weights and \( N_A \) is the Avogadro’s number. It was found that the reaction rate decreases as the degree of degradation increases. According to the authors, this observation could be explained by the fact that the
molecules yielded during pyrolysis are more stable than the initial long chains, or, alternatively, by the presence of a number of some weak links in the chain.

During the analysis of the products of pyrolysis, it was found that the products closely correspond to the empirical formula \((\text{CH}_2)_n\) of polyethylene itself. However, the degree of unsaturation changes significantly. The average number of double bonds per molecule stayed close to 1.0 for the bulk of the samples at all stages of degradation. The nature of double bonds was analyzed using infra-red absorption spectroscopy. Vinyl (\(\text{RCH} = \text{CH}_2\)), vinylene (\(\text{RCH} = \text{CHR}_1\)), and vinylidene (\(\text{RR}_1\text{C} = \text{CH}_2\)) groups were identified in the pyrolyzed samples. As for the dynamics of propagation of double bonds, it was observed that in the early stages of pyrolysis all three types of double bonds are formed, but when the average molecular weight decreased below about 1000, virtually no formation of new double bonds was observed, other than those in vinyl groups.

The authors also studied the dependence of the rate of rupture of C-C bonds in samples with different initial intrinsic viscosity (and, therefore, different average molecular weight) at various temperatures up to 360°C and observed the rate growth with the decrease of the initial molecular weight. This observation appeared to contradict the hypothesis that the deceleration of conversion with time occurs due to the increased stability of pyrolysis products compared to the initial polymer chains. In order to analyze the hypothesis about the crucial role of weak links in the pyrolysis initiation, they formulated a simple kinetic scheme that described the process of decay of chain links as a scission of two separate link types: the normal ones (the number of which in a sample can be denoted as \(n\)) and the weak ones (whose number is \(w\)). Under the assumption
that the rates of rupture of each type of link is proportional to the number of such links, the scheme could be formulated as a system of differential equations:

\[- \frac{dw}{dt} = k_w w; \quad (Eq. 1.5)\]

\[- \frac{dn}{dt} = k_n n , \quad (Eq. 1.6)\]

where \( t \) is time and \( k_w > k_n \). The total number of links of each type broken after time \( t \) can be expressed in terms of the initial chain length \( P_0 \) and the original fraction of weak links \( \alpha \):

\[ S_w = \alpha P_0 - w, \quad (Eq. 1.7) \]

\[ S_n = (1 - \alpha) P_0 - n. \quad (Eq. 1.8) \]

Thus, the total fraction of broken bonds \( S_T \) is

\[ \frac{S_T}{P_0} = \frac{S_w + S_n}{P_0} = 1 - e^{-k_n t} + \alpha e^{-k_n t} - \alpha e^{-k_w t}. \quad (Eq. 1.9) \]

The authors attempted to fit kinetic curves obtained at 315°C and 360°C with this expression for \( S_T/P_0 \) (Equation 1.9) but found that the fraction of weak links \( \alpha \) needed to be different for each temperature. They then supposed that the pyrolysis proceeds via a chain reaction initiated by the decay of a weak link. Then the effective value of \( \alpha \) would be equal to some initial concentration of weak links \( \alpha_0 \) multiplied by the kinetic chain length \( \eta_T \) (6) at the particular temperature of pyrolysis. The authors further speculated that since ethylene polymers are thermally unstable at temperatures as low as 290°C, whereas such alkanes as hexadecane are stable at 390°C (in the absence of a catalyst), the normal -CH\(_2\)-CH\(_2\)- links could not be counted as centers of
pyrolysis. The authors suggested that C-C bonds adjacent to carbonyl (RRC=O) or other oxygen-containing groups originating from the catalyst may serve as centers of pyrolysis initiation. As other potential weak links the authors suggested the C-C bonds adjacent to branching sites or impurities in the monomer. Thus, they proposed a scheme for the initiation of pyrolysis in which the decomposition starts at a carbonyl group by producing a primary alkyl radical, which, in turn, abstracts a hydrogen atom from a saturated chain:

\[
\text{(Rxn. 1.1)}
\]

(here * denotes a radical site, R, R1, and R2 are different alkyl radicals).

The secondary radical produced can fall apart producing a primary radical and an olefin:

\[
\text{(Rxn. 1.2)}
\]

(here R2 denotes a primary alkyl radical, H atoms are understood).

According to the authors, it is possible that depolymerization can mainly propagate through branching sites, the concentration of which in their PE samples they estimated as about one for every 50 carbon atoms:

\[
\text{(Rxn. 1.3)}
\]

(here, only the transferred H atom is shown explicitly, other hydrogens are understood).
The decay of the produced secondary radical can yield different types of double bonds:

\[
\begin{align*}
R_1R_2^*R_3 & \rightarrow R_1R_2 + 'R_3 \\
(Rxn. 1.4)
\end{align*}
\]

\[
\begin{align*}
R_1R_2^*R_3 & \rightarrow R_1R_2R_3 + 'R_2 \\
(Rxn. 1.5)
\end{align*}
\]

It is known that the hydrogen atoms on tertiary carbon atoms are more easily abstracted by radicals than those on secondary atoms (7). If the hydrogen is removed from a tertiary carbon atom, the tertiary radical can fall apart according to the following scheme:

\[
\begin{align*}
R_1R_2^*R_3 & \rightarrow R_1R_2 + 'R_3 \\
(Rxn. 1.6)
\end{align*}
\]

This scheme explains reasonably the fact that the concentrations of vinylene and vinylidene groups grow during the initial stages of the pyrolysis, since the abstraction of H atoms occurs more easily at branching sites. At the later stages, however, when the weak links (branching sites) are mostly consumed, the growth of vinylene and vinylidene groups ceases. The production of vinyl groups (originating mostly from the decay of secondary radicals with the radical site away from possible branching points), was observed at the later stages of pyrolysis as well.

In 1954 Madorsky (8) studied the thermal degradation of linear polyethylene in an evacuated molecular still over the temperature range 393 – 449°C. The pyrolysis experiments were conducted as follows: a polymer sample was preheated at 160°C for 1.5 hr to reject possible traces of volatiles. The sample was then heated to the desired pyrolysis temperature in the above-mentioned range; the duration of the heating process was 45 min. The experiment at constant
temperature lasted 30 min. As a result of the experiment, the following fractions were obtained:
fraction I, a residue (except when pyrolysis was conducted to completion); fraction II, volatile at
the pyrolysis temperature; fraction III, volatile at room temperature; fraction IV, not condensable
at the temperature of liquid nitrogen. Fraction III, in some cases, was separated by molecular
distillation at -80°C into a more volatile fraction IIIA and a less volatile fraction IIIB. During
pyrolysis PE yields mostly fraction II. Fraction IV yielded less that 0.1 % by weight of the polymer
sample, was analyzed in a mass spectrometer, and found to consist of hydrogen, air, CO, and CO₂.
Fraction III was also analyzed using the mass spectrometric method and was found to be a mixture
of saturated and unsaturated hydrocarbons with the number of carbon atoms in a molecule ranging
from 2 to 12.

A mechanism of thermal decomposition of short linear alkanes in the gas phase was
suggested by Rice and Rice (7). The mechanism involved formation of free radicals and abstraction
of hydrogen atoms by the radicals. This kinetic scheme was expanded onto pyrolysis of polymers
in the condensed phase by Simha and Wall (9). The scheme involved the following steps:

(a) *Initiation*. A unimolecular rupture of a C-C bond in the polymer chain:

\[
\begin{array}{c}
\text{R} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{R} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\end{array} \xrightarrow{\text{Rxn. 1.7}} \quad \begin{array}{c}
\text{R} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{R} \quad \text{H} \quad \text{H} \\
\end{array} + \begin{array}{c}
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\end{array}
\]

(here * denotes a carbon atom with an unpaired electron, and R is a long linear alkyl radical; the
breaking bond is crossed by two dashes).
Reaction 1.7 is the only reaction path by which free radicals can be produced in the bulk of a polymer.

(b) Propagation. This process is also referred to as unzipping, which in the case of PE is a special case of β-scission – a process during which a C-C bond breaks between the second and the third carbon atoms from the radical site. The Propagation step consists of the decay of a radical produced during the initiation step releasing of a molecule of the monomer (ethylene) and a shorter free radical:

\[
\text{(Rxn. 1.8)}
\]

(c) Free-radical transfer. This step can be both of the intermolecular and the intramolecular type. In the intramolecular type the H atom is abstracted by a radical from its own chain, while in the intermolecular type a free radical abstracts an H atom from another chain, as shown in the equation below (here the H atom marked by # sign is being transferred to the radical site of the primary long chain radical):

\[
\text{(Rxn. 1.9)}
\]

This process is a two-step process that consists of H abstraction followed by β-scission. In the Simha and Wall’s work, however, it is represented by a one-step process.
(d) **Termination.** This step occurs when two free radicals recombine and form a single covalent bond and, therefore, a polymer chain:

\[
2 \text{ radicals} \rightarrow 1 \text{ polymer chain} \quad \text{(Rxn. 1.10)}
\]

Madorsky ([10](#)) noted that the fate of a free radical that appears during the initiation reaction will be determined by two competing reactions: (i) propagation leading to the yield of monomer molecules, and (ii) transfer of H atoms followed by β-scission resulting in formation of saturated and unsaturated chain ends and a new free radical, as shown in the scheme in step (c) of Simha’s mechanism. Madorsky found that this mechanism provides a satisfactory explanation for the low yield of the monomer in the case of polyethylene degradation, but at the same time he questioned why the free radical does not undergo an unzipping process in the period between its production and the hydrogen transfer reaction. According to Madorsky’s opinion, the unzipping of the free radical would lead to a larger yield of monomer than was observed experimentally by Madorsky and Straus ([8](#)). In order to explain this, Madorsky evoked the mechanism described by Staudinger et al. for the decomposition of polystyrene ([11](#)). According to the Staudinger’s mechanism, most of the scissions of C-C bonds occur due to strains caused in polymer chains by thermal excitation. The scissions are accompanied by H transfer at the scission site in the case of polymers where hydrogen is abundant on the chains (such as PE); such H-transfer reactions are also known as disproportionation of radicals. An example of such a two-step process is Reaction 1.11 (the H atom marked by # sign is being transferred to the C atom marked by # sign):

\[
\begin{array}{c}
\text{R} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{R} \quad \text{H} \quad \text{H} \\
\text{R} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{R} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{R} \\
\end{array} + \begin{array}{c}
\text{R} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \\
\end{array}
\quad \text{(Rxn. 1.11)}
\]
This mechanism does not require formation of free radicals that could fall apart producing monomers.

Madorsky (10) proposed visualizing the process of thermal scission of polymers as follows. A polymer molecule, unlike a molecule of a shorter ordinary alkane, responds to the input of thermal energy not as a unit but in parts, so that some parts get more thermal energy (appearing in the form of vibrational, rotational, and translational motions) and some parts get less. At the same time the motions of the parts of polymer molecules are restricted due to the molecules’ size and the surrounding environment. This produces strains in the backbones of the molecules, that, in turn, cause scissions. In the case of a polymer abundant in hydrogen, such as PE, the scissions are accompanied by abstraction of H atoms from a carbon adjacent to the breaking C-C bond (known as the β-position).

In 1968 Tsuchiya and Sumi (12) studied the products of the thermal decomposition of linear polyethylene, which was pyrolyzed at 437°C for 20 min using an experimental apparatus similar to that used by Madorsky (8). The weight of the residue was 92.5%; the lighter products of C1 to C16 hydrocarbons totaling 2.5 wt % were analyzed using gas chromatography. The remainder, which was collected in a trap, was assumed to consist of compounds larger than C16 and was not analyzed. The authors provided mole percentages of three types of products – n-alkanes, 1-alkenes, and alkadienes – plotted against the number of C atoms in a molecule. The graphs have well expressed peaks at 3, 7, and 11 carbon atoms for n-alkanes, and 3, 6, and 10 carbon atoms for 1-alkenes. According to the authors, the high abundances of these compounds can be explained by introducing the backbiting reaction (also referred by the authors as “coiling”). The backbiting
reaction represents an intramolecular radical transfer, when a primary alkyl radical turns into a secondary radical by transferring a hydrogen atom from the middle of the chain to the end where the radical site was. Thus, after the radical site migrates from the first C atom to, e.g., the fifth, the secondary radical produced can decay by a $\beta$-scission mechanism releasing either a propyl radical and a long chain olefin or 1-hexene and a long alkyl radical:

$$\text{•CH}_2\text{-CH}_2\text{-CH}_2\text{-R} \rightarrow \text{CH}_3\text{-(CH}_2)_3\text{-CH(•)-CH}_2\text{-R} \rightarrow$$

$$\text{n-C}_3\text{H}_7\text{• } + \text{CH}_2\text{=CH-CH}_2\text{-R} \quad \text{(Rxn. 1.12)}$$

$$\text{•CH}_2\text{-CH}_2\text{-CH}_2\text{-R} \rightarrow \text{CH}_3\text{-(CH}_2)_3\text{-CH(•)-CH}_2\text{-R} \rightarrow \text{n-C}_6\text{H}_{12} + \text{•R} \quad \text{(Rxn. 1.13)}$$

(in these two reactions the first step is the intramolecular H transfer and the second step is the decomposition of the secondary radical; $R$ denotes an alkyl radical, (•) is the radical site).

The authors suggested that multiple peaks on the graphs indicate the occurrence of successive intramolecular radical transfer:

$$\text{•CH}_2\text{-CH}_2\text{-CH}_2\text{-R} \rightarrow \text{CH}_3\text{-(CH}_2)_3\text{-CH(•)-CH}_2\text{-R}' \rightarrow \text{CH}_3\text{-(CH}_2)_7\text{-CH(•)-CH}_2\text{-R}'' \rightarrow$$

$$\text{CH}_3\text{-(CH}_2)_{11}\text{-CH(•)-CH}_2\text{-R}'''. \quad \text{(Rxn. 1.14)}$$

In a manner similar to the scheme described above (Reactions 1.12 and 1.13), the secondary radicals produced as a result of successive backbiting reactions can decay producing correspondingly longer radicals and alkenes.

A large amount of 1-hexene (the result of the decay of the secondary radical produced by the radical transfer from the first to the fifth carbon atom) was also found in independent studies.
of the thermal cracking of n-hexadecane by Voge and Good (13) and Fabuss et al. (14). suggested that the intramolecular radical transfer from the first to the fifth carbon occurs with the greatest ease; a subsequent transfer from the fifth to the ninth position should also be easier than to the neighboring eighth or tenth positions. However, the authors expected the rate of the successive (secondary to secondary radical) transfer to be much lower than that of the initial (primary to secondary radical) transfer. They also considered three different mechanisms for the hexadecane degradation: (i) via C-C bond scission followed by disproportionation (the authors referred to it as “simultaneous saturation and unsaturation”), (ii) via intermolecular radical transfer followed by β-scission, and (iii) via the intramolecular radical transfer followed by β-scission. These three mechanisms are expected to produce different mole ratios of n-alkanes, 1-alkenes, and alkadienes: 1:2:1 in the case of the first mechanism as the predominant one, (1- α)²:2(1- α):1 in the case of the second one, and (1- α):1:0 in the case of the third one (here α is the fraction of n-alkane radicals consumed in steps other than H abstraction). Since the molar percentage of the alkadienes produced during PE pyrolysis in the course of their work was less than 0.1%, the authors concluded that intramolecular radical transfer (mechanism (iii)) is the predominant mechanism in the thermal decomposition of PE.

In 1968 Michajlov et al. (15) used a flash pyrolysis apparatus coupled with an in-line gas chromatograph to investigate the block structure of high-density polyethylene (HDPE) and low-density polyethylene (LDPE). The main structural difference between the two kinds of PE is the degree of branching: HDPE’s degree of branching is low, which determines its inclination to pack into crystalline structures; the degree of branching of LDPE is high, which means that the chains do not pack into crystalline structures as well. The authors pyrolyzed the polymers at 680ºC, which
provided rapid and complete decay of the samples. It was found that during pyrolysis LDPE and HDPE produce very similar fragments with the differences mainly in the relative concentrations of individual compounds: the abundance of branched isomers produced during the pyrolysis of LDPE is two to three times higher than those obtained from HDPE. It was also observed that LDPE produces more n-C3, n-C4, and n-C5 products (alkanes and olefins), whereas HDPE shows higher abundances of the fragments with carbon number 10 and above. According to the authors, this fact can be explained by the higher abundance of tertiary C atoms in LDPE and, therefore, higher abundances of pendant side alkyl groups with 3, 4, or 5 C atoms that tend to break off. They also discovered that fragments with the numbers of carbon atoms up to 50 can be detected among the products of pyrolysis for both types of polyethylene. A few pyrolysis experiments were conducted at higher (780°C and 920°C) temperatures, and it was observed that higher temperatures favor the yield of more short-chain fragments.

In 1982 Dickens (16) studied the pyrolysis of LDPE and HDPE in vacuum and in nitrogen flow using the method of factor-jump thermogravimetry (17) in an attempt to determine the apparent activation energies of the process. The degradation was conducted in a series of short isothermals (2-7% of weight loss per one isothermal) with the rates of degradation from 0.55 to 3 μg sec⁻¹. The pyrolysis experiments were conducted in the temperature range 410-475°C. The apparent overall activation energy of the pyrolysis process was found to be 65.4 ± 0.5 kcal mol⁻¹ for both LDPE and HDPE.

In order to describe the results of the experiments, Dickens developed a mechanistic description of the pyrolysis process, the crucial steps of which are similar to those of the
mechanisms that had been developed before (3), (10). In the author’s notation (P_n represents H(CH_2)_n, E’ is a primary radical; B’ is a secondary radical; I is an initiating group; S’ is a small radical able to produce volatile products by abstraction of H, R’ is an alkyl radical that can be primary or secondary.), the reaction scheme can be written as a sequence of the next steps:

\[ P_nH \rightarrow P'_m + P'_{n-m} \text{ (random backbone scission, rate constant } k_r) \]  \hspace{1cm} (Rxn. 1.15)

\[ (E') \hspace{1cm} (E') \]

\[ P'_m + P_nH \rightarrow P_mH + R' \text{ (hydrogen abstraction, rate constant } k_H) \]  \hspace{1cm} (Rxn. 1.16)

\[ (E' \text{ or } S') \hspace{1cm} (B') \]

\[ R'_n \rightarrow P_{m-2-CH=CH_2} + P'_{n-m} \text{ (} \beta \text{-scission of chain, rate constant } k_s) \]  \hspace{1cm} (Rxn. 1.17)

\[ (B') \hspace{1cm} (I) \hspace{1cm} (E') \]

\[ P'_n + P'_m \rightarrow P_{n-2-CH=CH_2} + P_{n-2-CH_2-CH_3} \text{ (disproportionation, rate constant } k_t) \]  \hspace{1cm} (Rxn. 1.18)

\[ (E') \hspace{1cm} (E') \]

\[ P_{n-CH=CH_2} \rightarrow P'_{n-1} + 'CH_2-CH=CH_2 \text{ (end initiation next to allylic group, rate constant } k_e) \]  \hspace{1cm} (Rxn. 1.19)

\[ (I) \hspace{1cm} (E') \hspace{1cm} (S') \]

The author derived kinetic equations for the concentrations of the radicals based on the mechanism described above using the following assumptions: (a) the initiation occurs only at the olefinic chain ends (it has to be noted that even though the author mentioned the reaction of random
backbone scission in his reaction scheme, he did not include this process in his mechanistic
description of pyrolysis process); (b) there is no influence of the change of the concentration of
the initiation groups with time; (c) the weight loss occurs only due to the scission of radicals; (d)
S’ radicals produce volatile products with a rate constant $k_v$, (e) termination is only by E’ radicals.
The rate of production of volatiles is given by

$$\frac{d[\text{volatiles}]}{dt} = \alpha k_s[B^*]$$

(Eq. 1.10)

(here $\alpha$ is a temperature-independent proportionality coefficient that takes into account the
probability that some of the scissions produce nonvolatile molecules).

Applying the steady-state approximation (6) to the concentrations of B’ and E’, one obtains:

$$\frac{d[B^*]}{dt} = k_h[E^*][PH] + k_h[S^*][PH] - k_s[B^*] = 0,$$

(Eq. 1.11)

$$\frac{d[E^*]}{dt} = k_e[I] + k_s[B^*] - k_h[E^*][PH] - k_t[E^*]^2 = 0,$$

(Eq. 1.12)

and

$$\frac{d[S^*]}{dt} = k_e[I] - k_h[S^*][PH] - k_v[S^*] = 0.$$

(Eq. 1.13)

From Equations 1.11 - 1.13 one can get the expressions for $[E^*]$, $[B^*]$, and the rate of
volatilization:

$$[E^*] = \frac{k_s[B^*]}{k_h[PH]},$$

(Eq. 1.14)
The author assumed Arrhenius behavior for each rate constant, making the expression for the apparent overall activation energy \( E \) of the degradation in terms of the activation energies of the component reactions

\[
E = E_H + \frac{1}{2} E_e - \frac{1}{2} E_t, 
\]  
(Eq. 1.17)

where the subscripts \( H \), \( e \), and \( t \) denote the \( H \) transfer, initiation next to the allylic group, and termination by disproportionation, respectively.

According to the author’s estimations based on the works of Benson (18), Kerr and Trotman-Dickenson (19), Kiang et al. (20), and Klein and Briscoe (21), the value of the activation energy for hydrogen abstraction by primary alkyl radicals (denoted as \( E_H \) above) exceeds that of hydrogen abstraction by secondary radicals by 6 to 20 kcal mol\(^{-1}\). Based on this estimation, the author proposed a kinetic scheme, where the primary radicals are proposed to be so reactive that they immediately abstract hydrogen atoms from the surrounding matrix of molten polymer, forming secondary radicals that, in turn, undergo \( \beta \)-scission or disproportionation. The corresponding kinetic equations with the steady-state approximation take the following forms:

\[
\frac{d[B^*]}{dt} = k_H[E^*][PH] - k_s[B^*] - k_e[B^*]^2 = 0
\]  
(Eq. 1.18)

and
\[ \frac{d[E^*]}{dt} = 2k_e[I] + k_s[B^*] - k_H[E^*][PH] = 0, \]  
(Eq. 1.19)

and their solutions are

\[ [B^*] = \sqrt{\frac{2k_e[I]}{k_t}} \]  
(Eq. 1.20)

and

\[ [E^*] = \frac{k_s[B^*]+2k_e[I]}{k_H[PH]}. \]  
(Eq. 1.21)

Then the kinetic equation for the mass loss takes the form

\[ \frac{d(\text{volatiles})}{dt} = \alpha k_S \sqrt{2[I] \frac{k_e}{k_t}} \]  
(Eq. 1.22)

and the expression for the overall activation energy becomes

\[ E = E_S + \frac{1}{2} E_e - \frac{1}{2} E_c. \]  
(Eq. 1.23)

Based on this equation and on the assumption that the initiation for the major part of the degradation is scission in the \( \beta \)-position with respect to the allylic group, Dickens estimated the activation energy of \( \beta \)-scission of secondary radicals to be 33 kcal mol\(^{-1} \). For the initial rates of pyrolysis in vacuum at temperatures below those used in his study, the author estimated the overall activation energy \( E \) to be 70.6 kcal mol\(^{-1} \). According to Dickens, the overall activation energies of 70.6 kcal mol\(^{-1} \) (estimated based on the mechanism described above) and 65.4 kcal mol\(^{-1} \) (experimentally observed by Dickens) are in fairly good agreement with those obtained by Madorsky (10). However, Dickens believes the newer values to be more reliable.
In 1997 Westerhout and coworkers (22) reviewed earlier TGA studies of polymer pyrolysis and conducted their own TGA experiments on polyethylene (both LDPE and HDPE), polypropylene, and polystyrene, as well as their kinetic modeling. Below, the details of the work concerning mostly the pyrolysis of polyethylene are reviewed.

Westerhout et al. critically analyzed earlier attempts to model TGA pyrolysis, such as the infinite number of parallel reactions model by Darivakis et al. (23), the weak bond model (3), consecutive reaction models (24, 25), and the Simha and Wall model (9) and found that the models have limited practical use because they do not describe the process of pyrolysis over a broad conversion range. The authors also found that the large number of unknown parameters that are necessary in order to achieve agreement between the model’s predictions and the experimental results are the main drawbacks for most of the aforementioned models. They also noticed that in most of TGA studies a standard power law model is used to describe the kinetics of pyrolysis, in which the mass m of the polymer changes with time according to the equation

$$\frac{dm}{dt} = -k_0 e^{-\frac{E_{act}}{kT}} m^n,$$

(Eq. 1.24)

where t is time, k0 is a preexponential factor, E_{act} is the activation energy of the process, and n is the order of reaction. Westerhout et al. warned that by using an apparatus such as TGA in kinetic studies, one determines not the intrinsic chemical reaction rate, but, in fact, the rate of evaporation of pyrolysis products, since not every bond scission leads to the formation of a product that is able to evaporate. Only small molecules are able to evaporate and therefore lead to the decrease of the polymer’s mass. Westerhout and coworkers pointed out that the kinetic parameters obtained using the simple power law model in earlier TGA studies can differ by an order of magnitude. Even
though such differences may appear due to the use of different types of PE and to the influence of the initial molecular weight, as well as to experimental errors, the authors described the use of the simple power law model as probably the most important reason for the observed differences in the kinetic parameters. Westerhout et al. asserted that the power law model is only applicable over a rather narrow conversion range (70-90%, according to the authors’ estimation, see below). Despite its narrow range of applicability, the power law model was used by many authors over a much broader range.

In their original work Westerhout et al. created two kinetic models: the simple empirical first-order power law model used to interpret the experimental TGA data and the Random Chain Dissociation (RCD) model that describes the kinetics on a more fundamental basis. The latter model implements a statistical reaction pathway approach that was used for the description of the kinetics of pyrolysis of lignin by McDermott and Klein (26). This model takes into account both chemical and physical processes occurring during pyrolysis. In this model different types of C-C bonds (at branching sites and in the non-branched parts of the chain) are given different scission rates with corresponding rate constants. The higher scission rate constants are assigned to those bonds that connect carbon atoms with side chains attached since the decay of those bonds leads to the formation of more stable (compared to alkyl primary radicals) secondary radicals. In order to keep the number of fitted parameters in their model low, the authors implemented a rather simple reaction scheme that does not include intramolecular, intermolecular, or cyclization reactions. They found that their RCD model combines the most relevant features of the models that had been proposed in other studies but keeps the number of fit parameters low. According to the authors, their RCD model does not just describe the rate of evaporation during TGA experiments but also
takes into consideration the difference between the evaporation and C-C scission rates, as Simha and Wall did in their model (9). The RCD model also accounts for the influence of weak bonds, as Oakes and Richards did (3). Westerhout and coworkers conducted their own rigorous TGA study of pyrolysis of HDPE and LDPE in the temperature range between 400 and 450°C under isothermal conditions and modeled the results with both the first-order model and the RCD model. They found that the first-order model fits the experimentally observed dependence of the conversion rate versus conversion well only at higher degrees of conversion (70-90%), whereas the RCD model qualitatively describes the dependence reasonably well over a much wider range of conversion (10-90%). They warned, however, that due to the fact that TGA experiments can be conducted only over a relatively narrow range of temperatures (about 50°C), one should expect a considerable mutual dependence of the preexponential factor and the activation energy (the kinetic compensation effect (16)). Due to this mutual dependence, the authors concluded that the activation energies for the pyrolysis process are on the order of 200 kJ mol\(^{-1}\) and the preexponential factors are on the order of 10\(^{-13}\) s\(^{-1}\). Another observation revealed that branching has a considerable effect on the reaction rate: a higher degree of branching leads to a higher conversion rate due to the fact that the formation of more stable secondary and tertiary radicals is more likely in branched polymers. It was also observed that the influence of the initial molecular weight distribution on the conversion rate is negligible (which seems to contradict the earlier observation made by Oakes and Richards (3)). The authors supported this observation by a closer analysis of the literature data. They also found that the influence of β-scission on the conversion rate can be considered as negligible since their RCD model does not take it into account but still fits the experimental results well.
A more detailed kinetic study of the pyrolysis of polyethylene and polypropylene was reported by Ranzi et al. (27). In this work they created a kinetic pyrolysis scheme that included initiation (C-C scission), H-abstraction, β-scission, and radical recombination reactions. The authors speculated that the kinetic parameters of the above-mentioned reactions should not differ from those of similar reactions that take place in the gas phase between short alkanes and alkyl radicals. They implemented gas-phase kinetic parameters in their mechanism, that provided analytical solutions to kinetic equations for the concentrations of the polymer molecules \( P_n \), olefin molecules \( O_n \), and \( \alpha,\omega \)-dialkene species \( D_n \), where \( n \) is the degree of polymerization. The results of the calculations were compared with the experimental data obtained from thermogravimetric analysis of PE pyrolysis available in the literature ((28), (29)), as well as obtained in the course of the original study by Ranzi and coworkers. They conducted a series of thermogravimetric experiments measuring the dynamics of weight loss of samples subject to well defined heating conditions (5 – 20°C min\(^{-1}\)) in a nitrogen atmosphere. The experiments lasted until the Residue Weight Fraction reached zero, i.e., the entire PE sample was converted into volatile products. The results of the modeling are in good agreement with the experimental data; however, only the Residue-Weight-Fraction dependence on temperature was modeled using the kinetic mechanism. No data were provided for the modeling of kinetics of particular chemical compounds.

In a subsequent work by the same group (30) the mechanism was improved by introducing a more detailed treatment of backbiting reactions into the kinetic scheme. The following figure
shows an example of a 1,4 intramolecular hydrogen shift (R denotes a long alkyl radical, * is a C atom with a radical site, H atoms are understood):

![Diagram of 1,4 intramolecular hydrogen shift](image)

(Rxn. 1.20)

Similar schemes are provided for 1,5- and 1,6-isomerization reactions. The authors pointed out that, from an energy point of view, the 1,4-hydrogen transfer is less favorable than the 1,5- and 1,6-transfer due to some extra strain energy. On the other hand, from an entropy point of view, the 1,4-transfer is more favorable compared to 1,5- and 1,6-transfer because a smaller number of rotors must be blocked for the transition cyclic structure to be formed. The authors also took into account successive H-transfer reactions that can occur in secondary radicals. According to them, the most probable successive intramolecular hydrogen abstraction mechanism is 5,9- followed by 9,13-transfer. In the course of the study a series of isothermal (500°C and 600°C) flash pyrolysis experiments was conducted. A weighed amount of PE was placed in a small quartz tube and pyrolyzed at in the flow of helium for up to 15 sec, which was sufficient for the complete conversion of the sample into volatile products. The pyrolizer was connected to a gas chromatograph that permitted measuring the abundances of particular products of pyrolysis. The agreement with the results of the mechanistic modeling (particularly, the distribution of molar fractions of volatile alkenes among the products of pyrolysis) was found to be very good.

A very thorough reexamination of the data on the pyrolysis of polyethylene is provided in the work by Poutsma (31). The free-radical pyrolysis mechanism presented in the article consists of six types of reactions:
1. initiation by a scission of a C-C bond producing two primary radicals;
2. β-scission of a primary radical producing a C$_2$H$_4$ molecule and a shorter primary radical;
3. H transfer reaction between a primary radical and a saturated chain followed by β-scission of the produced secondary radical (this sequence is also referred to as random scission) that leads to the formation of a long-chain olefin and a new primary radical;
4. a “near-end” backbiting (1-x intramolecular H transfer, where x denotes the number of the C atom from which the H atom is being transferred) followed by β-scission of a secondary radical and resulting in the production of a volatile alkane or alkene;
5. intramolecular H transfer of 1-n type, where n >> x in type 4;
6. a group of termination reactions that includes the recombination processes between primary and/or secondary radicals, disproportionation reactions producing alkanes and alkenes, and evaporation of radicals from the melt.

Discussing the initiation stage of the process, Poutsma analyzed a hypothesis that weak-link scissions (scissions of allylic C-C bonds adjacent to unsaturation or at branching points) have a crucial role in the low-temperature PE pyrolysis onset. He came to the conclusion that for a typical high-density polyethylene (HDPE) with the fraction of tertiary or quaternary carbon atoms ~10$^{-3}$, homolysis at branching points is noncompetitive with homolysis of C-C bonds between secondary carbon atoms because the slight increase of the C-C scission rate at a branching site is nullified by the low concentration of the branching sites themselves. As for the role of allylic C-C bonds, Poutsma considered it not significant because the concentration of allylic bonds increases
with time during pyrolysis (16), whereas the weak links are expected to be rapidly consumed. He also considered the contribution of molecular disproportionation, during which an H atom from a C-H bond is donated to an unsaturated linkage to form two radicals. Even though the significance of this reaction is recognized in the thermal decay of olefins and aromatics, Poutsma inferred that in the thermal decay of HDPE it is of secondary importance.

In the discussion of the later stages of the pyrolysis mechanism, Poutsma criticized the common assumption that the major termination species of the process are primary radicals. According to his estimations, the concentration of secondary radicals appearing in the system due to H transfer reactions must be greater than that of primary radicals, so their recombination should be the dominant termination process. It was also concluded by Poutsma that steps 3 (H transfer followed by β-scission) and 4 (near-end backbiting followed by β-scission) of the mechanism are the obvious sources of terminal vinyl groups in the degrading polymer; however, no fully satisfying mechanism exists to rationalize the formation of vinylene (RCH=CHR) and vinylidene (R₂C=CH₂) groups, the formation of which was observed by Oakes and Richards at 315-360°C (3).

In his work Poutsma conducted a computational modeling of the initial product distributions as a function of C atoms in a molecule at infinitesimal conversion over the temperature range 250–800°C. He assumed, as Faravelli and Ranzi had done (27, 30), that the estimates for propagation rate constants derived from small-molecule behavior in the gas phase can be transferred to the conditions of polymer melt (although Poutsma used newer values of the rate constants compared to those used by Faravelli and Ranzi). He admitted, however, that the evidence for this simplification is significant but not overwhelming. The results of the modeling
suggested that at the lower values of temperature (up to roughly 550°C) random scission totally dominates and only at higher temperatures do effective backbiting products emerge, along with the products of unzipping to an even lesser degree. Poutsma concluded that unzipping should be the least favored process at all T-values. The model also predicted that the distance of backbiting into the chain should decrease with increase of temperature. This conclusion is supported by experimental data for the flash pyrolysis of HDPE (15).

In 2008 Nemeth at al. (32) used tetracontane (C₄₀H₈₂) as a model for studying the pyrolysis of polyethylene. The authors constructed a kinetic scheme of the pyrolysis process similar to those suggested by Tsuchiya and Sumi (12), Ranzi and coworkers (27), and Faravelli and coworkers (30). The authors modeled the thermal degradation of tetracontane using a stiff differential equation solver and compared the modeled distribution of products to their experimental results of the pyrolysis of HDPE conducted at 500°C for 20 s in a pyrolyser coupled with a GC/MS instrument. They found that the model predicts an equimolar distribution of non-gaseous alkanes and alkenes with carbon numbers from 8 to 35 (The model also predicts exceptionally high molar ratios of C₃₆ and C₃₇ components, but those were admitted to be model artifacts due to the choice of tetracontane representing the polymer.). The experimentally observed distribution of non-gaseous products appears to be somewhat different from that predicted by the model, but in several carbon atom ranges, such as C₁₀-C₁₃, C₁₄-C₁₇, C₁₈-C₂₁, and C₂₂-C₂₈, the formation of 1-alkenes was characterized by the authors as quasi-equimolar. The authors mentioned that since the whole process of thermal degradation of the polymer is a long free radical chain process, the rate of recombination of radicals has no effect on the stationary radical concentrations (the contribution of recombination to the radical consumption was estimated as less than 0.01%). The concentrations
of the radicals are mainly determined by the consumption of the radicals in the reactions of chain propagation. The concentration of secondary alkyl radicals is significantly affected by the rate constant of $\beta$-scission since this is the only consumption reaction that is available to them. The reduction of the rate constant of $\beta$-scission is automatically followed by a corresponding rise of the stationary concentration of the radicals. The authors acknowledged that, due to the complexity of the system under study and the scarcity of available rate constants, their solution represents only a possible reaction mechanism. Their sensitivity analysis shows that, whereas the concentrations of alkanes and alkenes are more sensitive to the rate of $\beta$-scission, the concentrations of dienes mostly depend on the rates of H abstraction reactions.

In 2008 Kayacan and Dogan (33) studied the kinetics of the non-isothermal pyrolysis of HDPE and LDPE using TGA and analyzed the products of pyrolysis using Fourier-Transform Infrared Spectroscopy (FTIR) and $^1$H- and $^{13}$C-Nuclear Magnetic Resonance Spectroscopy (NMR) methods (34). During the pyrolysis PE samples were entirely degraded into gaseous and liquid fractions; only the liquid fraction was analyzed using FTIR and NMR. The FTIR method revealed the presence of aromatic and aliphatic C-H groups, aliphatic C-C bonds, methyl (CH$_3$), methylene (CH$_2$), carbonyl (C=O), carboxyl (COOH), and hydroxyl (OH) groups (the total percentage of all oxygen-containing groups was found to be about 7%). The $^1$H NMR analysis discovered the presence of aliphatic and aromatic H resonances occurring in 0-3 ppm and 4-8 ppm ranges, respectively (CDCl$_3$ was used as the solvent). Both regions contain multiple peaks of complicated structure, but the authors reported no attempts to assign any particular peaks to any specific structural elements or groups. Instead, they computed total integrals of both (aliphatic and aromatic) areas and estimated their ratio, thus obtaining the ratio of the number of aliphatic to the
number of aromatic hydrogen atoms in the liquid pyrolysis products. The ratio was found to be about 91:9 for LDPE and 92:8 for HDPE samples. The authors also conducted a similar $^{13}$C NMR study of the products and found that the ratio of aliphatic to aromatic carbon atoms was about 95:5 for LDPE and 93:7 for HDPE.

The most detailed mechanistic study of HDPE pyrolysis up to date is the work by Levine and Broadbelt (35). This work is also the first modeling study that presents the time evolution of specific HDPE pyrolysis products. The authors used the method of moments ((36), (37)) to fully capture the chain length distribution instead of tracking every possible chain in the system. The polymeric species were distinguished based on the structural characteristics of the chain that included saturated and unsaturated end groups, end-chain radicals, general mid-chain radicals, and specific mid-chain radicals with the radical site between the 2nd and 25th positions. Low weight molecular products (which included alkanes from methane CH$_4$ up to n-tricosane C$_{23}$H$_{54}$ and alkenes from ethylene C$_2$H$_4$ to 1-hexacosane C$_{26}$H$_{52}$) and radicals were tracked explicitly. The mechanism of HDPE pyrolysis was composed of the following reaction families:

1. bond fission
2. radical recombination
3. allyl bond fission
4. hydrogen abstraction by a radical
5. mid-chain $\beta$-scission
6. radical addition to a double bond
7. end-chain $\beta$-scission
8. disproportionation of two primary radicals
9. 1,4-hydrogen shift
10. 1,5-hydrogen shift
11. 1,6-hydrogen shift
12. 1,7-hydrogen shift
13. x,x+3-hydrogen shift
14. x,x+4-hydrogen shift
15. x,x+5-hydrogen shift.

The methodology used by Levine and Broadbelt to estimate the numerical values of rate constants was developed earlier by the same group during the study of polystyrene degradation (38). This method of estimation is based on the Evans-Polanyi (39) and Blowers-Masel (40) relationships and the group additivity method parameterized by Benson (18). For intra- and intermolecular H transfer Levine and Broadbelt used the frequency factors from the studies of Poutsma (31) and Faravelli (30) referred above, as well as from the work by Pfaendtner and Broadbelt (41).

In the Levine and Broadbelt's work the evolution of the products of PE pyrolysis was studied at degradation times of 30, 90, and 150 min at 420°C. The modeling results were compared with the results of the experimental pyrolysis of HDPE conducted by the same group earlier (42) during the study of the thermal degradation of pure HDPE and its mixture with 4-(1-naphthylmethyl)bibenzyl at 420°C. The experimental data for species with the number of carbon atoms in a molecule between 5 and 7 were either absent or considered by the authors as unreliable and therefore were excluded from comparison with the modeling results. The model results for the
molar yields of alkanes and alkenes with carbon numbers between 8 and 23 are within a factor of 1.35 of the corresponding experimental values, considered by the authors to be excellent agreement. As for the comparison of the experimental data and modeling results for the gaseous products (alkanes and alkenes with the number of carbon atoms up to 4), the agreement was found to be fair. The authors remarked that the determination of the concentrations of the gaseous products was more difficult than for the condensable products, possibly leading to less reliable experimental values. They also suggested that the poorer agreement between modeling and experiment for gaseous products could be explained by secondary gas phase reactions, such as the alkenes undergoing allyl bond fission forming shorter alkyl and allylic radicals. These radicals can, in their turn, form alkanes (particularly, methane and ethane) and propylene, both of which are underpredicted by the model at longer times.

Levine and Broadbelt also concluded that the unzipping pathway (reaction family 7) is of minimal significance compared to the backbiting (reaction families 9 to 15) and random scission (the reactions of family 4 followed by the reactions from family 5). The net rate of random scission turned out to be about 10 times higher than that of backbiting.

1.2 REACTIVE MOLECULAR DYNAMICS STUDIES OF PYROLYSIS OF POLYETHYLENE

One of the computational methods of studying complex chemical systems that is currently gaining popularity is Reactive Molecular Dynamics (RMD) (43). Unlike conventional Molecular Dynamics methods, the algorithms of RMD allow chemical reactions to occur, i.e., allow breaking and making bonds. The RMD methods can be divided into two categories: those based on a
reaction cutoff distance and those based on reactive empirical force fields (43). The methods from the first category are usually implemented in studies of mechanical properties of materials, such as density, elasticity, thermal expansion coefficients, etc. (see, for example, (44), (45)). The cutoff distance methods do not use any information on the potential energy surface, which makes them much less suitable for studying the dynamics of chemical reactions than the reactive force field methods from the second category. The attention of this review will be focused on the reactive force field RMD methods.

A number of reactive force field RMD methods are known to date. These include ReaxFF (46), Adiabatic Reactive Molecular Dynamics (ARMD (47)), Empirical Valence Bond model (EVB, (48)), Adaptive Intermolecular Reactive Empirical Bond Order potential (AIREBO, (49)), and others. Two older reviews are available in the literature on the methods of RMD and their applications. The review by Garrison and Srivastava (50) focuses on the reactions described with the London-Eyring-Polanyi-Sato (LEPS) potential (51) (reactions of hydrogen or oxygen atoms at metallic surfaces), as well as with the Stillinger-Weber (SW) (52) and Embedded Atom Method (EAM) (53) (silicone surface etching). The review by Brenner (54) is focused mainly on the theoretical details of Abell-Tersoff-Brenner (ATB) (55). A recent detailed state of the art review of force field RMD methods can be found in the work by Farah et al. (43). The detailed review given below is limited to those RMD methods that have been used in computational modeling studies of the chemical systems most relevant to the subject of the current work, i.e. the decomposition of alkane-based polymers or linear long-chain alkanes.
In 1990 Blaisten-Barojas and Nyden (56) conducted a molecular dynamics study of the reaction of depolymerization in polymers using a linear PE chain as the model substance. The authors used the united atom representation, in which each CH2 or CH3 group in the PE chain is substituted by a single spherical unit, the mass of which is the sum of the masses of the constituent atoms. The MD simulations were performed for a single polymer chain in vacuum at temperatures up to 2500°C. The authors used the Morse function $V_b = D\{1 - \exp(-\alpha(r - r_s))\}^2$ for the description of the bonding potential between the units that the chain consists of. Only two possible reaction channels were taken into account: thermal random scission of the bonds between the units and depolymerization (that can be compared with β-scission of primary alkyl radicals), during which a fragment that consisted of two units connected by a double bond was released. In the case of the random scission, a bond was considered to be torn when it stretched for a distance longer than 18 au (about 10 Å). In order to allow sequential depolymerization reactions to occur, a switching function was implemented that modified the pair potential terms $V_b$ on both sides of the dissociating bond by strengthening the two bonds adjacent to the dissociating bond and weakening the two next-nearest bonds. The initial configuration of the chain under study was chosen to be a zigzag with 113.3° angle (corresponding to that between the bonds of a C atom in sp3 hybridization state) between the bonds, 1.53 Å bond lengths, and all dihedral angles equal to 180°. The authors found that the polymer fragments yielded during the random scission and undergoing the subsequent depolymerization produce highly coiled agglomerates. While continuing to depolymerize, the agglomerates were also observed to cool and eventually quench in melted-like conformations. The authors admitted that a similar effect had been observed in atomic clusters at temperatures above the melting point (57), (58): the clusters cooled as atoms evaporated from
them. The fragments that did not form the coiled agglomerates and resided in rather stretched out conformations were found to stay hot and were considered by the authors as good candidates to continue degradation by chemical reactions other than depolymerization.

In 2003 the kinetics of the thermal decomposition of Poly(methyl methacrylate) (PMMA) in the condensed phase was studied by Stoliarov and coworkers (59) using the RMD method. The method was implemented with the computer program MD_REACT; periodic boundary conditions (PBC) were applied in order to simulate the condensed-phase processes. The authors report good overall agreement with the experimentally determined mechanism and product distribution for the thermal decomposition of PMMA. They also noted that the good agreement with the experiment was achieved despite the fact that the dynamically modified force field used in the work provides only a first-order approximation to the true potential energy surfaces of the chemical reactions involved in the study. According to the authors, the most interesting observation made in the course of the work is the influence of the condensed-phase macromolecular environment on the initiation of PMMA decay: the rate of backbone scission in the polymer observed in this study is significantly higher than that determined experimentally for small molecules in the gas phase. It is important to note that the reaction of polymer backbone scission was not the main object of study in this work; the RMD simulations were conducted until a significant (20 – 30%) degree of conversion was reached, allowing such reactions as beta-scission and radical recombination to occur as well, thus advancing the degradation process well beyond the backbone scission process.

The second part of the project of Stoliarov et al. (60) was devoted to the RMD study of the thermal decomposition of polyisobutylene (PIB) using the MD_REACT program. The authors
implemented an improved (with respect to their previous work (59)) RMD method that included a more comprehensive new bond selection algorithm and the valence restriction on the total bond order of a chemically active atom. In the course of the work the thermal decay of PIB chains of different lengths was studied, and it was observed that the activation energy of the backbone scission reaction decreases from 239 kJ mol\(^{-1}\) for PIB4 (a PIB chain consisting of four isobutylene monomers) to 111 kJ mol\(^{-1}\) for PIB150 (a PIB chain consisting of 150 monomers). The authors suggest that the decrease may be a consequence of increased angular and torsional stresses in the larger PIB molecules. According to this hypothesis, if the chain is broken, the stresses partially relax, thus reducing the amount of energy required for the scission of the backbone to occur. Similarly to the first part of the study, the range of chemical reactions available in the system was not limited to backbone scission only but also included numerous other reactions with the participation of the formed radicals, reagents, and products.

In another article by Nyden and coworkers (61) the thermal decomposition of several vinyl-based polymers (polyethylene (PE), polypropylene (PP), and poly(isobutylene) (PIB)) was studied using the RMD method. As in previous studies by the same group ( (59), (60), (61)), the MD_REACT program was used to perform RMD simulations with the PBC implemented to simulate condensed-phase conditions. The authors observed a dramatic increase in the activation energies for initiation and propagation processes as pendant methyl groups are substituted for hydrogen atoms. Thus, the reported values for \(E_{\text{act}}\) for chain scission are 42 kJ mol\(^{-1}\) for PIB, 99 kJ mol\(^{-1}\) for PP, and 181 kJ mol\(^{-1}\) for PE. One can see that the reported \(E_{\text{act}}\) for C-C bond scission in PE is significantly (by about 170 kJ mol\(^{-1}\)) lower than that obtained for shorter molecules of similar chemical nature in the gas phase (e.g., 363 kJ mol\(^{-1}\) for butane; the estimation is based on
the kinetic data for the reaction of recombination of ethyl radicals by Shafir et al. (62)). Nyden et al. refrained from providing any detailed explanation of the observed phenomenon concluding that the amount of computational results produced to date is not sufficient for developing a sound theoretical basis for the dynamics of the system under study.

In the most recent work by Smith, Bruns, Stoliarov, Nyden, Ezekoye, and Westmoreland (63) the influence of molecular weight on the kinetics of backbone scission was studied for a series of linear alkanes of various lengths in the condensed phase using the method of Reactive Molecular Dynamics. The authors developed an open source C++ code RxnMD that implemented a new RMDff reactive force field (64). The authors reported a considerable acceleration effect of the polymer chain: the rate of C-C scission increased by about an order of magnitude as the chain length of a single molecule in the system under study was increased from one monomer unit (PE-1) to one hundred monomer units (PE-100). As the values of the C-C scission rate constant were reported in Arrhenius form, i.e., \( k = A e^{-\frac{E_{act}}{RT}} \), it was found that the values of log A only varied by ~5% and did not show any systematic trend with the change of the polymer chain length. On the other hand, the values of \( E_{act} \) did show a trend, monotonically decreasing from 349 kJ mol\(^{-1}\) for PE-1 to 251 kJ mol\(^{-1}\) for PE-100 (all the simulations were conducted under the conditions of density values confined to the range 0.80 – 0.83 g cm\(^{-3}\)). The authors suggested a tentative explanation for the observed decrease in activation energies, according to which the longer chains store additional potential energy in the form of strain that accumulates in their angular and torsional modes. When a backbone bond is broken, the resulting increase in the mobility facilitates the release of the strain. Thus, bond dissociation energies may vary along the polymer chain and longer chains that accumulate more strain contain more weak bonds. This effect had been observed
previously (65) when relaxed potential energy scans were calculated using the multilayer ONIOM (B3LYP/6-31G(d,p):Amber) (66) method in which individual backbone C-C bonds of an annealed PE chain (forming a globule) were stretched beyond the point of dissociation. The scans indicated a broad distribution of bond dissociation energies; many of the scans exhibited abrupt drops in potential energy following the bond scission. This observation was found to be consistent with the previously described hypothesis of the important role of the release of accumulated strain by enabling conformational changes in the dissociating fragments.

Knyazev (67) conducted a systematic molecular dynamics study of the reaction of C-C bond decay in vacuum for a series of linear alkanes ranging from PE-1 to PE-1000 using the Gromacs molecular dynamics package (68). It was found that the rate of the reaction increases by up to an order of magnitude with the increase of the alkane chain length. This effect was hypothetically attributed to the centrifugal forces of torsional motions of molecular fragments separated by a C-C bond subject to rupture: the forces act on the bond pulling it apart and making the bond’s decay easier. However, as the author admits, the observed accelerating effect of chain length (up to an order of magnitude) is still unable to completely account for the experimentally measured rates of PE thermal decay, since this would require the rates of the C-C scission in the melt to increase by at least several orders of magnitude compared to those of small alkane molecules in vacuum.

In the work by Chenoweth, van Duin, and Goddard (69) the ReaxFF reactive force field (46) was used to study the oxidation of hydrocarbons, which by itself is a complex chemical process and includes thermal decomposition as a constituent part. This method had previously been used by the same group for studying the thermal decomposition of poly(dimethylsiloxane)
with considerable success (70), and in (69) the authors applied the same methodology for studying the oxidation of methane, propene, benzene, and o-xylene. It was found that ReaxFF obtains the correct reactivity trend (propene > o-xylene > methane > benzene), following the trend in the C-H bond strength in the hydrocarbons. The authors also reported that new initiation chemistry was observed for the fuel-rich oxidation compared to the oxidation of isolated hydrocarbon molecules at very low fuel-to-oxygen ratios.

In the work by Wang et al. (71) the ReaxFF method was applied to studying the pyrolysis and combustion of n-dodecane at different values of temperature and pressure. The authors discovered that the pyrolysis of n-dodecane is initiated mainly through two pathways: the cleavage of C-C bond leading to formation of small alkyl radicals and the dehydrogenation reaction to form an H atom and the corresponding n-C_{12}H_{25} radical (however, the statistical significance of the latter pathway is not discussed). The kinetics of the thermal cracking of n-dodecane was studied according to the simplified scheme

\[ \text{n-dodecane} \rightarrow \text{product}, \quad \text{(Rxn. 1.21)} \]

where the whole intermediate chemical mechanism is represented with just one chemical equation and the “product” means all final products of the ensuing complex kinetics. It was found that the rate constant of the pyrolysis decreases by about an order of magnitude with the decrease of the density of the system from 0.33 g cm\(^{-3}\) to 0.08 g cm\(^{-3}\). The authors also compared the results of conducted ReaxFF simulations with chemical kinetic modeling studies and found a reasonable correlation.
2 EXPERIMENTAL PART AND DETAILS OF MOLECULAR DYNAMICS SIMULATIONS

2.1 DETAILS OF REACTIVE MOLECULAR DYNAMICS SIMULATIONS

2.1.1 MOLECULAR SYSTEMS AND CONDITIONS

The reaction of C-C bond scission was studied for linear polyethylene (PE) molecules with the number of individual monomer units of 1 (ethane), 2 (n-butane), 2.5 (pentane), 25, 100, and 500. To investigate the effects of the condensed phase on the temperature dependence of the PE decomposition rate constants, the reaction of PE-500 was studied at the densities of 0.75 g cm⁻³ (the density of molten polyethylene (72)) and 0.50 g cm⁻³ (henceforth referred to as “reduced density”), as well as under vacuum conditions. These calculations covered the temperature range of 2300 K – 3100 K. To study the effects of the PE chain length on the rate constant values, calculations were also performed for shorter molecules, at a single temperature of 3100 K. The reaction of the C-C scission for the shorter molecules was studied under two sets of conditions: (1) the fixed density of 0.75 g cm⁻³, and (2) variable density adjusted for each molecular system to
keep a constant pressure of $1.8 \times 10^4$ bar, the pressure observed in the PE-500 system at 3100 K and the density of 0.75 g cm$^{-3}$. These conditions are referred to henceforth as “fixed density” and “fixed pressure,” respectively.

### 2.1.2 Force Field and Reactive Molecular Dynamics Simulation Procedures

Molecular dynamics (MD) simulations were carried out for isolated single molecules in vacuum, as well as using periodic boundary conditions for simulation of the processes in the condensed phase. Two types of MD calculations were performed in this work: the “reaction” and the “diffusion” simulations. The reasoning for using these two calculation types is provided below in section 2.3.

In the “reaction” MD simulations, the all-atom OPLS-AA force field (73), (74) was used for the parameterization of potential energy surfaces (PES). Either a harmonic potential or (to enable C-C scission) a Morse potential (see below) was employed for the description of the C-C stretch terms. MD calculations were performed using the GROMACS program package, version 3.3 (68). Each simulation consisted of three stages. In the first stage, potential energy minimization via the steepest descent method was performed. The second stage consisted of the simulation of the thermal motion of the molecule at a given temperature for a duration of 10-50 ps with randomized initial atomic velocities set according to the Maxwell-Boltzmann distribution. In order
to avoid any chemical reaction during this stage the Morse terms in the force field parameterization of the potential energy of interatomic interactions were substituted with harmonic potentials. The goal of the second stage was to create randomized starting molecular configurations for the third stage. In the third stage, the simulation of the thermal motion started during the second stage was continued at the same temperature. The transition between the stages involved transferring the coordinates and the velocities of all atoms obtained at the end of the second stage and using them as the initial configuration for the third stage. The difference in the dynamics during the second and the third stages was thus in the interaction potentials between carbon atoms in C-C bonds, which were changed from harmonic to Morse to enable C-C bond scission.

The “diffusion” MD simulations were performed to model separation of the two fragments of a polymer chain resulting from a broken C-C bond, with the attractive Morse potential between the fragments removed. These simulations were conducted in three stages, the first two being identical to those of the “reaction” simulations described above. The third stage of the “diffusion” simulations differed from that of the “reaction” simulations by a modification of the force field, in which the strength of one C-C bond in the PE chain was reduced to 0 kJ/mol (the “broken” bond). It is worth mentioning that the term “diffusion” is applied here for the lack of a better term: the process of separation of the molecular fragments connected by a “zero-strength” C-C bond most likely does not have a completely uniform Brownian character because the bending and the torsional terms of the OPLS-AA force field do not decrease as the distance between carbon atoms in the bond increases. This means that the motions of the chain fragments produced conserve some of the constraints from the time when the fragments constituted a single molecule, thus not allowing their motions to be completely independent from each other.
The rate of separation of fragments can be expected to be influenced by the position of the broken bond relative to the end of the molecular chain. Therefore, in the cases of butane (PE-2) and pentane the rates of separation of fragments produced due to the rupture of the middle and the terminal C-C bonds were determined separately. For the longer alkanes (PE-25, PE-100, and PE-500), only the bond in the middle of the chain was chosen as ruptured in such “diffusion” MD simulations, under the assumption of negligible influence of the terminal C-C bonds on the kinetics of the polymer decay.

The temperatures used in modeling ranged from 2300 to 3100 K; such high temperatures were necessary to make the MD reaction rates observable within the practicable range of times of molecular dynamics simulations. The temperature of the systems was controlled using the Berendsen thermostat algorithm (75) with the coupling time 0.5 ps.

The time integration step size of 0.25 fs was used in all simulations. Further decrease of the integration time step did not influence the determined values of the rate constants. Overall translational motion of the center of mass and rotation around the center of mass were removed in all calculations. Periodic boundary conditions with square periodic boxes were used in the simulations performed for the conditions of the condensed phase.

2.1.3 **DETERMINATION OF THE RATE CONSTANTS**

In any molecular dynamics determination of reaction rates, a criterion of reaction occurrence must be used to determine when a reactive event takes place. In earlier bond dissociation studies,
Figure 1. Dependences of the per-bond C-C scission rate constants on the values of the critical distance $R_C$ (bond dissociation criterion) obtained in molecular dynamics simulations of decomposition of PE-500 at 2900 K. Open triangles, gas phase conditions; filled circles, condensed phase with the density of 0.50 g cm$^{-3}$; open circles, condensed phase with the density of 0.75 g cm$^{-3}$. The Morse function plotted on the same scale illustrates different behavior of the $k_{\text{eff}}$ vs $R_C$ dependences in the regions dominated by strong attractive potential (short distances) and diffusional separation of fragments (long distances, weak potential).
separation of the two carbon atoms forming a bond by a critical distance (denoted as $R_C$ henceforth) was used as such criterion (67), (63). The rate constant is then calculated as the reciprocal of the average time between the beginning of the reactive simulation (the “third stage” in our computational procedure) and the moment when any of the C-C bonds is stretched beyond the critical distance. Even though the choice of such a critical distance is rather arbitrary, in the gas-phase (vacuum) simulations the resultant rate constant values are not sensitive to the value of $R_C$ (67). However, in the condensed phase the situation is quite different. As described below, effective rate constants ($k_{eff}$) obtained display noticeable dependences on the values of the critical distance $R_C$. The upper part of Figure 1 demonstrates such $k_{eff}(R_C)$ dependences obtained in the simulations of PE-500 decomposition at $T = 2900\ K$ and three values of density (0.75 and 0.50 g cm$^{-3}$ and vacuum); the dependence of the Morse potential on the bond distance is shown in the lower part of the figure. At short bond separations, where the attractive influence of the Morse potential is strong, all curves show strong dependences of $k_{eff}$ on $R_C$. At longer separations, the vacuum and the condensed phase results are qualitatively different. In the case of vacuum the effective rate constant nearly loses its dependence on the critical distance at separations beyond approximately 0.43 nm, which roughly corresponds to the Morse potential energy being within $\frac{1}{4}RT$ from its long-range asymptotic value. In the two cases corresponding to the condensed phase simulations, however, the dependence of $k_{eff}$ on $R_C$ continues well beyond this point. To illustrate the differences, linear regression fit lines are drawn through the five points of the long-range end of each of the dependences in Figure 1. For condensed phase simulations these linear fit lines have considerable nonzero slopes, unlike the case of the vacuum simulations.
One can distinguish two distinct regions in the qualitative behavior of the $k_{\text{eff}}$ vs. $R_c$ curves in Figure 1. The left-hand region is potential-controlled whereas the limiting behavior of the right-hand region can be characterized as diffusion-controlled. The behavior observed in the right-hand region for condensed phase simulations can also be described as influenced by the cage effect, where the presence of the surrounding parts of molecular chains limits the rate of separation of the fragments connected initially by the dissociated C-C bond and thus promotes the reverse fragment recombination. Cage effects present a challenge to determination of the rate constant; although the two limiting potential- and diffusion-controlled regions are clearly distinguishable, the placement of the border between them is ambiguous and so is the associated value of the rate constant.

In the current work, we present a method of “factoring out” the contributions of the cage effects and assigning meaningful rate constant values to condensed phase carbon-carbon bond scission reactions. The method uses the dependences of $k_{\text{eff}}$ on $R_c$ such as those shown in Figure 1 and the results of “diffusion” simulations described in section 2.1.2. The process of bond dissociation and fragment separation is represented with the following kinetic model consisting of two reactions.

$$\text{R-R} \rightleftharpoons [\text{R} \cdots \text{R}] \quad \text{(Rxn. 2.1, 2.-1)}$$
$$[\text{R} \cdots \text{R}] \rightarrow 2 \text{R} \text{ (at distance } R_c) \quad \text{(Rxn. 2.2)}$$

Reactions 2.1 and 2.-1 in the mechanism represent reversible dissociation of a linear alkane chain into two primary alkyl radicals that stay in the vicinity of each other (in a cage). Reaction 2.2 represents the process of diffusional separation of these radicals to the distance $R_c$. This
process of fragment separation is characterized by a rate constant $k_2$ (denoted as $k_D$ henceforth for the clarity of its association with the diffusion process) that depends on the value of $R_C$ whereas the rate constants of reactions 2.1 and 2.1., $k_1$ and $k_{-1}$, are independent of $R_C$. The mechanism of reactions 2.1 and 2.2 attempts to uncouple the effects of bond dissociation (reaction 2.1) and diffusional separation of fragments (reaction 2.2). Thus, $k_1$ here is the rate constant of alkane dissociation that is not influenced by cage effects. This analysis seeks to determine its value.

The process of diffusional separation of fragments (reaction 2.2) was modeled separately, as described in section 2.1.2. For each set of conditions, the values of $k_D(R_C)$ were determined for a set of $R_C$ values as the reciprocal of the average time $t_D$ between the beginning of the third stage of the molecular dynamics simulation and the time when the fragments reached the distance equal to $R_C$. A typical dependence of $k_D$ on $R_C$ and the corresponding dependence of $t_D$ on the square of $R_C$ is shown in Figure 2. The latter dependence displays a linear character at long separations ($0.25 - 0.65 \text{ nm}^2$) but curves at shorter (less than 0.25 nm$^2$) distances.

The linearity of the long-distance part of the $t_D$ vs. $(R_C)^2$ dependence indicates a certain degree of similarity between separation of alkane chain fragments in molecular dynamics simulations and the random motion of a Brownian particle. For a 3-dimentional Brownian motion, the dependence of the average first-passage time on the distance traveled $r$ (i.e., the time it takes for a Brownian particle to move to distance $r$ from its original position for the first time) is described by the equation

$$
\langle t \rangle = \frac{r^2}{6D} \quad (\text{Eq. 2.1})
$$
Figure 2. Dependence of the diffusion time $t_D$ on the square of the distance between carbon atoms in the “broken” bond (see text) at $T = 2900$ K, density of $0.75$ g cm$^{-3}$. Inset: the corresponding dependence of the diffusional separation rate constant on $R_C$. Error bars are $2\sigma$. 
where $D$ is the diffusion coefficient (76). It is interesting to note that this dependence has the same functional form as the equation relating the average square of the displacement $\langle r^2 \rangle$ with time ($t = \frac{\langle r^2 \rangle}{6D}$). The non-zero intercept between the linear fit line in Figure 2b and the X-axis is expected since the initial separation between the chain fragments is not zero and, on average, equals the C-C bond length. Considering the first-passage times $t_0$ and $t$ corresponding to two different distances $r_0$ and $r$, from equation I one obtains

$$\langle t \rangle - \langle t_0 \rangle = \frac{r^2}{6D} - \frac{r_0^2}{6D},$$

(Eq. 2.2)

where the second term in the right-hand side of the equation is a constant.

The deviation from linearity at short separations is likely to be caused by the influence of the angular and the torsional terms in the potential describing the interaction between the chain fragments; even though the Morse bonding term is removed in diffusional simulations, other terms remain as in the potential used for reactive simulations.

Using the mechanism of reactions 2.1, 2.-1, and 2.2 and the steady-state approximation for $[R\cdots R]$, one obtains the following equation for the effective constant of the overall process of dissociation and separation of fragments:

$$k_{\text{eff}} = \frac{k_1 k_D}{k_{-1} + k_D}$$

(Eq. 2.3)

Here, $k_1$ and $k_{-1}$ are the forward and the reverse rate constants of reaction (2.1,2.-1) and $k_D$ is the diffusion rate constant of reaction 2.2. Equation 2.3 can be transformed to the following form:
Since $k_D$ and $k_{\text{eff}}$ depend on the critical distance $R_C$ and $k_1$ and $k_{-1}$ do not, equation 2.4 facilitates analysis of the data on $k_{\text{eff}}$ and $k_D$ obtained in molecular dynamics simulations using different values of $R_C$. When these data are plotted in the $k_D/k_{\text{eff}}$ vs $k_D$ coordinates, one can expect a linear dependence with a slope equal to the reciprocal of $k_1$ and an Y-axis intercept equal to the reciprocal of the equilibrium constant for the reaction (2.1,2.-1). An example of a dependence of $k_D/k_{\text{eff}}$ on $k_D$ is presented in Figure 3. As can be seen from the plot, the $k_D/k_{\text{eff}}$ vs. $k_D$ dependence has a linear character only in the region of low values of $k_D$, which corresponds to larger separations of the radical fragments ($R_C = 0.5 – 0.8$ nm). This is the same range of $R_C$ values where the dependences of $k_{\text{eff}}$ or $R_C$ are controlled by diffusion (as opposed to the region controlled by the bonding potential, Figure 1) and the diffusional separation of the radical fragments demonstrates a Brownian behavior (i.e., a linear dependence on the coordinates of Figure 2). We interpret this combination of data in Figures 1 – 3 as an indication that the two-step kinetic mechanism of reactions 2.1, 2.-1, and 2.2 and equations 2.3 and 2.4 are applicable in the region of $R_C = 0.5 – 0.8$ nm, whereas at shorter fragment separations the values of $k_1$ and $k_{-1}$ are not truly independent of $R_C$. The effects of $R_C$ on $k_1$ and $k_{-1}$ at short distances between fragments are likely to be due to the influence of the bonding potential; these effects result in the nonlinearity of the $k_D/k_{\text{eff}}$ vs. $k_D$ dependences (the right-hand side of Figure 3).
Figure 3. Dependence of the $k_d/k_{\text{eff}}$ ratio on the $R_C$-dependent diffusion constant $k_D$ for $T = 3100$ K, density of 0.75 g cm$^{-3}$. The fitted part of the dependence corresponds to longer separations of the C-C bond (0.5 nm to 0.8 nm), where the influence of the C-C interaction potential on the motions of the radicals is negligible. Error bars are $1\sigma$. 
Table 1. The values of the per-bond C-C scission rate constant $k_1(s^{-1})$ obtained for PE-500 under the conditions of vacuum and condensed phase.

<table>
<thead>
<tr>
<th>T / K</th>
<th>Density / g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vacuum</td>
</tr>
<tr>
<td>2300</td>
<td>$(8.72 \pm 0.716) \times 10^6$</td>
</tr>
<tr>
<td>2500</td>
<td>$(3.68 \pm 0.362) \times 10^7$</td>
</tr>
<tr>
<td>2700</td>
<td>$(1.42 \pm 0.209) \times 10^8$</td>
</tr>
<tr>
<td>2900</td>
<td>$(2.83 \pm 0.504) \times 10^8$</td>
</tr>
<tr>
<td>3100</td>
<td>$(7.04 \pm 0.981) \times 10^8$</td>
</tr>
</tbody>
</table>

* Uncertainties are 2σ.

The values of $k_1$ and $k_{-1}$ for all conditions (temperature and PE density) used in RMD simulations were obtained from linear fits to the dependences of $k_D/k_{eff}$ on $k_D$ analogous to that demonstrated in Figure 3. Only the left-hand sides of such dependences corresponding to the diffusion-controlled range of $R_C$ fragment separations were used in the fits, for the reasons described above. The values of the rate constants obtained via the linear regression analysis are presented in Table 1.
2.2 EXPERIMENTAL STUDY OF HDPE PYROLYSIS

2.2.1 THE EXPERIMENTAL APPARATUS, METHODS, AND MATERIALS

The experimental techniques chosen to study the products of polyethylene pyrolysis are Gas Chromatography (GC) and Nuclear Magnetic Resonance (NMR). These techniques allow the study of both volatile and non-volatile products. The current research is the second experimental study that employs NMR for the analysis of pyrolysis products (NMR was also used in the work by Kayacan and Dogan (33) reviewed above, but the authors did not employ the whole potential of the method only using it to estimate the ratio of aliphatic to aromatic protons and carbons in the products of PE pyrolysis). The sensitivity and selectivity of this technique allow us to focus our research on the initial stages of the pyrolysis process, during which the rates of secondary reactions (the reactions involving the products of pyrolysis as reactants) are low. This fact makes the contribution of the secondary reactions to the dynamics of the process of pyrolysis negligible, thus greatly simplifying its mechanistic modeling.

HDPE samples were pyrolyzed in airtight reactors that consisted of a Pyrex test tube, stainless steel Cajon junction that provided a vacuum-tight glass-to-metal connection, and a Nupro shut-off gas valve. An HDPE sample was placed into the test tube, and the junction and the valve were used in order to connect the reactor to a vacuum pump that was necessary during the degassing process (see below), or evacuate air from the reactor and fill it with nitrogen for a pyrolysis experiment. It was necessary to fill the reactor with nitrogen to avoid leaking air inside the cavity with the HDPE sample; the pressure of the nitrogen inside the reactor exceeded the current atmospheric pressure by 5 Torr to ensure that no air leaked inside. During a typical
pyrolysis experiment the bottom of a sealed tube with an HDPE sample was immersed into a vessel filled with molten tin and kept there at constant temperature for some predefined time. An electric hot plate was used for heating the vessel with the tin. The use of the molten tin as the thermostat allowed the immersed reactor to be heated very rapidly from room temperature to the desired pyrolysis temperature. Due to the large mass of the molten tin (~5 kg), the immersion of the reactor did not cause any significant change in the temperature of the thermostat. The temperature of the tin was measured using a type K (chromel-alumel) thermocouple. The temperature was controlled using a Variac autotransformer regulating the voltage on the hot plate.

Figure 4. The apparatus used for pyrolysis experiments: the HDPE sample [1] is placed into the Pyrex tube [2] that is connected to the Nupro valve [5] via the stainless steel Cajon junction [3] and the metal tube [4]. The Pyrex tube [2] is immersed into the vessel with molten tin [6]. The tin, in turn, is stirred by the metal rod with the blades [7] and heated by the hot plate [8]. The temperature of the molten metal was measured with the thermocouple [9].
and by a variable flow of nitrogen gas directed onto the surface of the molten tin. The combination of these two methods of temperature control kept the temperature of the tin at the desired value within a 1°C range. A mechanical rotating rod with metal propeller-type blades was used to stir the molten tin in order to provide a homogeneous distribution of heat.

HDPE used in the experiments was granulated Aldrich HDPE, CAS 9002-88-4. Two granules of the HDPE were used as a typical sample for pyrolysis experiments; the total mass of a single sample was 0.040 ± 0.005 g.

Preliminary analysis showed that the HDPE used for the experiments contains considerable amounts of hydrocarbon gases trapped in bubbles inside of the granules; the abundances of the trapped gases may amount to a few percent of the abundances of the gases released during pyrolysis experiments. Thus, in order to avoid distortion of the results of the pyrolysis experiments by mixing the gases trapped in the HDPE samples due to the manufacturing process and those produced during the pyrolysis experiment, the samples were subjected to the procedure of degassing. The procedure consisted of keeping the reactor with the sample immersed into the crucible with molten tin at a temperature of about 280°C for at least 10 hours. This temperature is too low for pyrolysis onset (31), so the only process expected to occur in the molten HDPE was the escape of the trapped gases out of the melt. The reactor with the sample being degassed was connected to a vacuum pump that evacuated the gases during the entire degassing process.

In the work by Lowell and McCrum (77) the diffusion of short alkanes in linear polyethylene was studied. By extrapolation of the dependence of diffusivity on temperature to the temperature of degassing, one can conclude that the diffusivity of short alkanes during the
The degassing process is about $10^{-4}$ cm$^2$ sec$^{-1}$ (78). In fact, due to decrease of the viscosity of molten HDPE, the real value of diffusivity should be even greater, so the value approximated based on the literature data can be used as the lower estimate of the diffusivity. Given that the thickness of a typical sample of molten HDPE is a few millimeters, one can use the relation between the diffusivity $D$ of a particle, the average square of the particle’s displacement $<r^2>$, and the time $\tau$ that it takes for the particle to displace by the distance $r$

$$D = \frac{<r^2>}{6\tau},$$

(Eq. 2.5)

and conclude that the duration of the degassing procedure of approximately 10 hours seems to be a time period long enough for most of the gases trapped inside of the sample to escape.

The gaseous products of HDPE pyrolysis were analyzed using the Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GCMS) methods. The GCMS method allows the separation of different products in the gaseous mixture and the analysis of them individually using a mass spectrometer. Thus, the method permits the identification of peaks of the chromatogram with actual chemical compounds. Despite its convenience, however, the GCMS method could not be used routinely for analyzing the results of the experiments due to its lower sensitivity compared to the GC method (see the description below). A single pyrolyzed HDPE sample was analyzed using the GCMS method. The sample was pyrolyzed to a significant extent that produced large analyzable amounts of gaseous products. The GCMS analysis permitted the deduction of the actual chemical structures of the pyrolysis products, as well as the retention times of the products specific for the temperature program of the gas chromatograph and the chromatography column used (see below).
The GCMS apparatus consisted of a Hewlett Packard 5890 Series II gas chromatograph and a Hewlett Packard 5989B mass spectrometer. A GS-GASPRO column was used with He as the carrier gas. The chromatography experiment was conducted according to the following temperature program: after the injection of the sample, the chromatograph oven was kept at the initial temperature 50°C for 5 min. At the end of 5 min the oven was heated up with a rate 20°C min\(^{-1}\) until the temperature reached 200°C. This temperature was kept for 10 min, after which the experiment ended. Thus, the total duration of the experiment was 22.5 min.

The GC method with Flame Ionization Detector (FID) was routinely used for analyzing the gaseous products of HDPE pyrolysis. Unlike the GCMS method described above, the GC/FID method is unable to determine the structures of the products, but it has a much higher sensitivity. In the current work the GC method was used for analyzing the abundances of specific pyrolysis products. The apparatus used for GC analysis consisted of a Hewlett Packard 5890 Series II gas chromatograph with a GS-GASPRO column and an FID detector. A typical routine GC experiment was conducted according to the same temperature program as the GCMS experiment described above. The use of the same column and the same temperature program in both types of the experiments permitted the assumption that particular products have the same retention times both in the GCMS and GC experiments and brings into correspondence the peaks observed on chromatograms in GC experiments with particular chemical structures determined in the GCMS experiment described above. Nitrogen gas was used as the carrier gas and a mixture of hydrogen and air was used as the source of the flame in the FID detector.
After a pyrolysis experiment, a 1 ml gas-phase sample of the contents of the reactor was used for the GC analysis. In order to determine the abundances of gaseous products and account for the temporal change of the instrument’s sensitivity, a 0.5 ml injection of a calibration mixture was made before and after every injection of pyrolyzed samples. The calibration mixture consisted of methane (50% molar fraction), ethane (25% molar fraction), and ethylene (25% molar fraction). The abundances of the gaseous products were calculated under the assumption that the signal produced by a hydrocarbon in the FID detector is proportional to the number of carbon atoms in the hydrocarbon \(^{79}\), i.e., for example, 1 mmol of ethane \(\text{C}_2\text{H}_6\) is expected to produce a two times stronger signal than 1 mmol of methane \(\text{CH}_4\).

The method of Nuclear Magnetic Resonance (NMR) was used in the current work in two implementations: \(^1\text{H} \text{NMR} \) and \(^{13}\text{C} \text{NMR}\). The NMR was used for analyzing the condensed fraction of the products of pyrolysis of HDPE. The method is almost perfectly applicable for the purposes of the current research due to its ability to analyze different types of C-C bonds in organic substances, as well as their concentrations.

For a typical sample for NMR analysis a portion \((0.040 \pm 0.002 \text{ g})\) of the solid residue of the HDPE pyrolysis was used. The solvent used for the preparation of the sample was a mixture consisting of 40 wt % of 1,2,4-trichlorobenzene \(\text{C}_6\text{H}_3\text{Cl}_3\) (0.093 ml) and 60 wt % of deuterated benzene \(\text{C}_6\text{D}_6\) (0.252 ml), which is similar to the mixture of the solvents used by Qu et al. \(^{80}\) in their NMR study of cross-linking in LDPE. Actual quantities of the solvents were chosen such that the mass of the dissolved HDPE residue in the NMR sample was equal to 10 wt %. Due to the fact
that HDPE dissolves in the solvents only at elevated temperatures, the NMR tubes with the samples were flame sealed to avoid solvent evaporation.

The NMR experiments were conducted using a Bruker Ascend 400 spectrometer at 120°C. The spectrometer’s operating frequency is 400 MHz, and the experimental conditions for $^1$H and $^{13}$C experiments were chosen, respectively, as follows: pulse width, 10 $\mu$s and 14 $\mu$s; acquisition time, 1.47 s and 0.655 s; number of points, 32768 and 33078; spectral width, 28 ppm and 250 ppm; recycle delay, 1 s and 2 s; number of scans, 100 and 1024.

2.2.2 THE CHOICE OF EXPERIMENTAL CONDITIONS (PYROLYSIS TEMPERATURE AND TIME)

Pyrolysis experiments were conducted with previously degassed samples over the temperature range 400°C to 440°C; the time of pyrolysis varied from 5 min to 20 min. The lower limit of the temperature range is chosen to be 400°C because it corresponds to the temperature of HDPE pyrolysis onset (31). The pyrolysis temperature in different experiments was changed in increments of 10 degrees that corresponds to five separate values of temperature in the chosen temperature range: 400°C, 410°C, 420°C, 430°C, and 440°C. In order to ensure that even at the upper limit of the temperature range the contribution of the reactions of alkyl radicals with products of pyrolysis is negligible and the pyrolysis process is still in its initial stage, one can compare the rate of the reaction of alkyl radicals with the -CH$_2$- groups as the main initial reactants with that of the radicals with olefins that are among the products of pyrolysis and can react with the radicals. The abstraction reaction of alkyl radicals with olefins can produce allylic radicals that are stabilized
due to the delocalization of the unpaired electron. Because of the stabilization, the delocalized radicals have higher rates of production compared to the analogous non-delocalized radicals (39). Since the actual rate constants of the reactions in the condensed phase are not known, in order to estimate the ratio between the rate of reaction of alkanes with radicals (we will denote the corresponding rate as $v_{\text{alkane}}$) and the rate of reaction of olefins with radicals (the rate will be denoted as $v_{\text{olefin}}$), one can draw an analogy with the reactions in the gas phase. The closest and simplest analogy of the reactions of radicals with alkanes and olefins in the condensed phase will be the reactions of a hydrogen atom with propane $C_3H_8$ and propene $C_3H_6$ (Abstraction of an H atom in the methyl group in propene will produce an allyl radical which is the simplest example of a delocalized radical. We are interested in the reaction producing an allylic radical because, as mentioned above, the rate constant of allylic production is higher than that of non-delocalized radicals, and we require an upper-bound estimate for the rates of secondary reactions). At 700 K ($427^\circ\text{C}$) the rate constant $k_{\text{alkane}}$ of the reaction $C_3H_8 + H = H_2 + n-C_3H_7$ is $2.88 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (81), and the rate constant $k_{\text{olefin}}$ of the reaction $C_3H_6 + H = H_2 + C_3H_5$ is $6.24 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (82). The concentration of the -CH$_2$- groups in HDPE at the density of 0.75 g cm$^{-3}$ (which is the density of molten HDPE in the working temperature range of the current work (72)) is $\sim 3 \times 10^{22}$ molecule cm$^{-3}$, and the concentration of double bonds in HDPE pyrolyzed under the conditions accepted in the current work is not more than $3 \times 10^{18}$ molecule cm$^{-3}$ (see the Results part below); the concentrations will be denoted as [−CH$_2$−] and [C=C], respectively. Thus, the ratio of the reaction rates is

$$\frac{v_{\text{alkane}}}{v_{\text{olefin}}} = \frac{k_{\text{alkane}}[-\text{CH}_2-]}{k_{\text{olefin}}[\text{C=C}]} \approx 5000.$$  

(Eq. 2.6)
Thus, one can see that even at the high temperature limit of the current study the rate of the secondary reactions is about 5000 times lower than the rate of the primary processes.
3 RESULTS AND DISCUSSION

3.1 REACTIVE MOLECULAR DYNAMICS

3.1.1 RESULTS OF RMD SIMULATIONS

The results of molecular dynamics simulations of the reaction of C-C bond dissociation in PE-500 are presented in Figure 5 and Table 1. As can be seen from the Arrhenius plots, the reaction of C-C bond dissociation in the condensed phase is noticeably slower than in the gas phase, with differences of up to an order of magnitude. The condensed phase rate constants also demonstrate a strong dependence on the density, with much of the difference between the gas-phase rate constants and those obtained for the “normal” density of 0.75 g cm$^{-3}$ recovered if simulations are performed with the reduced density of 0.5 g cm$^{-3}$. It is worth emphasizing that the observed slowing of the scission reaction with increasing density is not a consequence of the cage effect because the latter has been accounted for in the kinetic analysis described above.

The Arrhenius parameters for the C-C backbone scission rate constant for PE-500 are given in Table 2. One can see that despite the differences in the central values of the obtained activation energies, their confidence intervals (determined as two standard errors of the mean) overlap. Since the value of RT for the temperature interval of the current study is about 20 kJ mol$^{-1}$, one can assert that the obtained activation energies differ by only 2RT from 348 kJ mol$^{-1}$, the value of the threshold of the Morse potential used in the force field to describe the C-C bond, which is similar
to a typical activation energy for C-C scission for small alkane molecules in the gas phase (83), (84), (85). The results of the study of C-C scission in PE molecules of varying length are presented in Table 3 and Figure 6. In the figure, diamonds represent the results obtained in simulations performed under the conditions of fixed density (0.75 g cm\(^{-3}\)). Circles represent the data obtained in simulations where densities of the PE with different chain lengths were varied to maintain the same pressure, \(1.8 \times 10^4\) bar, the pressure of PE-500 at the “normal” density of 0.75 g cm\(^{-3}\) at 3100 K.

As can be seen in Figure 6, the rate constant obtained under the fixed density conditions decrease by about an order of magnitude as the length of the polymer chain decreases from 500 monomers to one monomer. At the same time, the rate constants determined under the fixed pressure conditions do not show any statistically meaningful dependence on the length of the chain.
Figure 5. The Arrhenius plots of the per-bond C-C dissociation rate constants $k_1$ obtained in molecular dynamics simulation of PE-500 decomposition. Lines are Arrhenius fits through the data. Open circles and dashed line: gas phase conditions; filled circles and dotted line: condensed phase with the density of 0.5 g cm$^{-3}$; filled triangles and solid line: condensed phase with the density of 0.75 g cm$^{-3}$. Error bars are 2\(\sigma\).
Table 2. Arrhenius parameters \( a \) for C-C backbone scission in PE-500 determined for three values of density.

<table>
<thead>
<tr>
<th>Density / g cm(^{-3})</th>
<th>( A / s^{-1} )</th>
<th>( E_{\text{act}} / \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75 (normal)</td>
<td>((4.21 \pm 0.98) \times 10^{12})</td>
<td>275 ( \pm ) 28</td>
</tr>
<tr>
<td>0.5 (reduced)</td>
<td>((1.31 \pm 0.68) \times 10^{14})</td>
<td>326 ( \pm ) 60</td>
</tr>
<tr>
<td>0 (vacuum)</td>
<td>((2.06 \pm 0.46) \times 10^{14})</td>
<td>323 ( \pm ) 26</td>
</tr>
</tbody>
</table>

\( a \) Uncertainties are 2\( \sigma \).

Table 3. The values of the C-C bond decay rate constant obtained for systems of linear alkanes of varying chain lengths under the conditions of fixed density and fixed pressure at 3100 K.

<table>
<thead>
<tr>
<th>Molecular system</th>
<th>Log(k1 / s(^{-1}) ( a ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed density</td>
</tr>
<tr>
<td>500PE-1</td>
<td>6.91 ( \pm ) 0.24</td>
</tr>
<tr>
<td>250PE-2</td>
<td>7.19 ( \pm ) 0.06</td>
</tr>
<tr>
<td>200C-5</td>
<td>-----</td>
</tr>
<tr>
<td>20PE-25</td>
<td>8.06 ( \pm ) 0.21</td>
</tr>
<tr>
<td>5PE-100</td>
<td>7.90 ( \pm ) 0.12</td>
</tr>
<tr>
<td>PE-500</td>
<td>8.00 ( \pm ) 0.08</td>
</tr>
</tbody>
</table>

\( a \) Uncertainties are 2\( \sigma \).
Figure 6. The values of C-C scission rate constant obtained in MD simulations under the fixed density conditions with the density kept at 0.75 g cm\(^{-3}\) (circles) and under the fixed pressure conditions (pressure kept at 1.8\(\times\)10\(^4\) bar, squares). Both sets of simulations were performed at 3100 K. Error bars are 2\(\sigma\). Part (a): rate constants obtained using the kinetic mechanism described is Sec. 2.1.3. Part (b): rate constants obtained using the value of R\(_c\) fixed at 0.45 nm as the criterion of occurrence of the reaction (the chosen value of R\(_c\) corresponds to the length beyond which a C-C bond had to be stretched to reach 99\% of its dissociation energy in the work by Smith et al. (63)).
3.1.2 DISCUSSION OF RMD SIMULATIONS

An earlier systematic molecular dynamics study of the C-C bond scission in vacuum for a series of linear alkanes and polyethylene macromolecules by Knyazev (67) demonstrated that increasing chain length results in significant acceleration of the reaction, with an increase of up to an order of magnitude in the values of the per-bond rate constant, $k_{CC}$. This effect was tentatively attributed to centrifugal effects of torsional motions about the C-C bonds in the alkane chains. The differences between the gas phase and the condensed phase values of $k_{CC}$ observed in the current study are similar in value to those found in (67) between the smallest molecule considered (C$_2$H$_6$) and long-chain alkanes; both are approximately a factor of 10. It is tempting to surmise that the effect of reaction deceleration in the condensed phase is caused by the obstruction of the torsional degrees of freedom of the alkane chains. Thus, within the framework of this hypothesis, reaction acceleration observed in the gas phase with the chain length increasing from PE-1 (C$_2$H$_6$) to PE-25 and longer chains (up to PE-1000) should not occur in the condensed phase of polymer melt.

At a first glance, this conclusion appears to contradict the findings of Smith et al. (63), who observed significant differences between the per-bond C-C scission rates in short and long PE molecules in their condensed phase RMD study. In their work, the reaction accelerated significantly (up to two orders of magnitude) as the length of a PE chain increased from one to one hundred monomers. The PE molecules used in the simulations of Smith et al. had the chemical formulas C$_{2n}$H$_{4n}$, where $n$ is the number of monomers in the chain. The difference with the normal alkane formula C$_{2n}$H$_{4n+2}$ is due to the use of the CH$_2$ end-groups with sp$^3$ hybridized carbon atoms. Thus, the smallest PE-1 molecule of Smith et al. had the chemical formula C$_2$H$_4$, with a single (not
double) C-C bond and sp\textsuperscript{3} carbons. All calculations were performed with the density of PE melt maintained between 0.80 and 0.83 g cm\textsuperscript{-3}.

The temperature dependences of the C-C scission rate constant obtained in (63) for PE-1 and PE-100 are plotted in Figure 7 together with the results obtained in the current work for PE-500. The difference between the PE-1 and the PE-100 rate constants reach two orders of magnitude between 2500 and 2840 K, where the temperature ranges used by Smith et al. for these two chain lengths overlap. An experimental k(T) dependence reported by Kiefer et al. (86) is shown for comparison.

The main motivation for our study of the dependence of the per-bond C-C scission rate constant on the polyethylene chain length was to elucidate the apparent disagreement between the hypothesis of the effects of the condensed phase on the torsional degrees of freedom and the results of Smith et al. The results obtained in the current work for the fixed density conditions are in qualitative agreement with those of Smith et al.: the per-bond rate constant increases in the sequence PE-1, PE-2, PE-25, and tends to saturation for longer chains (Figure 6). At the same time, the rate constant values obtained under the fixed pressure conditions do not show any discernible dependence on the chain length, as can be seen from the same graph. We therefore conjecture that the influence of the chain length on the C-C scission rate constant is caused by the differences in the degree of molecular crowding or the availability of intermolecular space for molecular motion, including the motion required for extension of the C-C bonds during scission. The concept of molecular crowding is intuitively clear but difficult to define
Figure 7. The results obtained in the current work for PE-500 in vacuum (circles) and at the density of 0.75 g cm\(^{-3}\) (squares) plotted together with the results obtained by Smith et al. (63) for PE-1 fragments (heavy dashed line) and PE-100 molecule (heavy solid line). Heavy dotted line: experimental $k(T)$ dependence for ethane decomposition from Kiefer et al. (86).
quantitatively. One way to quantify it can be based on the pressure in the system – a higher degree of crowding would correspond to a higher pressure. Figure 8 illustrates the dependence of the pressure obtained in RMD simulations performed in this work for the fixed density conditions on the polyethylene chain length. The pressure increases by approximately a factor of two as the number of monomers in the chain decreases from 500 to one, demonstrating the corresponding increase in molecular crowding. The reason for this pressure / crowding increase is in the different dependences of the bonding and non-bonding potentials on interatomic distances. Figure 9 illustrates such dependences for carbon-carbon interactions, for the force fields used in the current work as well as by Smith et al. Non-bonding potentials in general result in larger interatomic distances, particularly at the translational energies in the thermal range. Replacing a long-chain molecule with a set of shorter ones while keeping the same number of carbon atoms results thus in higher degree of molecular crowding due to larger effective space occupied by these molecules. Another contribution to the higher degree of molecular crowding in the short-molecule systems used in the current work is due to the presence of additional hydrogen atoms.
It is thus likely that the differences between the rates of C-C scission obtained for a long-chain (PE-100) molecule and a collection of short (PE-1) molecules observed by Smith et al. (63) are caused, at least partially, by the differences in molecular crowding. As a chain consisting of one hundred monomers is replaced by one hundred C\textsubscript{2}H\textsubscript{4} fragments, the bonding interaction potential in every other C-C bond in the system effectively gets replaced by a nonbonding van der Waals potential, with larger effective atomic sizes. This leaves less free intermolecular space available for molecular motion.
As the results of the current work are compared with those of Smith et al., it is necessary to highlight some of the important differences in the methodologies used in the two studies. The force field used by the authors of (63) differs from that used in the current work. One important difference is in the more realistic description of the angular and the torsional potential terms.

**Figure 9.** Bonding and non-bonding potential terms for C-C interaction used in the current study (solid lines) and by Smith et al. (63) (dashed lines). Non-bonding potentials result in larger effective distances between carbon atoms. The horizontal dotted line corresponds to \(\frac{1}{2}RT\) at 3100K.
applied in (63). The force constants of these terms gradually diminish as the adjacent C-C bond is stretched, thus resulting in more “loose” (18) transition states for C-C scission and in larger values of the rate constants (Figure 7). These rate constants are, on average, in better agreement with the experimental gas-phase values obtained for the thermal decomposition of ethane by Kiefer et al. (86), as illustrated in the same figure. The OPLS-AA force field used in the current study does not allow for such a decrease in the bending and the torsional force constants as the carbon atoms in the bond separate. This difference in the force fields may also have an influence on the rate with which the mutual orientation of the fragments of the broken bond relaxes during the separation of the carbon atoms forming the bond.

Another important difference is in the method of determining the values of the rate constants. In the current study, a method based on the kinetic mechanism of reactions 2.1, 2.-1, and 2.2 was developed (section 2.1.3, equations 2.3 and 2.4, Figure 3). This method takes into account cage effects specific to the condensed phase of the polymer melt, which in this case means the influence of the finite rates of diffusional separation of radicals on the observed effective rate constants. The values of rate constants obtained after “factoring out” the cage effects are not affected by the influences of the choice of the separation criteria (critical distances), such as those illustrated in Figure 1. In the study of Smith et al., a critical distance of 0.45 nm (corresponding to the bond stretch beyond 99% of the dissociation energy) was used as the criterion of the occurrence of the scission reaction. Although the values of the rate constants obtained using the two methods necessarily differ, the important qualitative conclusions of the current work are not method-specific. Figure 1 demonstrates that even if a fixed value of the critical C-C distance is used as the
criterion of bond dissociation, the effective rate constants corresponding to the condensed phase conditions are approximately an order of magnitude lower than those obtained in vacuum.

Finally, the results of the current study do not provide for an unequivocal support or rejection of the hypothesis (67) that acceleration of C-C scission in the gas phase with increasing molecular chain length is caused by centrifugal effects of torsional motions. Indeed, the differences between the gas phase and the condensed phase values of per-bond rate constant observed in the current study for PE-500 are of the same value (an order of magnitude) as the differences between the gas-phase decomposition rates of the smallest PE molecule (PE-1, C$_2$H$_6$) and long-chain alkanes. This seems to support the above hypothesis because torsional degrees of freedom of long alkane chains can be expect to be obstructed in the condensed phase. However, as Figure 6 and the data in Table 3 demonstrate, in the condensed phase, an increase in pressure results in a higher degree of molecular crowding and decreasing values of the rate constant, which is not explained by the above hypothesis. Since the transition from the gas phase to the condensed phase is also accompanied by increase in pressure, the two effects may or may not be related and may be caused by the same or different phenomena.

3.2 EXPERIMENTAL STUDY

3.2.1 DESCRIPTION OF EXPERIMENTAL RESULTS

All experimental data obtained in the course of the current study can be found in Appendices A and B. Appendix A contains the data obtained using the method of Gas
Chromatography; Appendix B contains the data acquired via Nuclear Magnetic Resonance spectroscopy. It can be seen that the abundances of all gaseous products at all temperatures increase linearly with time (Figures 10 – 24). The kinetics of liquid phase products (Appendix B) is more complicated: whereas the molar fractions of CH₃, CH₄, vinylene, and vinylidene groups increase linearly with time, the molar fractions of vinyl groups tend to reach saturation at longer pyrolysis times (10 min and higher, see Figures 25 – 29).

Figures 10 – 24 depict gaseous products of HDPE pyrolysis, the abundances of which are listed in Tables 5 – 9 (Appendix A).
Figure 10. Gaseous products of HDPE pyrolysis obtained at 400°C: CH₄ (squares), C₂H₄ (circles), C₂H₆ (triangles), C₃H₆ (crosses), C₃H₈ (diamonds); the error bars represent 1σ.
Figure 11. Gaseous products of HDPE pyrolysis obtained at 400°C: C₄H₁₀ (squares), 1-C₄H₈ (circles), 2-C₄H₈ (triangles), 1-C₅H₁₀ (crosses), C₅H₁₂ (diamonds); the error bars represent 1σ.
Figure 12. Gaseous products of HDPE pyrolysis obtained at 400°C: $C_6H_{14}$ (squares), 1-$C_6H_{12}$ (circles), $C_7H_{16}$ (triangles), 1-$C_7H_{14}$ (diamonds), $C_8H_{18}$ (crosses); the error bars represent 1σ.
Figure 13. Gaseous products of HDPE pyrolysis obtained at 410°C: \( \text{CH}_4 \) (squares), \( \text{C}_2\text{H}_4 \) (circles), \( \text{C}_2\text{H}_6 \) (triangles), \( \text{C}_3\text{H}_6 \) (crosses), \( \text{C}_3\text{H}_8 \) (diamonds); the error bars represent \( 1 \sigma \).
Figure 14. Gaseous products of HDPE pyrolysis obtained at 410°C: C₄H₁₀ (squares), 1-C₄H₈ (circles), 2-C₄H₈ (triangles), 1-C₅H₁₀ (crosses), C₅H₁₂ (diamonds); the error bars represent 1σ.
Figure 15. Gaseous products of HDPE pyrolysis obtained at 410°C: $C_6H_{14}$ (squares), $1-C_6H_{12}$ (circles), $C_7H_{16}$ (triangles), $1-C_7H_{14}$ (diamonds), $C_8H_{18}$ (crosses); the error bars represent 1σ.
Figure 16. Gaseous products of HDPE pyrolysis obtained at 420°C: CH₄ (squares), C₂H₄ (circles), C₂H₆ (triangles), C₃H₆ (crosses), C₃H₈ (diamonds) ; the error bars represent 1σ.
Figure 17. Gaseous products of HDPE pyrolysis obtained at 420°C: C₄H₁₀ (squares), 1-C₄H₈ (circles), 2-C₄H₈ (triangles), 1-C₅H₁₀ (crosses), C₅H₁₂ (diamonds); the error bars represent 1σ.
Figure 18. Gaseous products of HDPE pyrolysis obtained at 420°C: C₆H₁₄ (squares), 1-C₆H₁₂ (circles), C₇H₁₆ (triangles), 1-C₇H₁₄ (diamonds), C₈H₁₈ (crosses); the error bars represent 1σ.
Figure 19. Gaseous products of HDPE pyrolysis obtained at 430°C: CH₄ (squares), C₂H₄ (circles), C₂H₆ (triangles), C₃H₆ (crosses), C₃H₈ (diamonds); the error bars represent 1σ.
Figure 20. Gaseous products of HDPE pyrolysis obtained at 430°C: C₄H₁₀ (squares), 1-C₄H₈ (circles), 2-C₄H₈ (triangles), 1-C₅H₁₀ (crosses), C₅H₁₂ (diamonds); the error bars represent 1σ.
Figure 21. Gaseous products of HDPE pyrolysis obtained at 430°C: C₆H₁₄ (squares), 1-C₆H₁₂ (circles), C₇H₁₆ (triangles), 1-C₇H₁₄ (diamonds), C₈H₁₈ (crosses); the error bars represent 1σ.
Figure 22. Gaseous products of HDPE pyrolysis obtained at 440°C: \( \text{CH}_4 \) (squares), \( \text{C}_2\text{H}_4 \) (circles), \( \text{C}_2\text{H}_6 \) (triangles), \( \text{C}_3\text{H}_6 \) (crosses), \( \text{C}_3\text{H}_8 \) (diamonds); the error bars represent 1\( \sigma \).
Figure 23. Gaseous products of HDPE pyrolysis obtained at 440°C: C₄H₁₀ (squares), 1-C₄H₈ (circles), 2-C₄H₈ (triangles), 1-C₅H₁₀ (crosses), C₅H₁₂ (diamonds); the error bars represent 1σ.
Figure 24. Gaseous products of HDPE pyrolysis obtained at 440°C: $\text{C}_6\text{H}_{14}$ (squares), 1-$\text{C}_6\text{H}_{12}$ (circles), $\text{C}_7\text{H}_{16}$ (triangles), 1-$\text{C}_7\text{H}_{14}$ (diamonds), $\text{C}_8\text{H}_{18}$ (crosses); the error bars represent 1σ.
Figures 25 – 29 depict molar fractions of olefinic groups detected in the liquid fraction of HDPE pyrolysis products.

**Figure 25.** Molar fractions of vinyl (squares), vinylene (circles), and vinylidene (triangles) groups obtained at 400°C; the error bars correspond to 1σ.
Figure 26. Molar fractions of vinyl (squares), vinylene (circles), and vinylidene (triangles) groups obtained at 410°C; the error bars correspond to 1σ.
Figure 27. Molar fractions of vinyl (squares), vinylene (circles), and vinylidene (triangles) groups obtained at 420°C; the error bars correspond to 1σ.
Figure 28. Molar fractions of vinyl (squares), vinylene (circles), and vinylidene (triangles) groups obtained at 430°C; the error bars correspond to 1σ.
Figure 29. Molar fractions of vinyl (squares), vinylene (circles), and vinylidene (triangles) groups obtained at 440°C; the error bars correspond to 1σ.
Figure 30. Molar fractions of CH$_3$ (squares) and CH$_Y$ (circles) groups determined for the liquid fraction of HDPE pyrolysis products at 400°C; uncertainties correspond to 1σ.
Figure 31. Molar fractions of CH₃ (squares) and CH₅ (circles) groups determined for the liquid fraction of HDPE pyrolysis products at 410°C; uncertainties correspond to 1σ.
Figure 32. Molar fractions of CH₃ (squares) and CH₅ (circles) groups determined for the liquid fraction of HDPE pyrolysis products at 420°C; uncertainties correspond to 1σ.
Figure 33. Molar fractions of CH₃ (squares) and CH₅ (circles) groups determined for the liquid fraction of HDPE pyrolysis products at 430°C; uncertainties correspond to 1σ.
Figure 34. Molar fractions of CH₃ (squares) and CH₅ (circles) groups determined for the liquid fraction of HDPE pyrolysis products at 440°C; uncertainties correspond to 1σ.
In order to model the process of pyrolysis of polyethylene the next mechanism was developed:

\[
\begin{align*}
R-R &\rightarrow 2 R_P & k_1 & \quad (Rxn. 3.1) \\
R_P &\rightarrow C_2H_4 + R_P & k_{βP} & \quad (Rxn. 3.2) \\
R_P + -CH_2- &\rightarrow -CH_3 + R_S & k_{HTa} & \quad (Rxn. 3.3) \\
R_S &\rightarrow R_P + Q & k_{βS} & \quad (Rxn. 3.4) \\
R_P + R_P &\rightarrow R-R & k_{RPP} & \quad (Rxn. 3.5) \\
R_P + R_S &\rightarrow CH_Y & k_{RPS} & \quad (Rxn. 3.6) \\
R_S + R_S &\rightarrow CH_H & k_{RSS} & \quad (Rxn. 3.7) \\
R_P + Q &\rightarrow R_S & k_{APT} & \quad (Rxn. 3.8) \\
R_P + Q &\rightarrow R_P^* & k_{APN} & \quad (Rxn. 3.9) \\
R_S + Q &\rightarrow R_S^* & k_{AST} & \quad (Rxn. 3.10) \\
R_S + Q &\rightarrow R_P^{**} & k_{ASN} & \quad (Rxn. 3.11)
\end{align*}
\]

Here, R-R denotes C-C bonds in a linear polyethylene chain; R_P and R_S are, respectively, primary and secondary radicals; -CH_2- and -CH_3 are -CH_2- and methyl groups (that also can be...
denoted as -CH$_3$) of a polyethylene chain; CH$_Y$ is a tertiary carbon atom with a single hydrogen and three polymer chains attached; CH$_1$ is a link between two tertiary atoms of the type R$_1$R$_2$HC-CHR$_3$R$_4$; Q is an olefinic polymer chain ending with a vinyl group; R$_P^*$ is a radical of the type RR$_1$HC-CH$_2$; R$_P^{**}$ is a radical of the type RR$_1$HC-R$_2$HC-CH$_2$; R$_S^*$ is a radical of the type RR$_1$HC-CH$_2$-CRH. The proposed mechanism was employed for estimating the values of the rate constants of the recombination of secondary radicals (k$_{RSS}$), addition of secondary radicals to the terminal C atom of a vinyl group (k$_{AST}$), and hydrogen transfer from -CH$_2$- groups to primary radicals (k$_{HTa}$). The modeling was based on the assumption of applicability of the values of the rate constants of C-C bond scission (k$_1$) and $\beta$-scission of primary and secondary radicals (k$_{\beta P}$ and k$_{\beta S}$, respectively) obtained in the gas phase in the modeling of liquid phase processes. Particular values of the rate constants used in the current model are listed in Table 4.

It can be seen that the process described by the mechanism above is a chain reaction in which the role of the initiation step is taken by Rxn. 3.1, Rxns. 3.2 – 3.4 and 3.8 – 3.11 are propagation steps, and Rxns. 3.5 – 3.7 are termination steps. For the radicals RP and RS the next kinetic equations can be written:

$$\frac{d[R_P]}{dt} = 2k_1[R - R] + k_{\beta S}[R_S] - k_{HTa}[R_P][CH_2] - 2k_{RPP}[R_P]^2 - k_{RPS}[R_P][R_S] - k_{APT}[R_P][Q] - k_{APN}[R_P][Q],$$ (Eq. 3.1)

$$\frac{d[R_S]}{dt} = k_{HTa}[R_P][CH_2] + k_{APT}[R_P][Q] - k_{\beta S}[R_S] - k_{RPS}[R_P][R_S] - k_{RSS}[R_S]^2 - k_{AST}[R_S][Q] - k_{ASN}[R_S][Q],$$ (Eq. 3.2)
where $k_1$ is the rate constant of C-C bond scission; $k_{BS}$ is the rate constant of $\beta$-scission of secondary radicals; $k_{APT}$, $k_{APN}$, $k_{AST}$, and $k_{ASN}$ are the rate constants of terminal and nonterminal addition of primary and secondary radicals to olefins, respectively; $k_{RPP}$, $k_{RPS}$, and $k_{RSS}$ are the rate constants of recombination of primary with primary, primary with secondary, and secondary with secondary radicals, respectively; $k_{HTa}$ is the rate constant of hydrogen transfer by primary radicals; $[Q]$ is the concentration of polymer chains with vinyl groups. Since both $R_P$ and $R_S$ are highly reactive intermediates, a steady-state approximation (6) can be applied to the rates of change of their concentrations. Mathematically, the steady-state approximation in the current case consists in declaring $\frac{d[R_P]}{dt}$ and $\frac{d[R_S]}{dt}$ being equal to zero, which turns Eqs. 3.1 and 3.2 from differential to algebraic. Based on the works by Saeys et al. (87), Knyazev and Slagle (88), and Awan et al. (89) it can be concluded that the rates of nonterminal addition of both primary and secondary radicals to vinyl groups are significantly lower than those of terminal addition, and, therefore, the contributions of Rxns. 3.9 and 3.11 to the concentrations of $R_P$ and $R_S$ can be neglected compared to those of Rxns. 3.8 and 3.10. Also, due to the fact that $[R_S] >> [R_P]$ (see below), it can be stated that the contributions of Rxns. 3.5 and 3.6 are negligible compared to that of Rxn. 3.7 and the contribution of Rxn. 3.8 is negligible compared to that of Rxn. 3.10. Thus, Eqs. 3.1 and 3.2 produce the following relations:

$$[R_S] = \sqrt{\frac{k_1[R-R]}{k_{RSS}}}, \quad \text{(Eq. 3.3)}$$

$$[R_P] = [R_S] \frac{k_{BS}}{k_{HTa}-[CH_2-]}, \quad \text{(Eq. 3.4)}$$
The reaction of C-C bond scission (Rxn. 3.1) is the reaction that initiates the process of pyrolysis. The products of this reaction are two primary radicals \( \text{R}_P \). Further fate of the radicals \( \text{R}_P \) is mostly determined by the rates of two processes: \( \beta \)-scission producing ethylene (Rxn. 3.2) and a transfer of a hydrogen atom from \(-\text{CH}_2-\) groups of surrounding polymer chains producing secondary radicals \( \text{R}_S \) and methyl groups (Rxn. 3.3). According to the kinetic mechanism described above, one can see that the only reaction resulting in production of \( \text{C}_2\text{H}_4 \) is the reaction of \( \beta \)-scission of primary radicals \( \text{R}_P \). The kinetic equation for the concentration of \( \text{C}_2\text{H}_4 \) can be written in the following form:

\[
\frac{d[\text{C}_2\text{H}_4]}{dt} = k_{\beta P}[\text{R}_P],
\]

(Eq. 3.5)

where \( k_{\beta P} \) is the rate constant of \( \beta \)-scission of primary radicals and square brackets denote concentration. Thus, the values of \([\text{R}_P]\) for every temperature can be obtained if one approximates kinetic curves of \( \text{C}_2\text{H}_4 \) by straight lines and divides their slopes by the values of the rate constant of \( \beta \)-scission of primary radicals (the values of \( k_{\beta P} \) used and the corresponding calculated values of \([\text{R}_P]\) can be found in Table 4).

Rxn. 3.8 describes the way of production of olefinic polymer molecules that have a vinyl group and are denoted as \( \text{Q} \). Since the molar fractions of \( \text{Q} \) in the liquid phase of pyrolysis products exceed those of gaseous products (particularly, ethylene) by about three orders of magnitude, it can be concluded that the rate of hydrogen transfer in the liquid phase is much higher than the rate of their \( \beta \)-scission. This means that, once being produced in the reaction of C-C scission, primary radicals \( \text{R}_P \) virtually immediately produce secondary radicals \( \text{R}_S \) by abstracting hydrogen atoms from nearby \(-\text{CH}_2-\) groups of surrounding polymer chains. Thus, the concentration of \( \text{R}_S \) has to be
much greater than that of \( R_P \) since most of \( R_P \) gets consumed in Rxn. 3.3 producing \( R_S \). Furthermore, based on the RMD studies conducted in the course of the current work, one can affirm that the rate constant of the reaction of C-C bond scission in the liquid phase can be approximated by that of C-C bond scission in the gas phase. Thus, the rate of production of \( R_P \) in Rxn. 3.1 can be estimated according to the kinetic equation for \([R_P]\):

\[
\frac{d[R_P]}{dt} = 2k_1[R - R].
\]  
(Eq. 3.6)

If one assumes that the whole unpyrolyzed polymer sample consists only of -CH\(_2\)- groups, the concentration of the latter can be estimated as

\[
[-CH_2 -] = [R - R] = \frac{\rho N_A}{m_{CH_2}} \approx 3.23 \cdot 10^{22} \text{ molecules cm}^{-3},
\]

where \( \rho \) is the density of molten polyethylene equal to 0.75 g cm\(^{-3} \) (72), \( m_{CH_2} \) is the mass of a -CH\(_2\)- group in atomic mass units, and \( N_A \) is the Avogadro constant. If one accepts that the values of \( k_1 \) in the temperature range of the current pyrolysis experiments is \( \approx 10^{-10} \text{ s}^{-1} \) (see Table 4), then the rate of the production of \( R_P \) via Rxn. 3.1 has to be \( \approx 10^{12} \text{ molecules cm}^{-3} \text{ s}^{-1} \). Now, the lower bound of the rate of production of \( R_P \) via \( \beta \)-scission of secondary radicals \( R_S \) can be estimated from the kinetic equation for \([R_P]\) based on Rxn. 3.4, which will look as

\[
\frac{d[R_P]}{dt} = k_{\beta S}[R_S],
\]  
(Eq. 3.7)

where \( k_{\beta S} \) denotes the rate constant of \( \beta \)-scission of secondary radicals. If one assumes that \([R_S] = [R_P]\) (which will significantly underestimate the concentration of \( R_S \)), then it can be seen that the rate of production of \( R_P \) via this channel is \( \approx 10^{15} \text{ molecules cm}^{-3} \text{ s}^{-1} \) that is about 1000 times faster
than the rate of production of \( R_P \) via the reaction of C-C scission. Thus, it can be asserted that the main source of the primary radicals \( R_P \) in the system under study is the reaction of \( \beta \)-scission of secondary radicals \( R_S \) (Rxn. 3.4 of the mechanism above).

Another product of hydrogen transfer from a -CH\(_2\)- group of the polymer to the primary radical is a methyl group. Based on the Rxn. 3.3, the kinetic equation for the concentration of methyl groups can be written as follows:

\[
\frac{d[-CH_3]}{dt} = k_{HTa}[R_P][-CH_2].
\]  
(Eq. 3.8)

Relation 3.4 can be employed here, which allows to rewrite Eq. 3.8 as

\[
\frac{d[-CH_3]}{dt} = k_{R_S}[R_S].
\]  
(Eq. 3.9)

Eq. 3.9 can be used to calculate the steady-state concentrations of \( R_S \) for every temperature (they can be found in Table 4).

Based on the mechanism proposed at the beginning of this section, a kinetic equation for \( Q \) can be constructed:

\[
\frac{d[Q]}{dt} = k_{R_S}[R_S] - k_{AST}[R_S][Q]
\]  
(Eq. 3.10)

(as before, due to the low concentration of \( R_P \), the contributions of Rxns. 3.8, 3.9, and 3.11 into the concentration of \( Q \) were considered neglectable). The solution of Eq. 3.10 is

\[
[Q] = \frac{k_{R_S}}{k_{AST}} + \left([Q]_0 - \frac{k_{R_S}}{k_{AST}}\right)e^{-k_{AST}[R_S]t},
\]  
(Eq. 3.11)
where $[Q]_0$ is the initial concentration of Q.

Eq. 3.11 was used for fitting experimental dependences of Q on time using the literature values of $k_\beta$ and $[R_s]$ obtained earlier from the experimental kinetics of -CH$_3$ as fixed parameters.

**Figure 35.** Experimental values of the molar fraction of Q (polymers containing a vinyl group) obtained at 400°C and the modeled dependence of the molar fraction of Q on temperature calculated using Eq. 3.11. Error bars are 1σ.
and $k_{AST}$ as the fitted parameter. The obtained values of $k_{AST}$ can be found in Table 4. Figures 35 – 39 depict the experimental dependences of $Q$ on time together with the function $[Q] = [Q](t)$ calculated according to Eq. 3.11 with fitted values of $k_{AST}$.

**Figure 36.** Experimental values of the molar fraction of $Q$ (polymers containing a vinyl group) obtained at 410°C and the modeled dependence of the molar fraction of $Q$ on temperature calculated using Eq. 3.11. Error bars are 1σ.
Figure 37. Experimental values of the molar fraction of Q (polymers containing a vinyl group) obtained at 420°C and the modeled dependence of the molar fraction of Q on temperature calculated using Eq. 3.11. Error bars are 1σ.
Figure 38. Experimental values of the molar fraction of Q (polymers containing a vinyl group) obtained at 430°C and the modeled dependence of the molar fraction of Q on temperature calculated using Eq. 3.11. Error bars are 1σ.
Figure 39. Experimental values of the molar fraction of Q (polymers containing a vinyl group) obtained at 440°C and the modeled dependence of the molar fraction of Q on temperature calculated using Eq. 3.11. Error bars are 1σ.

The values of $k_{HTa}$ and $k_{RSS}$ were calculated according to Eqs. 3.4 and 3.3 respectively and can be found in Table 4. The obtained values of $k_{AST}$ and $k_{HTa}$ are of the same order of magnitude as those obtained for the reaction of small olefins and radicals in the gas phase by Knyazev and
Slagle (88) and those obtained by Tsang and Hampson for the hydrogen abstraction from ethane by methyl radicals (90), respectively.

Table 4. \( k_1 \) is calculated based on the study of recombination of \( \text{C}_2\text{H}_5 \) radicals by Shafir et al. (62), \( k_{\beta P} \) is calculated based on the study of decomposition of n-\( \text{C}_4\text{H}_9 \) and iso-\( \text{C}_4\text{H}_9 \) by Knyazev and Slagle (88), \( k_{\beta S} \) is calculated based on the computational study of decomposition of normal hexyl radicals by Tsang et al. (91) (the values provided by Tsang et al. were multiplied by 2 due to the reaction path degeneracy).

<table>
<thead>
<tr>
<th>T, °C</th>
<th>( k_1 )</th>
<th>( k_{\beta P} )</th>
<th>( k_{\beta S} )</th>
<th>([R_P])</th>
<th>([R_S])</th>
<th>( k_{\text{AST}} )</th>
<th>( k_{\text{HTa}} )</th>
<th>( k_{\text{RSS}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1.48E-11</td>
<td>9.79E+03</td>
<td>2.85E+04</td>
<td>8.81E+08</td>
<td>1.93E+12</td>
<td>1.12E-15</td>
<td>1.93E-15</td>
<td>1.29E-13</td>
</tr>
<tr>
<td>410</td>
<td>3.83E-11</td>
<td>1.33E+04</td>
<td>3.91E+04</td>
<td>4.10E+09</td>
<td>2.96E+12</td>
<td>6.27E-16</td>
<td>8.75E-16</td>
<td>1.41E-13</td>
</tr>
<tr>
<td>420</td>
<td>9.63E-11</td>
<td>1.79E+04</td>
<td>5.31E+04</td>
<td>3.38E+09</td>
<td>2.68E+12</td>
<td>7.04E-16</td>
<td>1.31E-15</td>
<td>4.32E-13</td>
</tr>
<tr>
<td>430</td>
<td>2.36E-10</td>
<td>2.38E+04</td>
<td>7.16E+04</td>
<td>4.46E+09</td>
<td>3.48E+12</td>
<td>1.23E-15</td>
<td>1.73E-15</td>
<td>6.29E-13</td>
</tr>
<tr>
<td>440</td>
<td>5.63E-10</td>
<td>3.15E+04</td>
<td>9.56E+04</td>
<td>1.13E+10</td>
<td>3.98E+12</td>
<td>1.10E-15</td>
<td>1.04E-15</td>
<td>1.15E-12</td>
</tr>
</tbody>
</table>
4 CONCLUSION

A Reactive Molecular Dynamics study of the reaction of C-C bond scission under the conditions of polymer melt conducted in the course of the current work showed that the values of the rate constant of the C-C scission reaction are approximately equal to those obtained for short alkanes in the gas phase. Therefore, the current study justifies the use of the gas phase C-C scission rate constant in the kinetic modeling of polymer pyrolysis.

The current work is the first experimental study in which the initial stages of pyrolysis of polyethylene were investigated at various temperatures using the methods of Gas Chromatography and Nuclear Magnetic Resonance. The methods permitted measuring the quantities of various gaseous and liquid products of pyrolysis, whereas the fact that even at the highest temperature employed in the study the pyrolysis process is still at its initial stages permitted to develop a simple kinetic mechanism with a minimal number of unknown parameters and successfully use it for the description of the kinetics of observed products. The kinetic analysis of the process of pyrolysis allowed to estimate rate constants of such important elementary processes as the addition of alkyl radicals to olefins, the recombination of alkyl radicals, and the abstraction of hydrogen atoms by alkyl radicals under the conditions of the liquid phase. Since the current study is the first experimental work the goal of which is the determination of rate constants of elementary processes under the conditions of polymer melt, it is impossible to compare the obtained values of the rate constants with the results of different research groups to test their validity. However, the values of the determined rate constants were found to be in reasonable agreement with the rate constants obtained for similar processes for short molecules and radicals in the gas phase.
5 APPENDIX A

Tables 5 – 9 list the abundances of gaseous pyrolysis products obtained at different temperatures and different pyrolysis times; y denotes the molar fraction of a product calculated as the ratio of the number of moles of the product released to the number of moles of CH₂ groups in a given HDPE sample, σ denotes a single standard error of the mean.
Table 5. Gaseous products of pyrolysis obtained at 400°C. y denotes the molar fraction, \( \sigma \) is one standard error of the mean.

<table>
<thead>
<tr>
<th>Pyrolysis product</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>y</td>
<td>( \sigma )</td>
<td>y</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>6.57E-08</td>
<td>5.6E-09</td>
<td>1.10E-07</td>
<td>8.0E-09</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>1.38E-07</td>
<td>1.1E-08</td>
<td>2.51E-07</td>
<td>2.1E-08</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>1.09E-07</td>
<td>1.1E-08</td>
<td>1.93E-07</td>
<td>1.7E-08</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>2.61E-07</td>
<td>2.2E-08</td>
<td>4.99E-07</td>
<td>4.2E-08</td>
</tr>
<tr>
<td>C(_3)H(_6)</td>
<td>1.94E-07</td>
<td>2.1E-08</td>
<td>4.31E-07</td>
<td>3.8E-08</td>
</tr>
<tr>
<td>C(_4)H(_10)</td>
<td>1.40E-07</td>
<td>1.3E-08</td>
<td>2.79E-07</td>
<td>2.5E-08</td>
</tr>
<tr>
<td>C(_4)H(_8)</td>
<td>7.90E-08</td>
<td>7.0E-09</td>
<td>1.57E-07</td>
<td>1.4E-08</td>
</tr>
<tr>
<td>1-C(_4)H(_8)</td>
<td>2.57E-08</td>
<td>2.5E-09</td>
<td>5.68E-08</td>
<td>5.0E-09</td>
</tr>
<tr>
<td>2-C(_4)H(_8)</td>
<td>2.58E-07</td>
<td>2.8E-08</td>
<td>5.07E-07</td>
<td>4.3E-08</td>
</tr>
<tr>
<td>C(_5)H(_12)</td>
<td>7.40E-08</td>
<td>7.3E-09</td>
<td>1.47E-07</td>
<td>1.3E-08</td>
</tr>
<tr>
<td>1-C(_5)H(_10)</td>
<td>1.31E-07</td>
<td>2.1E-08</td>
<td>2.55E-07</td>
<td>9.0E-09</td>
</tr>
<tr>
<td>1-C(_6)H(_12)</td>
<td>2.16E-07</td>
<td>2.3E-08</td>
<td>4.31E-07</td>
<td>3.8E-08</td>
</tr>
<tr>
<td>C(_7)H(_16)</td>
<td>2.84E-08</td>
<td>2.7E-09</td>
<td>6.16E-08</td>
<td>5.5E-09</td>
</tr>
<tr>
<td>1-C(_7)H(_14)</td>
<td>3.10E-08</td>
<td>3.0E-09</td>
<td>5.91E-08</td>
<td>5.2E-09</td>
</tr>
<tr>
<td>C(_8)H(_18)</td>
<td>1.57E-08</td>
<td>2.0E-09</td>
<td>3.47E-08</td>
<td>3.7E-09</td>
</tr>
</tbody>
</table>
Table 6. Gaseous products of pyrolysis obtained at 410°C. y denotes the molar fraction, σ is one standard error of the mean.

<table>
<thead>
<tr>
<th>pyrolysis product</th>
<th>pyrolysis time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>y</td>
</tr>
<tr>
<td>CH4</td>
<td>2.63E-07</td>
</tr>
<tr>
<td>C2H6</td>
<td>6.29E-07</td>
</tr>
<tr>
<td>C2H4</td>
<td>6.41E-07</td>
</tr>
<tr>
<td>C3H8</td>
<td>1.36E-06</td>
</tr>
<tr>
<td>C3H6</td>
<td>1.30E-06</td>
</tr>
<tr>
<td>C4H10</td>
<td>1.03E-06</td>
</tr>
<tr>
<td>1-C4H8</td>
<td>4.52E-07</td>
</tr>
<tr>
<td>2-C4H8</td>
<td>1.93E-07</td>
</tr>
<tr>
<td>C5H12</td>
<td>1.20E-06</td>
</tr>
<tr>
<td>1-C5H10</td>
<td>4.23E-07</td>
</tr>
<tr>
<td>C6H14</td>
<td>5.92E-07</td>
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<tr>
<td>1-C6H12</td>
<td>1.35E-06</td>
</tr>
<tr>
<td>C7H16</td>
<td>2.28E-07</td>
</tr>
<tr>
<td>1-C7H14</td>
<td>2.34E-07</td>
</tr>
<tr>
<td>C8H18</td>
<td>1.33E-07</td>
</tr>
</tbody>
</table>
Table 7. Gaseous products of pyrolysis obtained at 420°C. $y$ denotes the molar fraction, $\sigma$ is one standard error of the mean.

<table>
<thead>
<tr>
<th>pyrolysis product</th>
<th>5 (y, $\sigma$)</th>
<th>10 (y, $\sigma$)</th>
<th>15 (y, $\sigma$)</th>
<th>20 (y, $\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>4.15E-07, 4.9E-08</td>
<td>6.33E-07, 1.04E-07</td>
<td>1.01E-06, 1.6E-07</td>
<td>1.56E-06, 2.2E-07</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>6.69E-07, 1.1E-08</td>
<td>1.19E-06, 2.4E-07</td>
<td>1.87E-06, 2.5E-07</td>
<td>3.06E-06, 3.9E-07</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>6.11E-07, 1.4E-08</td>
<td>1.10E-06, 1.9E-07</td>
<td>1.66E-06, 2.6E-07</td>
<td>2.49E-06, 3.3E-07</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>1.32E-06, 5.8E-08</td>
<td>2.41E-06, 5.2E-07</td>
<td>3.52E-06, 4.2E-07</td>
<td>5.54E-06, 6.6E-07</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>1.18E-06, 6.8E-08</td>
<td>2.62E-06, 5.3E-07</td>
<td>4.30E-06, 6.0E-07</td>
<td>7.13E-06, 8.5E-07</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>7.08E-07, 3.2E-08</td>
<td>1.34E-06, 2.8E-07</td>
<td>1.93E-06, 2.5E-07</td>
<td>3.10E-06, 3.7E-07</td>
</tr>
<tr>
<td>1-C$_4$H$_8$</td>
<td>3.84E-07, 2.0E-08</td>
<td>8.00E-07, 1.51E-07</td>
<td>1.22E-06, 1.9E-07</td>
<td>2.01E-06, 2.4E-07</td>
</tr>
<tr>
<td>2-C$_4$H$_8$</td>
<td>1.42E-07, 1.2E-08</td>
<td>3.61E-07, 6.6E-08</td>
<td>5.65E-07, 1.06E-07</td>
<td>9.54E-07, 1.16E-07</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{12}$</td>
<td>1.06E-06, 8.0E-08</td>
<td>1.88E-06, 3.9E-07</td>
<td>2.42E-06, 3.6E-07</td>
<td>3.77E-06, 4.1E-07</td>
</tr>
<tr>
<td>1-C$<em>5$H$</em>{10}$</td>
<td>3.45E-07, 2.4E-08</td>
<td>6.82E-07, 1.26E-07</td>
<td>9.56E-07, 2.4E-07</td>
<td>1.56E-06, 1.8E-07</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{14}$</td>
<td>4.42E-07, 5.4E-08</td>
<td>8.08E-07, 1.51E-07</td>
<td>1.07E-06, 2.9E-07</td>
<td>1.59E-06, 1.7E-07</td>
</tr>
<tr>
<td>1-C$<em>6$H$</em>{12}$</td>
<td>9.23E-07, 1.32E-07</td>
<td>1.68E-06, 3.2E-07</td>
<td>2.09E-06, 6.0E-07</td>
<td>3.14E-06, 3.4E-07</td>
</tr>
<tr>
<td>C$<em>7$H$</em>{16}$</td>
<td>1.60E-07, 3.3E-08</td>
<td>3.00E-07, 4.9E-08</td>
<td>3.76E-07, 1.22E-07</td>
<td>5.70E-07, 5.7E-08</td>
</tr>
<tr>
<td>1-C$<em>7$H$</em>{14}$</td>
<td>1.55E-07, 2.8E-08</td>
<td>2.95E-07, 4.4E-08</td>
<td>3.57E-07, 1.20E-07</td>
<td>5.26E-07, 5.6E-08</td>
</tr>
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<td>C$<em>8$H$</em>{18}$</td>
<td>8.47E-08, 2.06E-08</td>
<td>1.56E-07, 2.3E-08</td>
<td>1.74E-07, 6.5E-08</td>
<td>2.61E-07, 2.5E-08</td>
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</table>
Table 8. Gaseous products of pyrolysis obtained at 430°C. y denotes the molar fraction, σ is one standard error of the mean.

<table>
<thead>
<tr>
<th>pyrolysis product</th>
<th>pyrolysis time, min</th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td></td>
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</tr>
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<td>σ</td>
<td>y</td>
<td>σ</td>
<td>y</td>
<td>σ</td>
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<td>3.6E-07</td>
<td>6.04E-06</td>
<td>6.6E-07</td>
</tr>
<tr>
<td>C₃H₆</td>
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<td>3.6E-07</td>
<td>4.13E-06</td>
<td>4.3E-07</td>
<td>7.86E-06</td>
<td>8.3E-07</td>
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<tr>
<td>C₄H₁₀</td>
<td>1.16E-06</td>
<td>1.8E-07</td>
<td>1.94E-06</td>
<td>2.0E-07</td>
<td>3.31E-06</td>
<td>3.7E-07</td>
</tr>
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<td>1-C₄H₈</td>
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<td>1.00E-07</td>
<td>1.18E-06</td>
<td>1.1E-07</td>
<td>2.25E-06</td>
<td>2.3E-07</td>
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<td>C₅H₁₂</td>
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<td>3.8E-07</td>
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<tr>
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<td>7.3E-08</td>
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<td>1.74E-06</td>
<td>1.7E-07</td>
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<td>1.60E-06</td>
<td>1.6E-07</td>
</tr>
<tr>
<td>1-C₆H₁₂</td>
<td>1.33E-06</td>
<td>1.5E-07</td>
<td>2.26E-06</td>
<td>2.5E-07</td>
<td>3.33E-06</td>
<td>3.3E-07</td>
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<tr>
<td>C₇H₁₆</td>
<td>2.35E-07</td>
<td>3.0E-08</td>
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<td>5.91E-07</td>
<td>6.3E-08</td>
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<tr>
<td>1-C₇H₁₄</td>
<td>2.18E-07</td>
<td>2.6E-08</td>
<td>3.97E-07</td>
<td>4.4E-08</td>
<td>5.69E-07</td>
<td>5.5E-08</td>
</tr>
<tr>
<td>C₈H₁₈</td>
<td>1.16E-07</td>
<td>1.7E-08</td>
<td>1.94E-07</td>
<td>2.4E-08</td>
<td>2.37E-07</td>
<td>2.7E-08</td>
</tr>
</tbody>
</table>
Table 9. Gaseous products of pyrolysis obtained at 440°C. y denotes the molar fraction, \( \sigma \) is one standard error of the mean.

<table>
<thead>
<tr>
<th>pyrolysis product</th>
<th>pyrolysis time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
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<tr>
<td></td>
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<tr>
<td>CH4</td>
<td>1.13E-06</td>
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<tr>
<td>C2H6</td>
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<td>C2H4</td>
<td>2.47E-06</td>
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<tr>
<td>C3H8</td>
<td>5.28E-06</td>
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<tr>
<td>C3H6</td>
<td>5.44E-06</td>
</tr>
<tr>
<td>C4H10</td>
<td>2.72E-06</td>
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<tr>
<td>1-C4H8</td>
<td>1.62E-06</td>
</tr>
<tr>
<td>2-C4H8</td>
<td>7.21E-07</td>
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<td>1-C5H10</td>
<td>1.37E-06</td>
</tr>
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<td>C6H14</td>
<td>1.44E-06</td>
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<tr>
<td>1-C6H12</td>
<td>3.21E-06</td>
</tr>
<tr>
<td>C7H16</td>
<td>6.61E-07</td>
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<tr>
<td>1-C7H14</td>
<td>6.29E-07</td>
</tr>
<tr>
<td>C8H18</td>
<td>2.79E-07</td>
</tr>
</tbody>
</table>
Tables 10 – 14 contain the results of $^1$H NMR analysis of the liquid fraction of pyrolysis products obtained at various times and temperatures; $\kappa$ denotes the ratio of the signal of a particular proton to the signal of the protons of CH$_2$ groups, $\sigma$ represents one standard error of the mean. The “H atom type” column represents the types of hydrogen atoms to which particular signals in 1H NMR spectra are assigned. Thus, RC{H}=CH$_2$ and RCH=C{H}$_2$ denote the signals of the nonterminal and terminal H atoms of the vinyl group, respectively (chemical shift ranges are 5.6 – 6.0 ppm and 4.8 – 5.1 ppm, respectively), RC{H}=C{H}R$_1$ denotes the signal of the H atoms of the vinylene group (the chemical shift range 5.2 – 5.6 ppm), and RR$_1$C=C{H}$_2$ denotes the signals of the H atoms of the vinylidene group (the chemical shift range 4.7 – 4.8 ppm).
Table 10. The results of $^1$H NMR analysis of the liquid fraction of HDPE pyrolysis products obtained at 400°C.

<table>
<thead>
<tr>
<th>H atom type</th>
<th>pyrolysis time, min</th>
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<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>κ</td>
<td>σ</td>
<td>κ</td>
<td>σ</td>
<td>κ</td>
</tr>
<tr>
<td>RC{H}=CH₂</td>
<td></td>
<td>5.20E-05</td>
<td>3.2E-06</td>
<td>1.84E-04</td>
<td>1.1E-05</td>
<td>3.00E-04</td>
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<tr>
<td>RC{H}=C{H}R₁</td>
<td></td>
<td>6.34E-05</td>
<td>6.9E-06</td>
<td>9.99E-05</td>
<td>1.08E-05</td>
<td>1.30E-04</td>
</tr>
<tr>
<td>RCH=C{H}₂</td>
<td></td>
<td>1.07E-04</td>
<td>9.E-06</td>
<td>4.05E-04</td>
<td>1.7E-05</td>
<td>6.37E-04</td>
</tr>
<tr>
<td>RR₁C=C{H}₂</td>
<td></td>
<td>1.94E-05</td>
<td>1.0E-05</td>
<td>3.85E-05</td>
<td>1.3E-06</td>
<td>5.95E-05</td>
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</table>

Table 11. The results of $^1$H NMR analysis of the liquid fraction of HDPE pyrolysis products obtained at 410°C.

<table>
<thead>
<tr>
<th>H atom type</th>
<th>pyrolysis time, min</th>
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<th>20</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>κ</td>
<td>σ</td>
<td>κ</td>
<td>σ</td>
<td>κ</td>
</tr>
<tr>
<td>RC{H}=CH₂</td>
<td></td>
<td>5.20E-05</td>
<td>3.2E-06</td>
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<td>-</td>
<td>6.74E-04</td>
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<td>RC{H}=C{H}R₁</td>
<td></td>
<td>6.34E-05</td>
<td>6.9E-06</td>
<td>1.90E-04</td>
<td>-</td>
<td>3.33E-04</td>
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<tr>
<td>RCH=C{H}₂</td>
<td></td>
<td>1.07E-04</td>
<td>9.E-06</td>
<td>1.21E-03</td>
<td>-</td>
<td>1.52E-03</td>
</tr>
<tr>
<td>RR₁C=C{H}₂</td>
<td></td>
<td>1.94E-05</td>
<td>1.03E-05</td>
<td>6.35E-05</td>
<td>-</td>
<td>1.03E-04</td>
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</table>
Table 12. The results of $^1$H NMR analysis of the liquid fraction of HDPE pyrolysis products obtained at 420°C.

<table>
<thead>
<tr>
<th>H atom type</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>κ</td>
</tr>
<tr>
<td>RC{H}=CH$_2$</td>
<td>5.20E-05</td>
</tr>
<tr>
<td>RC{H}=C{H}R$_1$</td>
<td>6.34E-05</td>
</tr>
<tr>
<td>RCH=C{H}$_2$</td>
<td>1.07E-04</td>
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<td>RR$_2$C=C{H}$_2$</td>
<td>1.94E-05</td>
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</table>

Table 13. The results of $^1$H NMR analysis of the liquid fraction of HDPE pyrolysis products obtained at 430°C.

<table>
<thead>
<tr>
<th>H atom type</th>
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</thead>
<tbody>
<tr>
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</tr>
<tr>
<td></td>
<td>κ</td>
</tr>
<tr>
<td>RC{H}=CH$_2$</td>
<td>5.20E-05</td>
</tr>
<tr>
<td>RC{H}=C{H}R$_1$</td>
<td>6.34E-05</td>
</tr>
<tr>
<td>RCH=C{H}$_2$</td>
<td>1.07E-04</td>
</tr>
<tr>
<td>RR$_2$C=C{H}$_2$</td>
<td>1.94E-05</td>
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</tbody>
</table>
Table 14. The results of $^1$H NMR analysis of the liquid fraction of HDPE pyrolysis products obtained at 440°C.

<table>
<thead>
<tr>
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</thead>
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<tr>
<td></td>
<td>κ</td>
</tr>
<tr>
<td>RC=CH₂</td>
<td>5.20E-05</td>
</tr>
<tr>
<td>RC=CH_1R₈</td>
<td>6.34E-05</td>
</tr>
<tr>
<td>RCH=C=CH₂</td>
<td>1.07E-04</td>
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<tr>
<td>RR₁C=C=CH₂</td>
<td>1.94E-05</td>
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</tbody>
</table>

Tables 15 – 19 contain the values of molar fractions of the three types of double bonds (vinyl, vinylene, and vinylidene) denoted as $\chi$ and their uncertainties denoted as $\sigma$, which represent one standard error of the mean. In the case of vinylene and vinylidene groups the values of the molar fractions were determined as the ratio of the $^1$H NMR signals of hydrogen atoms of these groups $s(H)$ to the signals of hydrogen atoms of the CH₂ group $s(CH₂)$:

$$\chi = \frac{s(H)}{s(CH₂)}.$$

Since the vinyl group, unlike the vinylene and vinylidene groups that have two hydrogen atoms, has three hydrogen atoms, its molar fraction was determined as the sum of the ratios of the signals of its hydrogen atoms ($s(1H)$ and $s(2H)$) to the signal of the CH₂ group $s(CH₂)$ multiplied by a factor of $\frac{2}{3}$:

$$\chi = \frac{2 s(1H) + s(2H)}{3 s(CH₂)}.$$
Table 15. Molar fractions of unsaturated groups in the liquid phase of the pyrolysis products obtained at 400°C.

<table>
<thead>
<tr>
<th>double bond type</th>
<th>pyrolysis time, min</th>
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<tbody>
<tr>
<td></td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
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<td>3.93E-04</td>
<td>1.86E-05</td>
<td>6.24E-04</td>
<td>4.51E-05</td>
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<tr>
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<td>6.89E-06</td>
<td>9.99E-05</td>
<td>1.08E-05</td>
<td>1.30E-04</td>
<td>6.53E-06</td>
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<tr>
<td>vinylidene</td>
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<td>1.03E-05</td>
<td>3.85E-05</td>
<td>1.34E-06</td>
<td>5.95E-05</td>
<td>3.57E-06</td>
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</table>

Table 16. Molar fractions of unsaturated groups in the liquid phase of the pyrolysis products obtained at 410°C.

<table>
<thead>
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<th>15</th>
<th>20</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
</tr>
<tr>
<td>vinyl</td>
<td>1.06E-04</td>
<td>8.00E-06</td>
<td>1.17E-03</td>
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<td>1.90E-04</td>
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<td>3.33E-04</td>
<td>5.66E-06</td>
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<td>1.94E-05</td>
<td>1.03E-05</td>
<td>6.35E-05</td>
<td>-</td>
<td>1.03E-04</td>
<td>1.85E-05</td>
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</table>
### Table 17. Molar fractions of unsaturated groups in the liquid phase of the pyrolysis products obtained at 420°C.

<table>
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<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
</tr>
<tr>
<td>vinyl</td>
<td>1.06E-04</td>
<td>8.00E-06</td>
<td>1.22E-03</td>
<td>4.56E-05</td>
<td>1.69E-03</td>
<td>6.25E-05</td>
</tr>
<tr>
<td>vinylene</td>
<td>6.34E-05</td>
<td>6.89E-06</td>
<td>2.10E-04</td>
<td>1.10E-05</td>
<td>4.46E-04</td>
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</tr>
<tr>
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<td>1.94E-05</td>
<td>1.03E-05</td>
<td>8.85E-05</td>
<td>5.47E-06</td>
<td>1.57E-04</td>
<td>1.40E-05</td>
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</table>

### Table 18. Molar fractions of unsaturated groups in the liquid phase of the pyrolysis products obtained at 430°C.

<table>
<thead>
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<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
</tr>
<tr>
<td>vinyl</td>
<td>1.06E-04</td>
<td>8.00E-06</td>
<td>1.25E-03</td>
<td>7.66E-05</td>
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<td>7.64E-05</td>
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<tr>
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<td>6.89E-06</td>
<td>2.49E-04</td>
<td>1.18E-05</td>
<td>4.33E-04</td>
<td>3.56E-05</td>
</tr>
<tr>
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<td>1.94E-05</td>
<td>1.03E-05</td>
<td>9.43E-05</td>
<td>1.83E-06</td>
<td>1.45E-04</td>
<td>7.39E-06</td>
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</tbody>
</table>
Table 19. Molar fractions of unsaturated groups in the liquid phase of the pyrolysis products obtained at 440°C.

<table>
<thead>
<tr>
<th>double bond type</th>
<th>pyrolysis time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>χ</td>
<td>σ</td>
</tr>
<tr>
<td>vinyl</td>
<td>1.06E-04</td>
</tr>
<tr>
<td>vinylene</td>
<td>6.34E-05</td>
</tr>
<tr>
<td>vinylidene</td>
<td>1.94E-05</td>
</tr>
</tbody>
</table>

Tables 20 – 24 contain the results of $^{13}$C NMR analysis of the liquid fraction of HDPE pyrolysis products; $κ$ denotes the ratio of the signal of a particular type of carbon atom to the signal of the carbons of CH$_2$ groups, $σ$ represents one standard error of the mean. The identification of particular resonances in the spectra was based on the work by Qu et al. (80). In Qu’s notation (that was also preserved in Tables 19 – 23) CH$_Y$ denotes a signal of a tertiary carbon atom, $α$ and $β$ are the carbon atoms in the polymer chains joined in CH$_Y$ that follow down the chain immediately after the junction; 1S is an ending C atom of a long saturated polymer chain, 2S and 3S are the C atoms that follow down the chain immediately after 1S; 1B$_6$ is an ending atom of a butyl branch.
Table 20. Signals identified in $^{13}$C NMR spectra of the liquid phase of the HDPE pyrolysis products obtained at 400°C.

<table>
<thead>
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<th>C atom type</th>
<th>pyrolysis time, min</th>
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<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>κ</td>
<td>σ</td>
<td>κ</td>
<td>σ</td>
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<tr>
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Table 21. Signals identified in 13C NMR spectra of the liquid phase of the HDPE pyrolysis products obtained at 410°C.

<table>
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<td>κ</td>
<td>σ</td>
<td>κ</td>
<td>σ</td>
<td>κ</td>
</tr>
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<td>CHy</td>
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<td>9.40E-03</td>
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<td>1.04E-02</td>
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</tr>
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<td>8.8E-04</td>
<td>1.18E-02</td>
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Table 22. Signals identified in 13C NMR spectra of the liquid phase of the HDPE pyrolysis products obtained at 420°C.

<table>
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<tr>
<th>C atom type</th>
<th>( \kappa )</th>
<th>( \sigma )</th>
<th>( \kappa )</th>
<th>( \sigma )</th>
<th>( \kappa )</th>
<th>( \sigma )</th>
<th>( \kappa )</th>
<th>( \sigma )</th>
</tr>
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<td>4.6E-04</td>
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<td>5.6E-04</td>
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</tr>
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<td>( \beta )</td>
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<td>1.45E-02</td>
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</tr>
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<td>4.5E-04</td>
<td>7.43E-03</td>
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<td>7.41E-03</td>
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<td>1.1E-03</td>
</tr>
<tr>
<td>1S+1Bb</td>
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<td>9.14E-03</td>
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Table 23. Signals identified in 13C NMR spectra of the liquid phase of the HDPE pyrolysis products obtained at 430°C.

<table>
<thead>
<tr>
<th>C atom type</th>
<th>pyrolysis time, min</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
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<tr>
<td></td>
<td>κ</td>
</tr>
<tr>
<td>CHy</td>
<td>3.08E-03</td>
</tr>
<tr>
<td>α</td>
<td>9.09E-03</td>
</tr>
<tr>
<td>3S</td>
<td>3.57E-03</td>
</tr>
<tr>
<td>β</td>
<td>1.02E-02</td>
</tr>
<tr>
<td>2S</td>
<td>4.15E-03</td>
</tr>
<tr>
<td>1S+1Bb</td>
<td>3.41E-03</td>
</tr>
</tbody>
</table>
Table 24. Signals identified in 13C NMR spectra of the liquid phase of the HDPE pyrolysis products obtained at 440°C.

<table>
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<tr>
<th>C atom type</th>
<th>pyrolysis time, min</th>
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<tbody>
<tr>
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<td>0</td>
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<tr>
<td></td>
<td>κ</td>
</tr>
<tr>
<td>CHy</td>
<td>3.08E-03</td>
</tr>
<tr>
<td>α</td>
<td>9.09E-03</td>
</tr>
<tr>
<td>3S</td>
<td>3.57E-03</td>
</tr>
<tr>
<td>β</td>
<td>1.02E-02</td>
</tr>
<tr>
<td>1S+1Bb</td>
<td>3.41E-03</td>
</tr>
</tbody>
</table>
Tables 25 – 29 contain the values of molar fractions of CHy and CH3 groups denoted as \( \chi \) with their standard errors of the mean denoted as \( \sigma \). The molar fractions of CH3 groups were calculated as an average value of \( \kappa \) of 1S + 1Bb, 2S, and 3S signals (since every polymer chain ending has one 1S, 2S, and 3S atom). The molar fraction of CHy was calculated according to the formula

\[
\chi = \frac{1}{3} \left( \kappa(CH_y) + \frac{1}{3} \kappa(\alpha) + \frac{1}{3} \kappa(\beta) \right),
\]

where \( \kappa(CH_y) \), \( \kappa(\alpha) \), and \( \kappa(\beta) \) are the ratios of the signals of CHy, \( \alpha \), and \( \beta \) carbon atoms, respectively (can be found in Tables 19 – 23). The coefficient \( \frac{1}{3} \) before \( \kappa(\alpha) \) and \( \kappa(\beta) \) follows from the fact that every tertiary carbon atom is a junction of three polymer chains and therefore there are three \( \alpha \) and \( \beta \) carbon atoms per one junction.

**Table 25.** The molar fractions of CH3 and CHy groups obtained in the liquid phase of the products of HDPE pyrolysis conducted at 400°C.

<table>
<thead>
<tr>
<th>group type</th>
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<tr>
<td></td>
<td>( \chi )</td>
<td>( \sigma )</td>
<td>( \chi )</td>
<td>( \sigma )</td>
<td>( \chi )</td>
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<td>3.11E-03</td>
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**Table 26.** The molar fractions of CH₃ and CH₄ groups obtained in the liquid phase of the products of HDPE pyrolysis conducted at 410°C.

<table>
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<th>group type</th>
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<td>CH₃</td>
<td>(\chi) 3.71E-03</td>
<td>(\sigma) 4.1E-04</td>
<td>(\chi) 5.84E-03</td>
<td>(\sigma) 3.7E-04</td>
<td>(\chi) 7.35E-03</td>
<td>(\sigma) 7.1E-04</td>
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<tr>
<td>CH₄</td>
<td>(\chi) 3.17E-03</td>
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<td>(\chi) 3.33E-03</td>
<td>(\sigma) 3.4E-04</td>
<td>(\chi) 3.60E-03</td>
<td>(\sigma) 1.6E-04</td>
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</table>

**Table 27.** The molar fractions of CH₃ and CH₄ groups obtained in the liquid phase of the products of HDPE pyrolysis conducted at 420°C.

<table>
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<tr>
<th>group type</th>
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<td>10</td>
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<tr>
<td>CH₃</td>
<td>(\chi) 3.71E-03</td>
<td>(\sigma) 4.1E-04</td>
<td>(\chi) 7.19E-03</td>
<td>(\sigma) 1.08E-03</td>
<td>(\chi) 7.19E-03</td>
<td>(\sigma) 6.3E-04</td>
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<tr>
<td>CH₄</td>
<td>(\chi) 3.17E-03</td>
<td>(\sigma) 3.1E-04</td>
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<td>(\chi) 3.84E-03</td>
<td>(\sigma) 2.6E-04</td>
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**Table 28.** The molar fractions of CH₃ and CH₄ groups obtained in the liquid phase of the products of HDPE pyrolysis conducted at 430°C.

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<tr>
<td>CH₃</td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
<td>χ</td>
<td>σ</td>
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</tr>
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**Table 29.** The molar fractions of CH₃ and CH₄ groups obtained in the liquid phase of the products of HDPE pyrolysis conducted at 440°C.

<table>
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</tr>
<tr>
<td>CH₃</td>
<td>χ</td>
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<td>χ</td>
<td>σ</td>
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7 BIBLIOGRAPHY


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