



Autocatalysis in thermal decomposition of polymers



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ABSTRACT

Possibility of replicating polymer decomposition by a single global reaction greatly simplifies pyrolysis modeling. Apparent kinetic parameters are normally derived from the microscale experiments with linear heating program, and the n -th order reaction is routinely assumed thereby strongly affecting the numerical values of the kinetic parameters. In this work, we demonstrate inconsistency of the n -th order reaction assumption and reveal the autocatalytic behavior in thermal degradation of polyethylene, polystyrene and polycarbonate. The autocatalysis manifests itself in non-monotonicity of the conversion function, which markedly increases in a wide range of conversions. Although the iso-conversional approach makes it possible to explicitly recover the conversion function from the measurements, this option has not been used in most of the previous studies. Meanwhile, proper approximation of the experimentally derived conversion function results in excellent replication of the measured reaction rates, with the same kinetic parameters, in a range of the heating rates. Thus developed thermal decomposition kinetic models are provided in this paper for three kinds of polyethylene (LDPE, HDPE, and UHMWPE), seven kinds of polystyrene, polycarbonate, and two kinds of polymethylmethacrylate with different molecular weights. Although the pyrolysis of the polymers with different molecular weights proceeds differently, no systematic correlation of the pyrolysis characteristics (conversion-averaged apparent activation energy, heat of combustion, peak reaction rates and temperatures etc.) with the molecular weight has been observed for polystyrene. Peak reaction rates and temperatures varied in opposite directions for polyethylene and polymethylmethacrylate.

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1. Introduction

Thermal decomposition is the inherent and triggering stage of polymer combustion being either controlled in waste utilization and solid fuel propulsion or uncontrolled in fires. Practical modeling of polymer decomposition is normally based on formal kinetic models [1], which include global reactions converting virgin material to volatiles and, possibly, char. This implies the need to reliably determine apparent kinetic parameters applicable in a range of heating rates. For this purpose, the measurement data obtained by thermogravimetry (TGA) and the microscale combustion calorimetry (MCC) are normally used. A number of data processing strategies have been developed including model-fitting and

model-free approaches, as well as the simplified peak value based methods [2].

The literature review outlined below shows that, in spite of the long term research and vast amount of published studies, inconsistency of global kinetic models and apparent kinetic parameters can be concluded even for basic and presumably well-studied practical polymers such as PE, PS, PC, PMMA, among others. Such an inconsistency of the reaction model results in:

1. Inability to predict TGA/MCC thermal decomposition data at different heating rates with the same kinetic parameters.
2. Qualitatively incorrect shape of the conversion function in the reaction rate equation (conversion rate of change vs. conversion).
3. Unacceptable sensitivity of the apparent kinetic parameters to the method used in its derivation, strong variations of the reported values obtained by the different methods.

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4. Unrealistic values of the apparent activation energies contradicting to those derived by model-free iso-conversional methods.

The purpose of this work is to highlight the importance of proper choice of the above-mentioned conversion function in pyrolysis modeling. To date, the n -th order reaction is assumed in overwhelming majority of the studies focusing on formal kinetic modeling of polymer pyrolysis, with very few exceptions. However, thermal decomposition of many important polymers does not obey the n -th order reaction and, instead, exhibits the autocatalytic reaction acceleration in a wide range of conversion. For example, in Refs. [3,4] it was already demonstrated for a particular type of polystyrene. Based on the MCC measurement data, in this work we show it for several kinds of polyethylene and polystyrene, as well as for polycarbonate. In contrast, we demonstrate that polymethylmethacrylate is the example of polymer that decomposes in accordance with the n -th order reaction model.

The additional objective of this work is to explore the effect of the molecular weight of a polymer on its pyrolysis; the existing literature does not suggest a definite conclusion whether it might be a possible reason of considerable differences between the kinetic data reported for the same polymer names in different studies.

2. Formal kinetics approach in pyrolysis modeling

2.1. The bias in favor of the n -th order reaction model

In this review, we restrict ourselves to the studies in which the formal kinetics approach is applied to pyrolysis modeling, and thermal decomposition is represented by a single global reaction. Recently, it has been demonstrated in Ref. [5] that this approach can be generalized to replicate multi-step pyrolysis of arbitrary complexity, if the dependencies of the apparent activation energy and the product of pre-exponential factor and the conversion function on conversion are accounted for. Here we consider a conventional approach with constant values of the kinetic parameters, which is only applicable to single-step reactions.

For polyethylene and polystyrene, a review of kinetic models and summary of the kinetic parameters published before 2000s can be found in Refs. [6] [7], and [8]. In particular, only the studies, which used the n -th order reaction model, were presented in Refs. [6] and [7]. As a result, the reported kinetic constants differ greatly over the conversion range, being very sensitive to the method applied to process measurement data. Rather strong variation of the rate constants was also observed thereby implying possible influence of molecular weight and measurement errors. Most importantly, it was highlighted in Ref. [6] that the use of the simple n -th order reaction model over a large conversion range is probably the major reason of the observed differences.

In spite of the above conclusion, the n -th order reaction model dominates in majority of more recent studies and is used to process TGA data, for example, in Ref. [9] (for HDPE, LDPE and LLDPE) [10], (HDPE) [11], (LLDPE) [12] (LDPE) [13], (PS), and [14] (HDPE), among many others. Apparent activation energies of 333–343, 187–199 and 219–230 kJ/mol were reported in Ref. [9] for thermal degradation of HDPE, LDPE and LLDPE, respectively. In Ref. [15], conversion-average activation energy 226.36 kJ/mol was obtained by applying the method of Friedman to TGA data, and the reaction order 0.582 was obtained using the measured peak values. Note, however, that kinetic data obtained in Refs. [9] and [15] by different methods are also very different. In Ref. [14], none of the methods applied to process TGA data were found to have an acceptable agreement with the experimental data, and, to tackle the problem,

an alternative iso-conversional procedure was proposed. It has to be highlighted, however, that this problem cannot be remedied by refining the data processing method if the n -th order reaction model fundamentally fails.

Given the conventional bias in favor of the n -th order reaction model, Refs. [16,17] and [18] are the notable exceptions. In particular, in Ref. [16], the autocatalytic expression for conversion function, $f(\alpha) = (1 - \alpha)^n \alpha^m$, is applied in processing TGA results for mixtures of polymers including polycarbonate. Based on the pyrolysis data for polytetrafluoroethylene and polyethylene, Ref. [17] acknowledges that the n -order kinetic law is not universal and may lead to wrong values of the kinetic parameters, thereby restricting model applicability to the case for which the model is calibrated. In Ref. [18] the same conclusion was made for thermal degradation of polybutylene terephthalate, and it was attributed to the random scission mechanism. Acceleratory phase at the beginning of the polystyrene pyrolysis was noticed in Ref. [1].

2.2. The effect of molecular weight

The effect of molecular weight has been observed in a number of studies including earlier work by Kokta et al. Ref. [19], in which polystyrene decomposition was studied by TGA. It was shown that the maximum rate and the activation energy of the decomposition increase up to molecular weights of about 360 kg/mol and then level off. Apparent activation energy of 42 ± 5 kcal/mol was determined. However, in Ref. [20], no dependence of the activation energy on molecular weight was found, although the peak temperature correlated well with the molecular weight. More recently in Ref. [21], the activation energy was shown to increase with the molecular weight. Below 370 °C, activation energies between 160 and 190 kJ/mol were found, whilst above 370 °C, the values between 200 and 320 kJ/mol were obtained.

In thermal degradation of polymethylmethacrylates studied by Kashiwagi et al. in Ref. [22], it has been noticed that, depending on the manufacturing procedure and the polymerization method, some abnormal linkages may develop, which are weaker than those in normal monomer chain. These weak linkages initiate depolymerization at lower temperatures thereby producing minor peaks in DTG curves. Also, the initial molecular weight distribution can have a large polydispersity and even be bimodal, which implies that the mean molecular weight may not be a comprehensive characteristic of the polymer structure. Comparison of three similarly produced PMMA polymers with the molecular weights of 44.6, 176 and 320 kg/mol in Ref. [22] shown that the increase of the initial molecular weight causes reduction of the minor DTG peaks with more pronounced domination of the major peak. Note, however, that in the more recent study by Ferriol et al. Ref. [23], rather strong multiple peaks were recorded for molecular weight as high as 996 kg/mol, albeit at relatively low heating rates. In Ref. [24], it was concluded that, in linear heating, the increase of the initial molecular weight causes the maximum degradation rate to reduce and to occur at lower temperatures.

In Ref. [23], PMMA decomposition was represented by four independent n -th order reactions, and their kinetic parameters were recovered by the multi-dimensional non-linear fitting. That made it possible to obtain excellent replication of the TGA data but did not provide information on possibility of applying a global single-reaction model, presumably valid at the heating rates higher than those (below 10 K/min) used in Ref. [23]. Indeed, at higher heating rates different reactions will overlap in temperature range, thereby justifying use of the single-step global reaction model. It can therefore be concluded that the effect of the initial molecular weight on *global* kinetic parameters of polymer decomposition has not been systematically addressed.

While reviewing the literature, researchers often concluded widely varying kinetic parameters with little correlation between them (for example, see Ref. [21]). It is therefore important to allow for the structural differences of the polymers produced by different polymerization methods, and the molecular weight is one of the relevant indicators. In this work, we explore the effect of different molecular weights on thermal decomposition of polyethylene, polystyrene, and polymethylmethacrylate.

3. Methodology

Flammable polymers studied in this work are listed in Table 1. These polymers are selected since their pyrolysis can be approximated by a single-step reaction model. Since any impurities and/or additives strongly affect the decomposition kinetics, we use the substances for which the manufacturing technology implies high (close to 100%) purity of the end product. In case of UHMWPE, the expected impurity is due to the remains of metal (Ti, Mg, Al)-organic catalyzers. As reported by the manufacturer, the mass fraction of the associated compounds in UHMWPE does not exceed 0.0006.

In the MCC apparatus, the mg-scale samples were exposed to the constant rate heating in nitrogen flow. Oxygen is added to the volatile-nitrogen flow in the proportion of 20% O₂ to 80% N₂. Pyrolysis volatiles are then completely oxidized in the combustion chamber, and the oxygen consumption rate is measured. Using the assumption of the constant heat of combustion per unit mass of oxygen consumed (taken equal to $\Delta h_{c,O_2} = 13.1$ kJ/g O₂), the specific heat release rate, \dot{q} , is recorded as a function of time, t , and sample temperature, T .

The measurement procedure for each heating rate follows that described in ASTM D7309-07a [25]. Although it coincides with that used in Ref. [5], it is briefly described below for clarity. Each measurement was performed at least 3 times to ensure repeatability of heat release rate-temperature curves and to assess average value and standard deviation. The measured dependencies of heat release rate on sample temperature, $\dot{q}(T)$, were pre-processed by applying the following operations: (i) interpolation to the sample temperature values aliquot 1 °C; (ii) subtracting the baseline (straight line between the sample temperature before the onset and after completion of the process); (iii) averaging over identical runs and evaluating standard deviation. Pre-processing of the MCC measurement data included evaluating transient (conversion, reaction rate), integral (total heat release, effective heat release capacity) and other (peak temperature, 10%, 50%, and 90% conversion temperatures) characteristics of material decomposition.

The measurement results are illustrated in Fig. 1, which shows dependencies of the heat release rate on time, $\dot{q}(t)$, obtained for polystyrene at different heating rates. Qualitatively similar single-peak dependencies were obtained for all the materials studied, which is the first indication of applicability the single-reaction pyrolysis model.

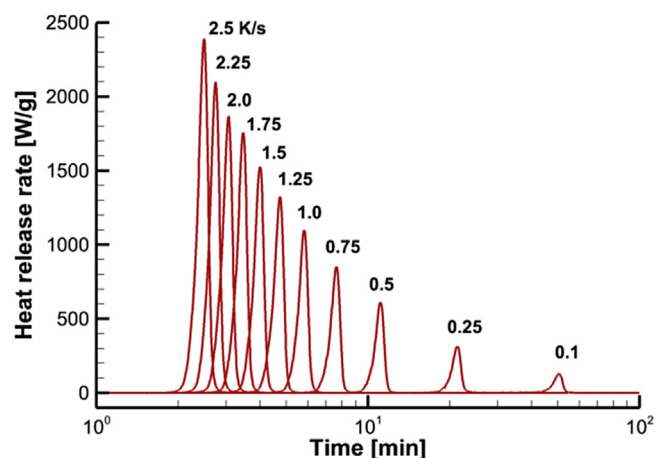


Fig. 1. MCC measurements for polystyrene, Mw = 980 kg/mol (each line is the average of several runs, the baseline is subtracted).

All the polymers considered here melt before the thermal decomposition run-away. Given the small sample mass, the layer of the molten substance is sufficiently thin to allow for the relatively high heating rates of order of 1 K/s. To derive the kinetic parameters, four heating rates 0.25, 0.5, 1 and 1.5 K/s were considered.

Although we only use the MCC data in this work, these data are closely related to the TGA measurements for the same materials since the chemical composition (and therefore their heat of combustion) does not vary significantly during the pyrolysis. This assumption is equivalent to the assumption of the single-step pyrolysis.

The heat release rate is coupled with the sample mass loss rate as

$$\dot{q} = \Delta q \left(-\frac{1}{m_0} \frac{dm}{dt} \right), \quad (1)$$

where m_0 is the initial sample mass, m is the current mass of solid material, and Δq is the heat of combustion per unit mass of combustible volatiles. Using the definition of the mass-based global conversion,

$$\alpha_m = \frac{m_0 - m}{m_0 - m_\infty} = \frac{1 - m/m_0}{1 - \nu_r},$$

and the mass-based gasification reaction rate,

$$\dot{r}_m = \frac{d\alpha_m}{dt}, \quad (2)$$

Eq. (1) is written as

$$\dot{q} = \Delta q \dot{r}_m, \quad (3)$$

Table 1

Materials (samples designated by* are not used in data processing as explained in the text).

Designation	Name	Molecular weight, kg/mol	Manufacturer	Sample mass, mg
LDPE	Low density polyethylene	50	Scientific Polymer Products Inc.	1.1–2.5
HDPE	High density polyethylene	125	Scientific Polymer Products Inc.	1.4–3.7
UHMWPE	Ultra high molecular weight polyethylene	2500	Boreskov Institute of Catalysis SB RAS	1.4–3.3
PS	Polystyrene	1.2*, 45*, 190, 210, 260, 311, 759, 980 and 2636	Scientific Polymer Products Inc.	1–3.5
PC	Poly(bisphenol-A-carbonate)	45	Scientific Polymer Products Inc.	4–6
PMMA35	Poly(methyl methacrylate)	35	Scientific Polymer Products Inc.	5–7
PMMA350	Poly(methyl methacrylate)	350	Sigma Aldrich Inc.	3–13

where $\Delta q' = \Delta q(1 - \nu_r)$ and $\nu_r = m_\infty/m_0$ is the residue mass fraction.

While processing the MCC measurement data, the heat release-based global conversion,

$$\alpha_q = \frac{\int_{T_0}^T \dot{q}(T) dT}{\int_{T_0}^{\infty} \dot{q}(T) dT} = \frac{1}{\overline{\Delta q'}} \int_0^{\alpha_m} \Delta q' d\alpha_m, \quad (4)$$

is evaluated. Both mass-based and heat release rate-based conversions are related to each other as

$$\overline{\Delta q'} d\alpha_q = \Delta q' d\alpha_m, \quad (5)$$

where $\overline{\Delta q'} = \int_0^\infty \dot{q} dt$ the integral heat of combustion per unit mass of the original sample. According to the above definitions,

$$\dot{q} = \Delta q' \dot{r}_m = \Delta q' \frac{d\alpha_m}{dt} = \overline{\Delta q'} \frac{d\alpha_q}{dt} = \overline{\Delta q'} \dot{r}_q, \quad (6)$$

where

$$\dot{r}_q = \frac{d\alpha_q}{dt} \quad (7)$$

is the heat release-based reaction rate.

As is shown in Ref. [5], the reaction rates (\dot{r}_m and \dot{r}_q), and conversions (α_m and α_q) derived from TGA and MCC data for the same material are identical if $\Delta q' = \overline{\Delta q'}$. Since this condition is approximately obeyed for the materials studied in this work, we will omit the subscripts m and q hereafter.

Thermal degradation of the original sample is described by a single global reaction, producing solid residual and combustible gas volatiles. The reaction rate defined by either Eq. (2) or (7) is modeled as

$$\dot{r} = Af(\alpha) \exp\left(-\frac{E_a}{RT}\right), \quad (8)$$

where the information on pyrolysis kinetics is accumulated in the numerical values of activation energy, E_a , pre-exponential factor, A , and in the conversion function, $f(\alpha)$, showing conversion dependence of the reaction rate (also called a reaction model).

To derive the values of E_a , A and to obtain $f(\alpha)$, we apply the methodology developed in our previous papers [3,4] consisting of three steps:

1. Evaluation of the apparent activation energy using the iso-conversional approach.
2. Formulation of the conversion function by fitting the measured dependence of reaction rate on conversion.
3. Given the activation energy and the kinetic function, evaluation of the pre-exponential factor.

The *first step* utilizes the method of Friedman which, unlike some of the other popular techniques, does not require any additional assumptions and approximations. The logarithmic form of Eq. (8) is used:

$$\ln r_i = -\left(\frac{E_a}{RT}\right)_i + \ln(Af(\alpha))_i, \quad (9)$$

where subscript i corresponds to a particular conversion, α_i . For a single heating rate, Eq. (9) yields a single point in the plot of $y = \ln r$ against $x = 1/T$. Multiple points produced by multiple heating rates

are approximated by the straight lines, $y(x) = a_i x + b_i$, and each line corresponds to a particular conversion, α_i . Values for a_i and b_i are obtained by the sum of the least squares procedure, thereby providing $E(\alpha_i) = a_i R$ and $\ln(Af(\alpha))_i = b_i$. Standard deviation is assessed as described in Ref. [3]. This procedure is illustrated in Fig. 2a and b, using the measurement data shown in Fig. 1.

Note, that in case of the single-step pyrolysis variation of the apparent activation energy with conversion is weak, which makes it possible to use the single constant value. We evaluate this value by averaging the conversion-dependent activation energy, $E_a(\alpha)$, over the conversion range $0.1 < \alpha < 0.9$. Conversion-averaged apparent activation energy is also shown by the dashed line in Fig. 2, b.

Most importantly, the iso-conversional approach makes it possible to explicitly recover the conversion function, $f(\alpha)$, from the measurements. This is done in the *second step* by plotting the dependencies $Af(\alpha) = r(\alpha) \exp(E_a/RT(\alpha))$ where $T(\alpha)$ and $r(\alpha)$ are measured at different heating rates. These dependencies (normalized by the $f(1/2)$ value) are shown below in Fig. 5, Fig. 9, Fig. 11 a, and Fig. 14, a, for different polymers studied. The $f(\alpha)$ dependencies appear to be very close to each other regardless of the heating rate, and it makes it readily possible to approximate the dependencies by one of the following functions,

$$1. \text{ n-th order } f(\alpha) = (1 - \alpha)^n, \quad (10)$$

$$2. \text{ autocatalytic } f(\alpha) = (1 - \alpha)^n (\alpha^m + \alpha^*) \quad (11)$$

each corresponding a particular reaction model.

Finally, pre-exponential factor, A , is obtained in the *third step* by substituting the peak values, r_p , T_p and α_p corresponding to the maximum reaction rate, to Eq. (8): $A = r_p \exp(E_a/RT_p) / f(\alpha_p)$. Pre-exponential factors obtained from this equality for all the heating rates are averaged.

The experience of using this procedure have shown that use of a computationally expensive multidimensional non-linear optimization (model fitting) produced very similar results (for example, see Ref. [4]) in case of single-step reactions.

Sample performance at the heating rate β is modeled by the set of ODEs,

$$\frac{dT}{dt} = \beta, T(0) = T_0, \quad (12)$$

$$\frac{d\alpha}{dt} = Af(\alpha) \exp\left(-\frac{E_a(\alpha)}{RT}\right), \alpha(0) = 0, \quad (13)$$

which is solved numerically to validate a pyrolysis kinetic model.

The measurement data and the kinetic parameters are summarized, respectively, in Tables 2 and 3 given in Appendixes.

4. Results and discussion

4.1. Polyethylene

Three kinds of polyethylene with significantly different molecular weights are considered as shown in Table 1. MCC measurement data for these materials are exemplified in Fig. 3 for the heating rate of 1 K/s. From the data summarized in Table 2 it can be deduced that the peak temperature, T_p , and the peak heat release rate, \dot{q}_p , increase with the molecular weight. It can be noted that this trend is opposite to that for polymethylmethacrylate (cf. Ref. [24] and data shown below in this work). Note also that variation of $\overline{\Delta q'}$ with the molecular weight does not exhibit a clear trend.

The dependence of the apparent activation energy on global

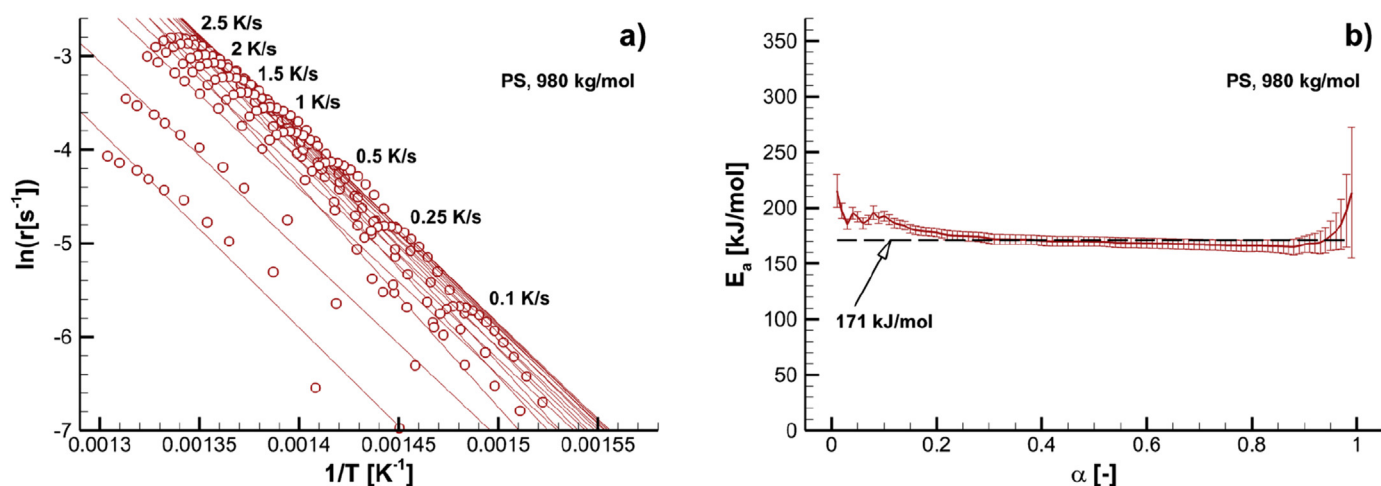


Fig. 2. Derivation of the apparent activation energy of polystyrene (980 kg/mol) pyrolysis in nitrogen by the method of Friedman: a) – straight regression lines fitting iso-conversional reaction rate-temperature data; b) – dependence of the activation energy on conversion.

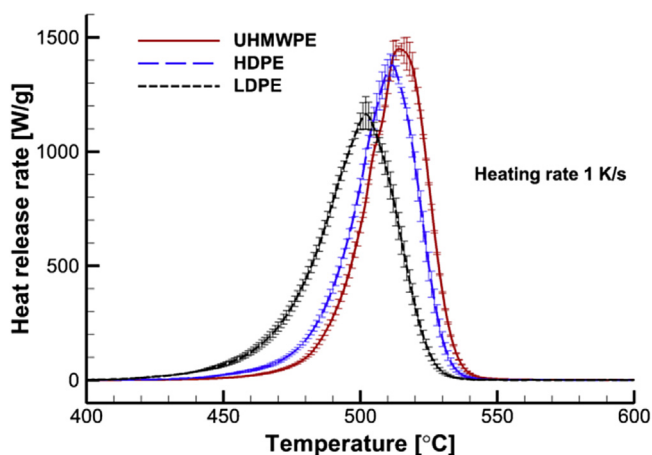


Fig. 3. MCC measurements for three types of polyethylene at the heating rate of 1 K/s. Vertical bars show standard deviation of multiple identical measurements.

conversion (derived by the method of Friedman as explained above) is demonstrated in Fig. 4a and b, which also shows comparison to the literature data derived by the same technique from the TGA data. It can be seen that all three substances exhibit quite close dependencies of the apparent activation energies, albeit, on average, the values for UHMWPE are lower. This observation does not conform with the conventional opinion (for example, see Ref. [8]) that the effective activation energy of PE degradation tends to increase with the molecular weight, at least in the range of molecular weights considered here. It can also be concluded that the values obtained in this work fall in the range of previously published data, which are, however, very widely scattered.

The important conclusion stems from Fig. 5, which clearly shows that up to $\alpha = 0.4$ conversion function (which is derived directly from the measurements) increases with conversion. This is a sharp manifestation of the autocatalytic behavior of the global reaction, which cannot be approximated by the n -th order function, i.e. by Eq. (10). As the above literature review shows, this peculiarity of PE pyrolysis has been mainly overlooked in previous studies. Instead of conventionally used n -th order reaction model, the autocatalytic reaction model should be applied, and the fitting parameters (n , m , and α^*) are shown in Fig. 5 and in Table 3.

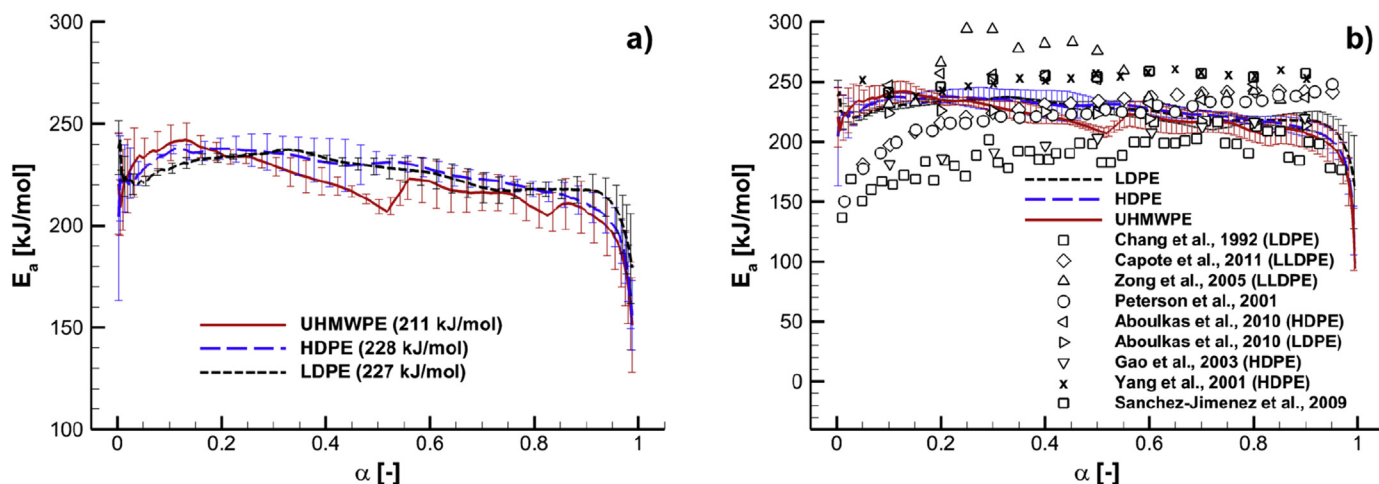


Fig. 4. The dependence of the apparent activation energy on global conversion in polyethylene pyrolysis in nitrogen. a) – data of this work for LDPE, HDPE, UHMWPE (vertical bars show standard deviation, conversion-averaged activation energies are given in brackets); b) – the same as a) and the literature data (symbols, Refs. [8,10–12,17,20,27,32]).

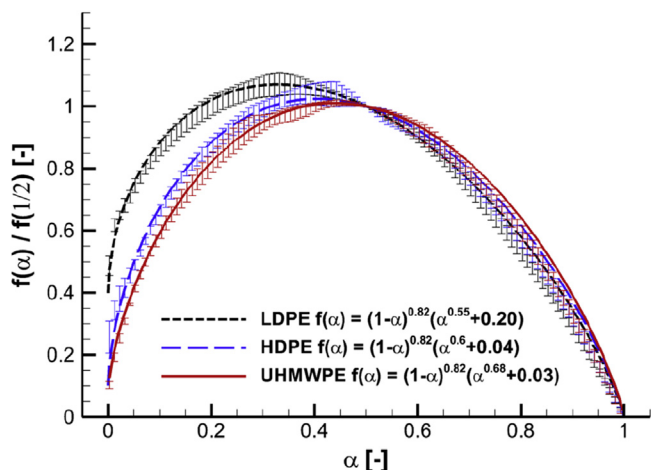


Fig. 5. Normalized conversion function for polyethylene pyrolysis in nitrogen. Vertical bars – standard deviation for different heating rates. Lines – approximation by the autocatalytic function.

Given the proper selection of the conversion function, excellent agreement is obtained between the single-reaction model, Eqs. 12 and 13, and the MCC measurement data (Fig. 6). Note, that the same kinetic model performs well for all the heating rates considered, which cannot be achieved with the n -th order reaction.

4.2. Polystyrene

Autocatalytic behavior of polystyrene pyrolysis has already been addressed in Refs. [3,4,26]. In this work we further extend this study by considering nine polystyrenes of the same manufacturer having remarkably different molecular weights (see Table 1). As Fig. 7 shows, most of the substances exhibited similar performance in the MCC tests, while the “lightest” substances with the molecular weights 1.2 and 45 kg/mol appeared to be very different. Due to this anomalous behavior, we did not use the measurement data for these two substances, which are shown below for the reference only.

The dependencies of the apparent activation energies on conversion are presented in Fig. 8, a, which shows the bunch of the similar curves, with some exceptions. The standard deviation is only shown for a single curve to avoid overloading since its value is similar for other curves. Comparison of the apparent activation energy to published data was given in Ref. [3] and is not therefore provided here. Conversion-averaged activation energies for different molecular weights are close to each other (Fig. 8, b). Similar to the conclusion made above for PE, no clear correlation with the molecular weight has been observed.

The conversion function increases at low conversions and it therefore cannot be represented by the n -th order dependence. Rather, the autocatalytic function, Eq. (11), can correctly approximate the measurement data. It is particularly noticeable that

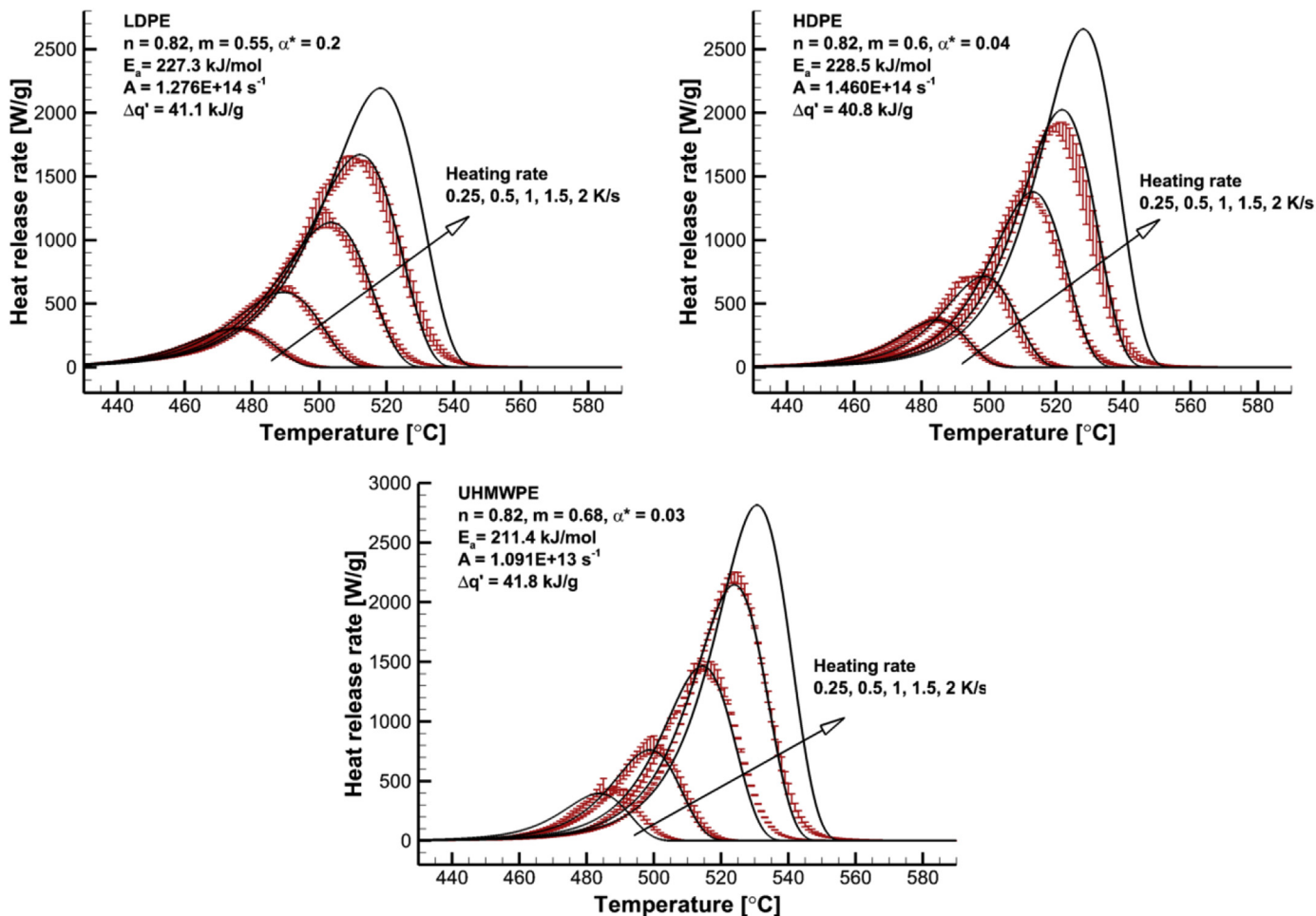


Fig. 6. MCC measurement data and kinetic model predictions for LDPE, HDPE and UHMWPE at different heating rates. Vertical bars – standard deviation of multiple identical measurements, solid lines – predictions by the autocatalytic reaction model with the kinetic parameters as shown.

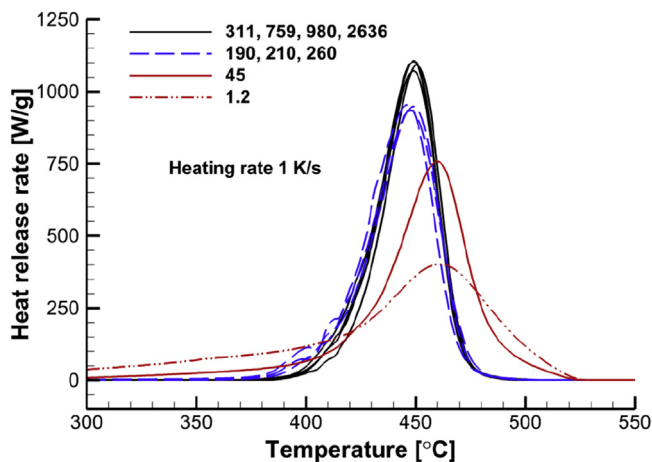


Fig. 7. MCC measurement data for polystyrenes with different molecular weights.

conversion functions for all the substances (with the above-mentioned exceptions) collapse to the same curve, for which numerical values $n = 0.9$, $m = 0.6$ and $\alpha_* = 0.05$ have been selected based on Fig. 9.

Thus derived autocatalytic kinetic model performs very well in a wide range of the heating rates, which is demonstrated by the comparison with the measurement data in Fig. 10, a. A special study (see also Ref. [4]) has shown that the n -order reaction model, albeit being able to fit the measurement at a *single* heating rate, fails if applied at different heating rates (Fig. 10, b). The fundamental reason is that the n -th order conversion function is qualitatively inconsistent with the measurement data.

4.3. Polycarbonate

For polycarbonate, we observed the behavior being qualitatively very similar to that of PE and PS. As shown in Fig. 11, a, apparent activation energies vary within the literature range (which is again rather wide), and the conversion function (Fig. 11, b) is of clearly autocatalytic type. The autocatalytic kinetic model provides very good replication of the measurement data for all the heating rates considered (Fig. 12), except the very end of the process ($\alpha > 0.8$) when most of volatiles is already released.

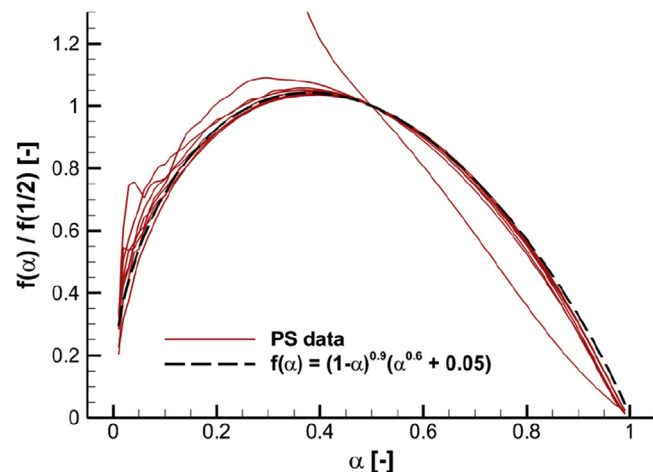
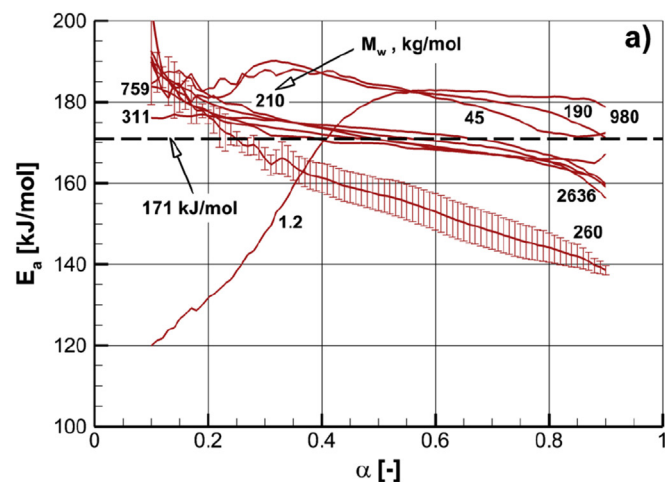


Fig. 9. Derivation of the kinetic function for polystyrene pyrolysis in nitrogen. Solid lines – measurement data for polystyrenes having average molecular weight 1.2, 45, 190, 210, 260, 311, 759, 980 and 2636 kg/mol (each line shows data averaged over four heating rates of 0.25, 0.5, 1 and 2 K/s). The anomalous line corresponds to the polymer with molecular weight 1.2 kg/mol.

4.4. Polymethylmethacrylate

We provide the results of kinetic modeling for PMMA pyrolysis in order to demonstrate the example when the n -th order reaction is adequate to the measurement data. Two substances with considerably different molecular weights of 35 and 350 kg/mol are considered (Table 1). The measurement data shown in Fig. 13 are noticeably different, and the effect of the molecular weight is qualitatively in agreement with the trend observed in Ref. [24].

In both cases, particularly for PMMA35, a smaller peak precedes the major one, and the former is ignored by the single-reaction approach accepted here. Activation energies are compared in Fig. 14, which also shows good agreement with the data reported in Ref. [23] for PMMA350. Conversion-averaged activation energy for PMMA35 (212 kJ/mol) is considerably higher than that for PMMA350 (177 kJ/mol).

Dissimilar to PE, PS and PC, pyrolysis of PMMA is characterized by a monotonically decreasing conversion function over the entire conversion range (see Fig. 14b and c), excluding small conversions

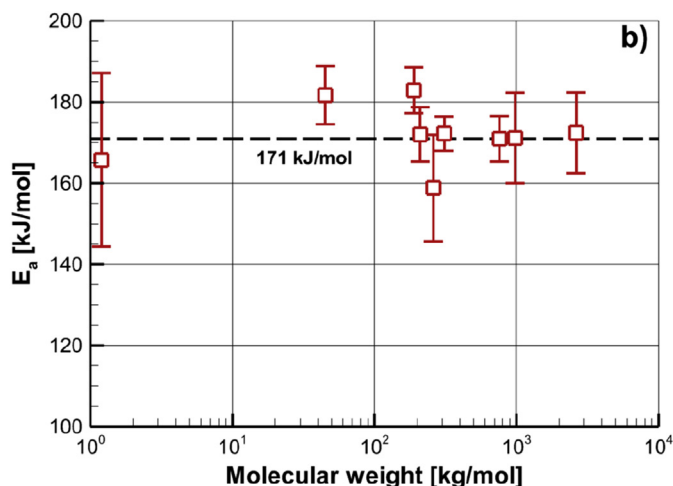


Fig. 8. Apparent activation energy of polystyrene pyrolysis in nitrogen: a) – the dependence on conversion; b) – values averaged over 0.1 to 0.9 conversion range. Vertical bars show standard deviation.

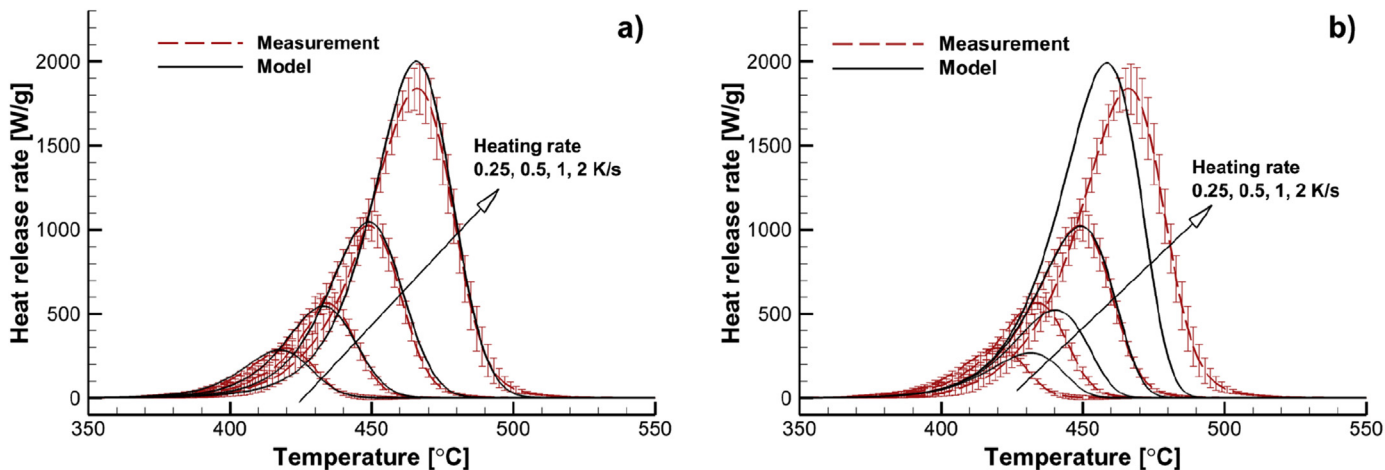


Fig. 10. Performance of the autocatalytic (a) and the first order (b) reaction models for polystyrene pyrolysis in nitrogen at the heating rates of 0.25, 0.5, 1, and 2 K/s. Dashed lines – average data for seven polystyrenes with molecular weights from 190 to 2363 kg/mol (vertical bars show the standard deviation). Solid lines – simulations. The first order reaction model is fitted to the single heating of 1 K/s only ($E_a = 319$ kJ/mol, $\ln A[s^{-1}] = 50.5$).

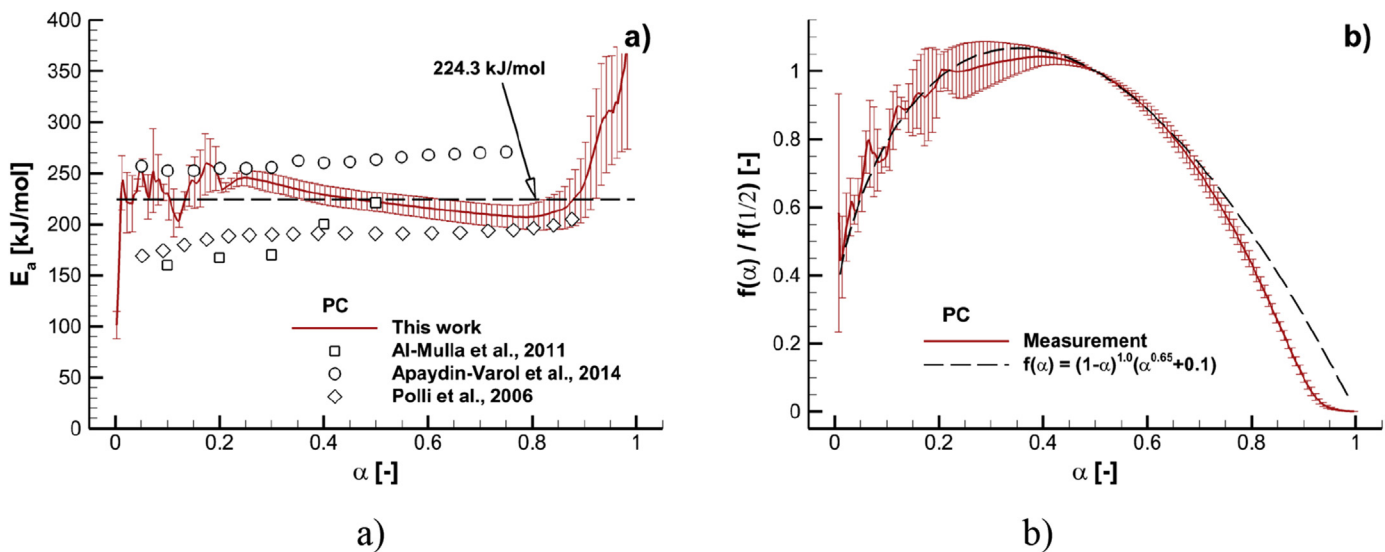


Fig. 11. The dependence of the apparent activation energy on global conversion (a) and the normalized conversion function (b) for polycarbonate pyrolysis in nitrogen. Vertical bars – standard deviation for different heating rates. Symbols – data from Refs. [28–30].

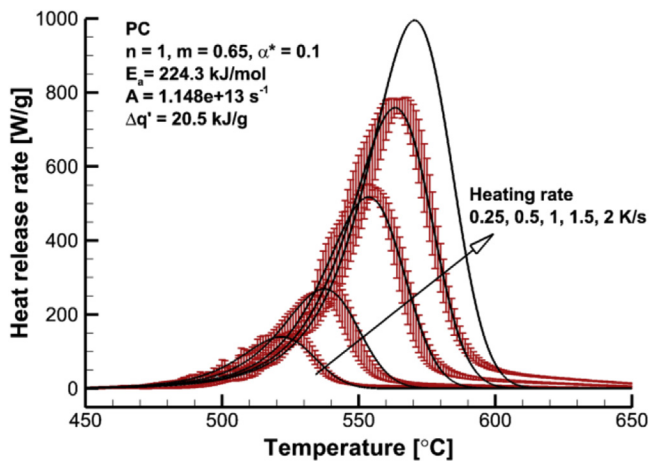


Fig. 12. MCC measurement data and kinetic model predictions for polycarbonate at different heating rates. Vertical bars – standard deviation of multiple identical measurements, solid lines – predictions by the autocatalytic reaction model with the kinetic parameters as shown.

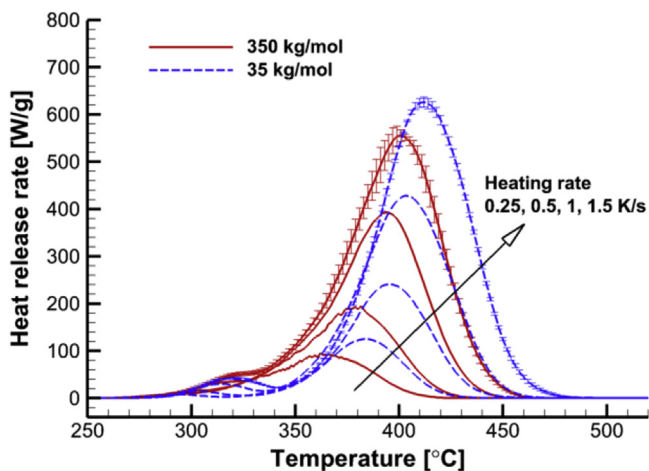


Fig. 13. MCC measurements for two types of polymethylmethacrylate at the heating rates of 0.25, 0.5, 1 and 1.5 K/s. Vertical bars show standard deviation of multiple identical measurements.

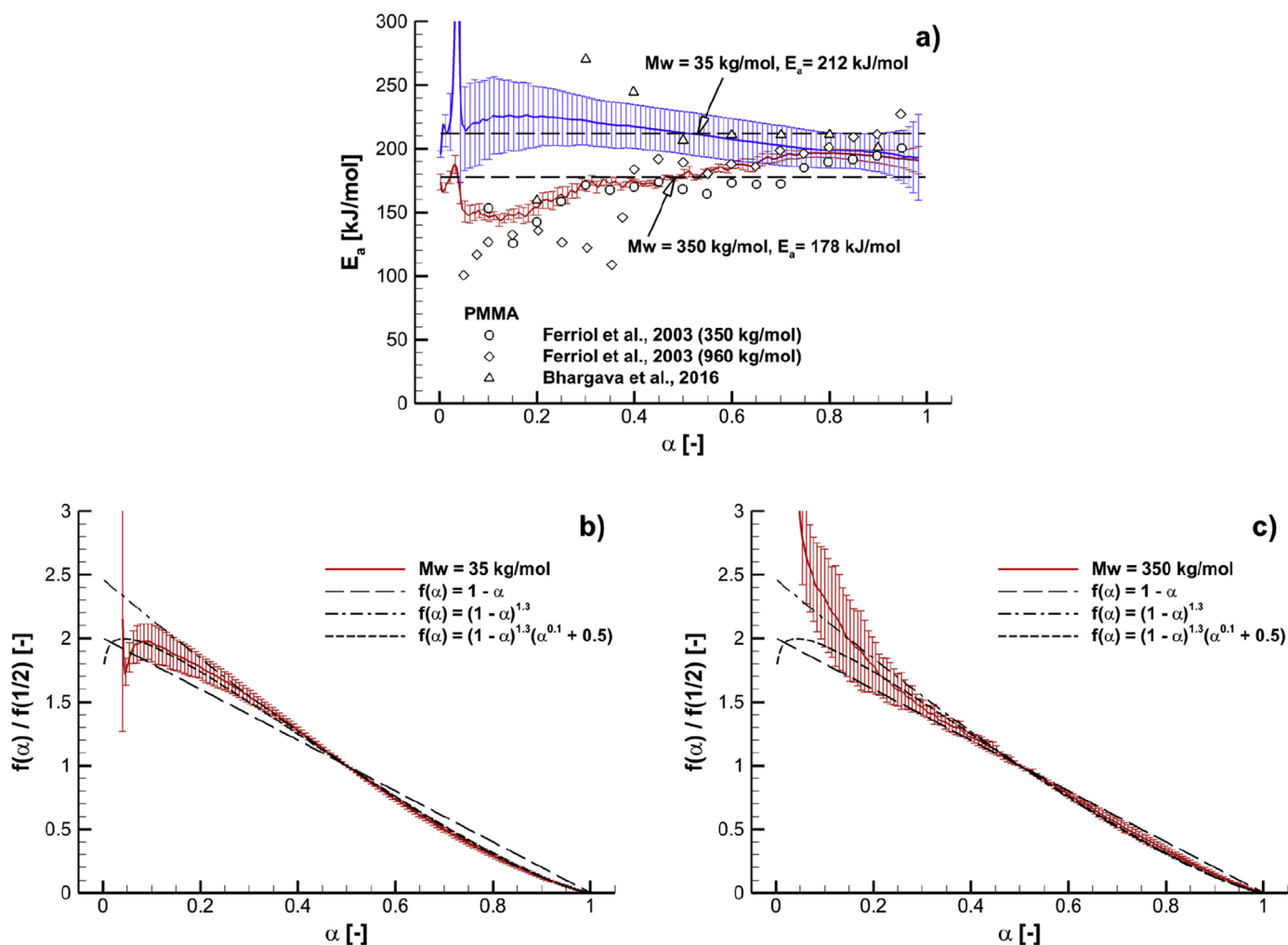


Fig. 14. The dependence of the apparent activation energy on global conversion (a) and the normalized conversion function (b, c) for PMMA pyrolysis in nitrogen (two molecular weights 35 and 350 kg/mol). Vertical bars – standard deviation for different heating rates. Symbols – data from Refs. [23,31].

for which the data is strongly affected by the experimental uncertainty. Apparent reaction order is quite close to 1, thereby justifying use of the first order reaction model as widely accepted in practice. However, we found that assigning $n = 1.3$ results in better

agreement with the measurement data (Fig. 15). Note that the conversion function appears to be practically the same for both PMMA35 and PMMA350, in spite of the difference in activation energies.

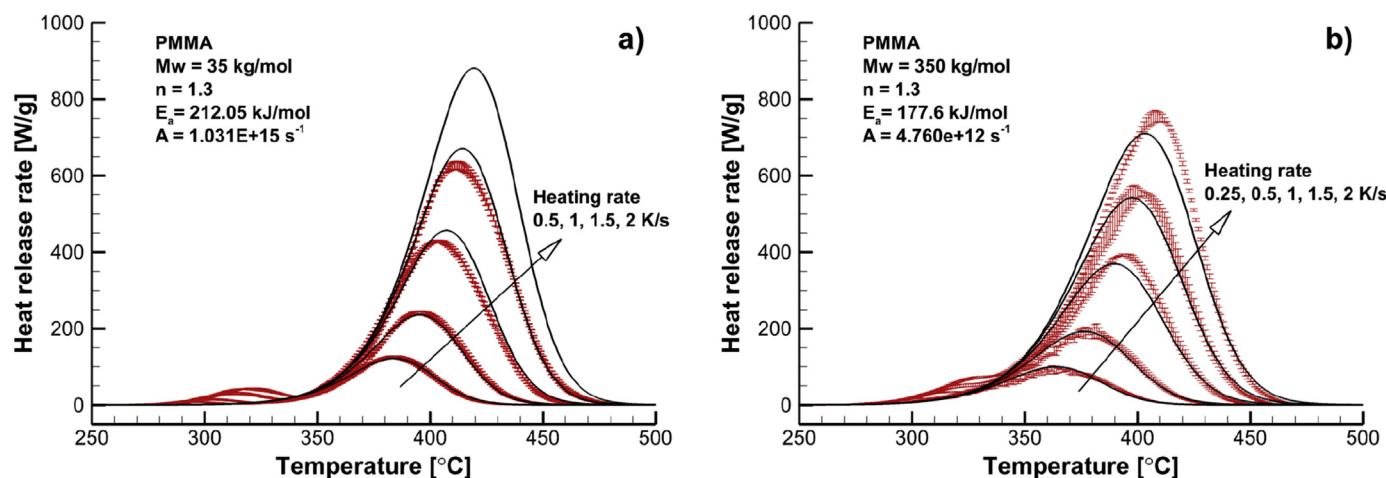


Fig. 15. MCC measurement data and kinetic model predictions for PMMA at different heating rates. Vertical bars – standard deviation of multiple identical measurements, solid lines – predictions by the autocatalytic reaction model with the kinetic parameters as shown.

5. Conclusions

For the polymers considered in this work, we observed qualitatively different behavior while the samples undergo pyrolysis in nitrogen. Three kinds of polyethylene, seven kinds of polystyrene, and the polycarbonate are shown to belong to the group of materials with clearly expressed autocatalytic reaction type. This was recognized by inspecting the non-monotonic dependencies of the conversion functions, $f(\alpha)$, on conversion, α ; in a wide range of conversions, $0 < \alpha < 0.4$, conversion function was found to increase. This peculiarity has been overlooked in most of the previous studies in which the n -th order reaction model was routinely (and, quite likely, erroneously) applied.

In this work we show that it might be a possible reason of inconsistency and wide scatter of the kinetic parameters reported in the existing literature; we also suggest the kinetic parameters (see Table 3), which, dissimilar to many previously published data, accurately replicate measurement data in a range of heating rates achievable in mg-scale thermal analysis.

In contrast, for two kinds of polymethylmethacrylate studied in this work, the n -th order reaction model predictions followed closely the measurement data, which shown monotonic decrease of the conversion function.

Exploring the fundamental reason of such a qualitatively different behavior of different polymers would require the in-depth comparative analysis of depolymerization mechanisms characteristic for each material, which is beyond the scope of this paper. However, refining the knowledge on proper selection of the conversion function is extremely important to formulate a self-consistent global pyrolysis kinetic model that performs uniformly well in a practically realizable range heating rates occurring in polymer combustion.

In deriving a consistent global kinetic model of polymer decomposition, we demonstrate the efficiency of the three-step procedure, including (i) evaluation of the conversion-averaged apparent activation energy by the iso-conversional method of Friedman, (ii) analytical formulation of the conversion function, and (iii) obtaining the pre-exponential factor averaged over the multiple heating rates. This procedure is recommended in case of the single-step pyrolysis, which is diagnosed by the single peak reaction rate-temperature dependencies and the weak variation of the activation energy with conversion.

As a corollary, the effect of polymer molecular weight on its pyrolysis has been examined. The data obtained in this work do not conform to the existing opinion on systematic increase of the apparent activation energy with the molecular weight. The overall trend in transformation of the reaction rate-temperature dependencies is shown to be opposite for PE and PMMA, for which the peak reaction rates and temperatures moved in opposite directions with variation of the initial molecular weight. No systematic correlation of the pyrolysis characteristics (conversion-averaged apparent activation energy, heat of combustion, peak reaction rates and temperatures etc.) with the molecular weight has been observed for polystyrene.

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Appendix 1. Summary of MCC measurement results

Table 2
MCC measurement results^a.

Measured quantity	Material						
	LDPE	HDPE	UHMWPE	PS980	PC	PMMA35	PMMA350
ν_r , –	0	0	0	0	0.24 ± 0.02	0	0
$\overline{\Delta q}$, kJ/g	41.1 ± 0.6	40.8 ± 0.4	41.8 ± 0.2	38.3 ± 0.3	20.4 ± 0.5	24.6 ± 0.2	22.4 ± 0.3
$\Delta \overline{q}$, kJ/g	41.1 ± 0.6	40.8 ± 0.4	41.8 ± 0.2	38.3 ± 0.3	26.8 ± 0.5	24.6 ± 0.2	22.4 ± 0.3
Heating rate 0.25 K/s							
\dot{q}_p , W/g	304 ± 8	370 ± 16	464 ± 58	313 ± 2	149 ± 6	125 ± 3	95 ± 7
T_p , °C	476 ± 1	485 ± 1	486 ± 2	420 ± 1	525 ± 2	385 ± 2	362 ± 2
$T_{50\%}$, °C	471	481	485	417	521	381	360
\dot{q}_p/β , kJ/(kg K) ^b	1213	1474	1849	1252	589	498	380
$HRC_{10-90\%}$, kJ/(kg K)	1010	1208	1452	1083	432	442	330
Heating rate 0.5 K/s							
\dot{q}_p , W/g	618 ± 16	722 ± 21	811 ± 69	609 ± 15	264 ± 16	241 ± 4	194 ± 18
T_p , °C	489 ± 2	498 ± 1	501 ± 1	433 ± 1	537 ± 3	396 ± 1	379 ± 3
$T_{50\%}$, °C	485	494	497	430	534	394	374
\dot{q}_p/β , kJ/(kg K) ^b	1235	1442	1621	1222	525	483	389
$HRC_{10-90\%}$, kJ/(kg K)	1011	1245	1348	1079	432	432	329
Heating rate 1 K/s							
\dot{q}_p , W/g	1168 ± 72	1378 ± 41	1450 ± 12	1105 ± 37	534 ± 15	428 ± 3	393 ± 3
T_p , °C	502 ± 1	512 ± 1	524 ± 1	449 ± 1	555 ± 2	403 ± 1	393 ± 2
$T_{50\%}$, °C	498	508	513	445	552	401	388
\dot{q}_p/β , kJ/(kg K) ^b	1170	1381	1478	1112	532	433	395
$HRC_{10-90\%}$, kJ/(kg K)	959	1163	1300	983	438	386	331
Heating rate 1.5 K/s							
\dot{q}_p , W/g	1623 ± 17	1881 ± 30	2210 ± 42	1525	762 ± 19	626 ± 11	555 ± 12
T_p , °C	511 ± 2	520 ± 2	532 ± 1	460 ± 1	565 ± 3	411 ± 1	401 ± 2
$T_{50\%}$, °C	507	517	529	456	562	410	396
\dot{q}_p/β , kJ/(kg K) ^b	1085	1257	1221	1027	505	423	373
$HRC_{10-90\%}$, kJ/(kg K)	947	1076	1099	922	419	382	316

^a $T_{50\%}$ is the temperature corresponding to 50% conversion. $HRC_{10-90\%}$ is the effective heat release capacity defined as $HRC_{10-90\%} = \overline{\Delta q} / \Delta T_p$, where ΔT_p is the temperature difference between 10% and 90% conversions (see Ref. [5] for details).

^b \dot{q}_p/β is evaluated based on actual time-averaged heating rate, which may have minor deviation from the nominal value shown in the table.

Appendix 2. Kinetic model summary

Table 3
Kinetic parameters.

Polymer	E_a , kJ/mol	$\ln A[s^{-1}]$	n	m	α^*
LDPE	227.3	32.48	0.82	0.55	0.2
HDPE	228.5	32.61	0.82	0.6	0.04
UHMWPE	211.8	30.01	0.82	0.68	0.03
PS	171.5	26.08	0.9	0.6	0.02
PC	224.3	30.07	1.0	0.65	0.1
PMMA35	212.05	34.57	1.3	0	0
PMMA350	177.6	29.19	1.3	0	0

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