# Accepted Manuscript


Autocatalysis in thermal decomposition of polymers

A. Yu Snegirev, V.A. Talalov, V.V. Stepanov, O.P. Korobeinichev, I.E. Gerasimov, A.G. Shmakov

PII: S0141-3910(17)30008-3

DOI: 10.1016/j.polymdegradstab.2017.01.008

Reference: PDST 8147

To appear in: *Polymer Degradation and Stability*

Received Date: 2 November 2016

Revised Date: 10 January 2017

Accepted Date: 15 January 2017

Please cite this article as: Snegirev AY, Talalov VA, Stepanov VV, Korobeinichev OP, Gerasimov IE, Shmakov AG, Autocatalysis in thermal decomposition of polymers, *Polymer Degradation and Stability* (2017), doi: 10.1016/j.polymdegradstab.2017.01.008.

# Autocatalysis in thermal decomposition of polymers

A.Yu. Snegirev[a],*, V.A. Talalov[a], V.V. Stepanov[a],
O.P. Korobeinichev[b], I.E. Gerasimov[b], A.G. Shmakov[b]

[a] Peter the Great Saint-Petersburg Polytechnic University, Department of Fluid Dynamics, Combustion and Heat Transfer, Polytechnicheskaya 29, Saint-Petersburg 195251, Russia

[b] Voevodsky Institute of Chemical Kinetics and Combustion, Institutskaya 3, Novosibirsk 630090, Russia

[*] Corresponding author: Alexander Snegirev
Email: a.snegirev@phmf.spbstu.ru Tel.: +7 921 6494754

## 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.

*Key words*: autocatalysis; thermal degradation; pyrolysis; global reaction; polyethylene; polystyrene; polycarbonate; polymethylmethacrylate; microscale combustion calorimetry; thermal analysis

## 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