

## Thermokinetics

A software module for the kinetic analysis of thermal measurements. All types of thermal data acquired using Thermogravimetry (TG), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Mass Spectrometry (MS in the so-called MID mode), FTIR, Dilatometry (DIL), Rheometry (Rheo) or Dielectric Analysis (DEA) can be evaluated.

The kinetic analysis allows to find the set of kinetic parameters e.g. number of steps, contribution of each step to the total effect of the process such as step enthalpy or step mass loss; reaction type, activation energy and reaction order for each step. Then this information will be used to solve the problems of predictions or optimization.

### Two main tasks of Thermokinetics

#### – predict the system behaviour for new temperature program (Prediction)

The user should input the temperature program and the software will make a simulation of the system behaviour. Without Thermokinetics software it is necessary to carry out the new measurement for each new temperature program, but with the software it can be simulate very fast. The following values can be predicted:

- measurement output (signal),
- partial reactions
  - Partial Mass Loss,
  - Partial Area, etc.,
- concentration of the reactants

The predictions can be done for one or several isothermal measurements, for dynamic measurements like heating, for isothermal or dynamic segment with daily temperature oscillations and for any sequence from such temperature segments.

#### – find temperature program for given system behaviour (Optimization)

It is the typical problem for the production process when the temperature program must be found for optimal time and optimal quality. Without Thermokinetics software it is necessary to make adjustment of the temperature program and measure several times in the hope to archive expected signal curve. The software saves your time and finds such temperature program:

- for given reaction rate
- for given output signal
- for given rate of final product production

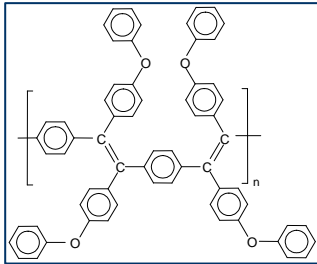
### Application fields:

Industries, where production or storage process depends on temperature

- food, medicines, recycling
- ceramics, metallurgy,
- polymers, plastics,
- epoxy resins:
- automotive industry,
- air plane production,
- building of bridges,
- road construction
- safety analysis, explosives

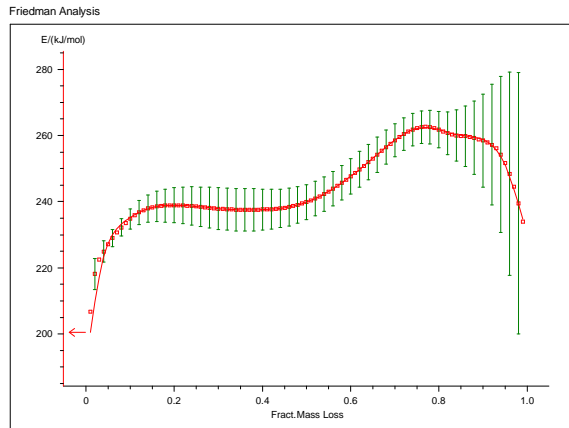
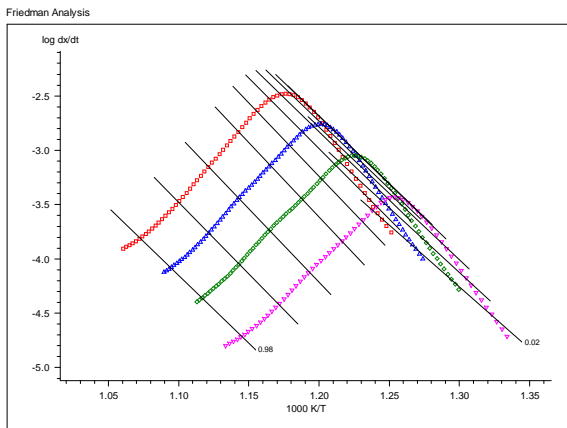


# Example1: Thermal decomposition of DPOP-PPV and its approximation with the aid of multivariate nonlinear regression



## Measurement type: TGA

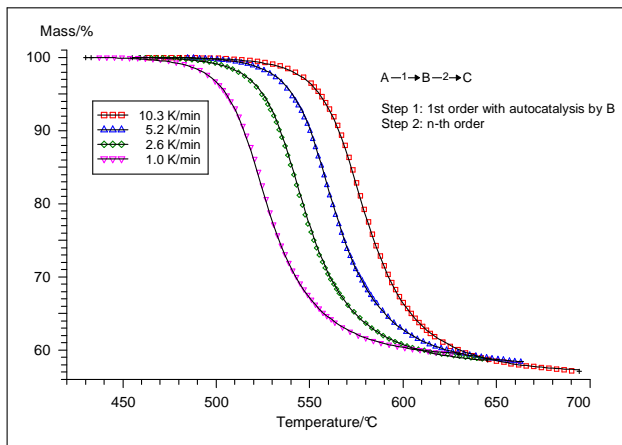
Poly(1,4-phenylenevinylene) and its derivatives, which are represented as polymers with a linear conjugated main chain consisting of alternating phenylene and vinylene units have attracted increasing interest in the past years. A typical representative of this group is the poly[1,4-phenylene-1,2-di(4-phenoxyphenyl)-vinylene] (**DPOP-PPV**). Here the high thermal stability conjugated for polymers is of interest. Even in air DPOP-PPV is stable up to **450°C**. The thermogravimetric decomposition of DPOP-PPV are measured in a He gas stream (20 ml/min) with heating rates of 1 up to 10 K/min and initial weights of about 10 mg. These measurements characterize the polymer as being highly thermostable. Its thermal decomposition starts only above 400°C and the main decomposition takes place at 550°C.



## Model-free analysis according to Friedman:

Activation energy plot contains two horizontal parts corresponding to the two consecutive steps with activation energies about 235kJ/mol and 260kJ/mol.

NETZSCH Thermokinetics Decomposition of DPOP-PPV

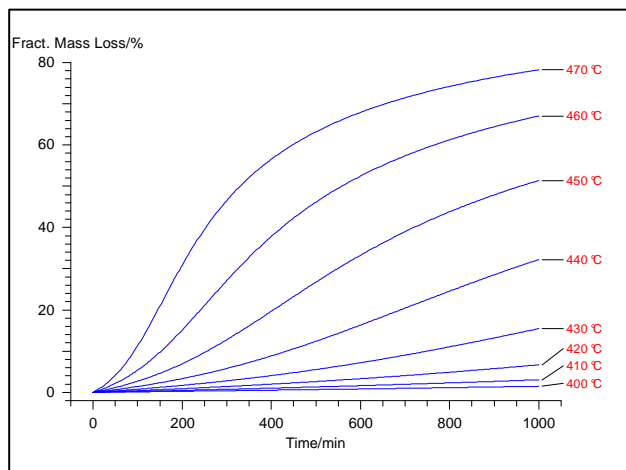


## Kinetic Analysis:

Process of two consecutive steps, the first one is autocatalytical reaction with activation energy 230kJ/mol, the second one is the reaction of 2-th order with activation energy 259kJ/mol. Contribution of the first step to the total reaction enthalpy is 51%.

Results of the evaluation are

- perfect description of experimental results of different heating rates with the same kinetic model
- the optimal parameters and their standard errors,
- statistical values as correlation coefficient and average fit error,
- F test for the significance test for the best model,
- graphic representation of the curve fit.



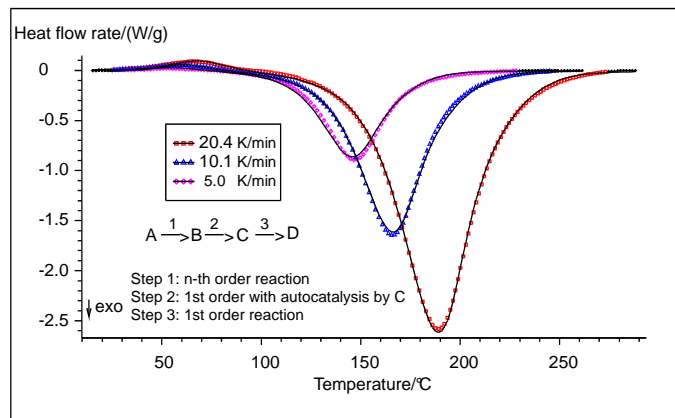
## Isothermal predictions:

The isotherms of two-step model show a sigmoidal course. This confirms the known fact, that a sigmoidal course being typical for autocatalytically activated processes and two-step processes. Here both prerequisites coincide. However, the second step of two-step processes must deliver a considerable portion for the signal.

Due to the sigmoidal course the low values of the partial mass loss for the two-step model need more time than for the single step model. In contrast, the two-step model reaches higher values faster than the single-step model.

## Example2: Kinetic analysis of the curing of an epoxy resin

Curing of Epoxy Resin



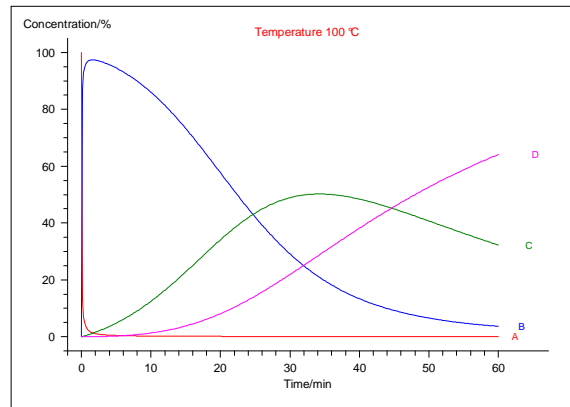
Measurement type: DSC

Epoxy resins are a group of widely used organic materials in the industry. The knowledge, how long is the curing time, under which conditions the user receives the full curing or a defined level of cure - these are points of interest, for which the kinetics gives an answer

Model-free analysis can not be used for this case because there are strong limitations of this method, caused by its kernel.

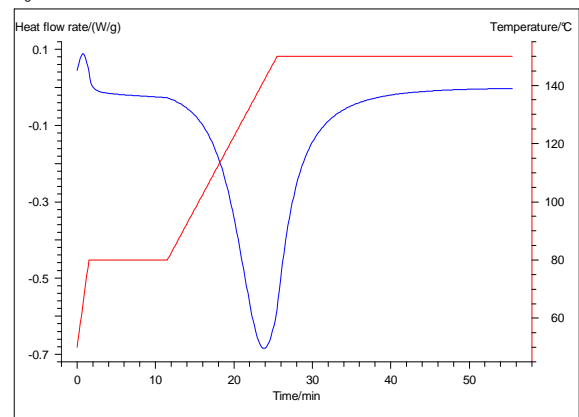
The almost perfect fit is achieved only after inclusion of the melting of the resin (between 50 and 90°C) as a formal nth-order reaction. The start of the actual curing is described well by a first-order reaction with autocatalysis.

Isothermal Reactants vs. Time



Isothermal prediction of reactants for 60 min a temperature from 100°C.

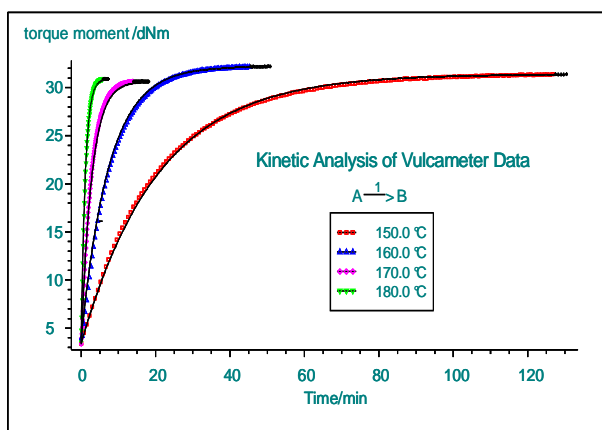
Signal vs. Time



Prediction according to a temperature program

## Example3: Vulcanization of natural rubber

Natural Rubber



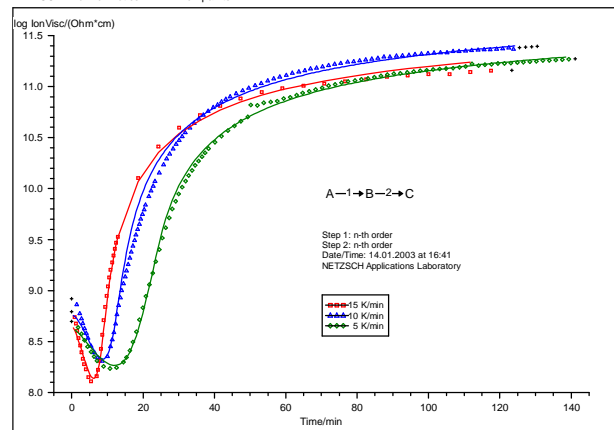
Measurement type: Rheometry

Isothermal measurement of torque moment

Kinetic model created for each of both examples can be used for further predictions

## Example4: Curing of powder paints

NETZSCH Thermokinetics DEA on paints



Measurement type: Dielectric analysis(DEA)

Dynamic measurements of the ion viscosity

## Example5: Simulation of rate controlled mass loss (RCM)

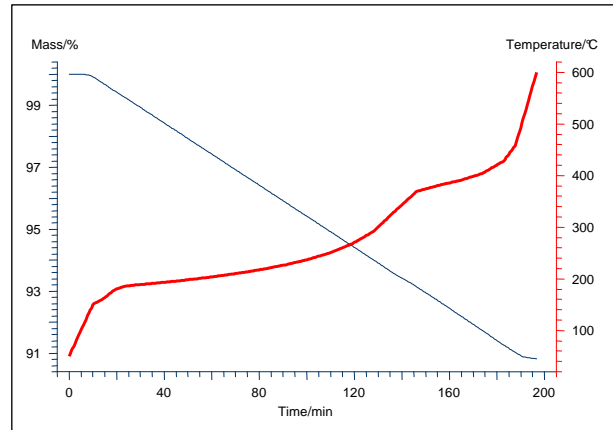
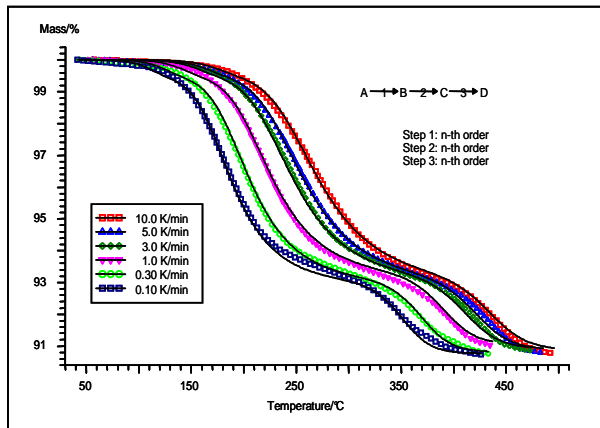
### Measurement type: TGA

In sinter metallurgy a polymeric binder is added to metal powder for a better adhesion. This binder is carefully removed during the first phase of the sinter process to avoid microcracking by emerging gases.

In the present project 6 measurements are carried out with heating rates of 0.1, 0.3, 1, 3, 5 and 10 K/min in the N<sub>2</sub>-atmosphere. The sample masses are in the range of 75 to 91 mg.

If the burn out of a polymere binder of a ceramic body is carried out with a constant mass loss (RCM - Rate Controlled Mass Change) then often the quality-reducing micro-cracks can be avoided.

NETZSCH Thermokinetics Burnout of Polymeric Binder



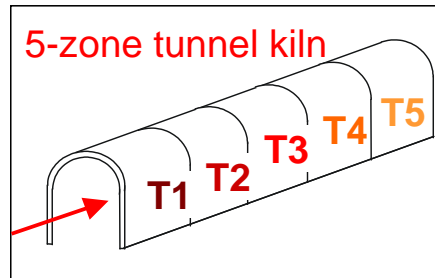
### Kinetic Analysis:

The three-step kinetic model is created for description of system behavior.

### RCM simulation:

Predicted temperature program for the constant rate of mass change 0,05%/min.

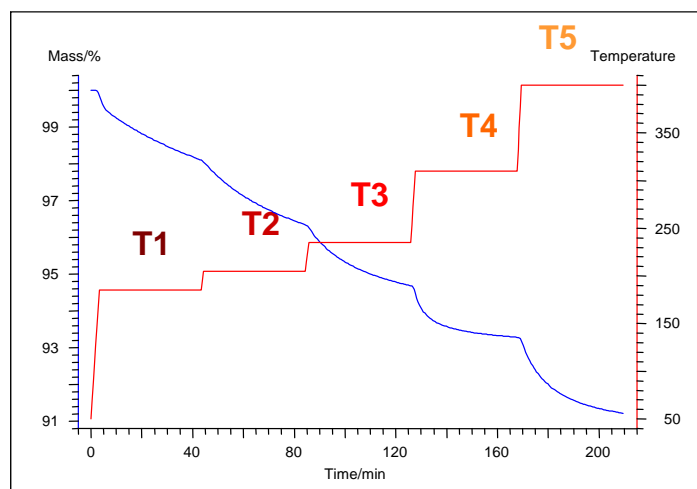
## Example6: Mass loss prediction for the production process



### Measurement type: TGA

The burnout process is often executed in a tunnel kiln. Therefore, the duration of staying in each zone of the furnace is the same.

What are the 5 temperatures, for which the rate of the mass loss is approximately constant ?



### Mass loss prediction in the tunnel kiln

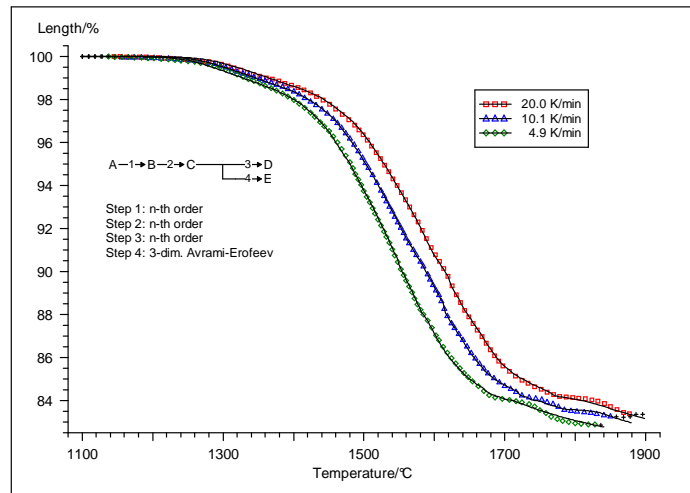
The temperature program corresponds to the sample temperature in the tunnel kiln with 5 zones. Kinetic model from the previous example is used for simulation.

The engineer can simulate the mass loss in the sample moved through the kiln for the any temperature values T1...T5. He will easy evaluate what happens if the temperature of any zone will be higher or lower then the usual temperature.

Here the reaction rate is almost constant during the first three zones. The last two zones contain non-constant reaction rate and they are most critical for the production quality.

## Example 7: Sintering Process Optimization for High-Tech Ceramics (Si<sub>3</sub>N<sub>4</sub>)

NETZSCH Thermokinetics Sintering of Silicium Nitride



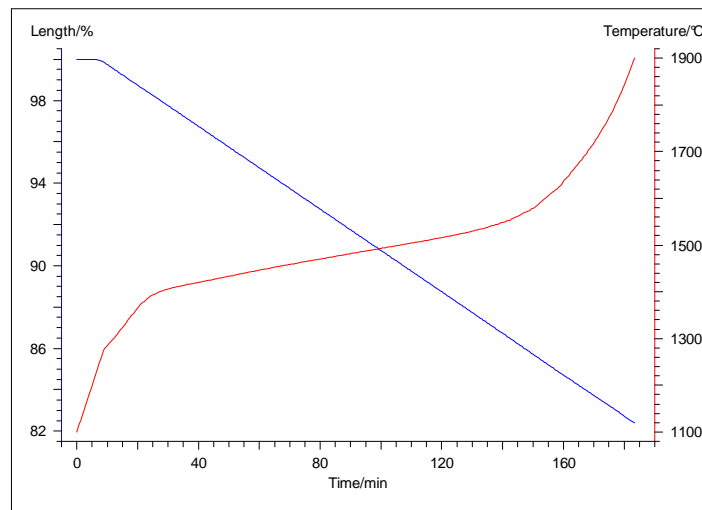
### Measurement type: DIL

In the production of modern high performance technical a green body is frequently manufactured ceramics by mixing a ceramic powder and a binder material. The green body is fired afterwards to achieve the final product. The temperature program during the firing process most of all during binder burnout and sintering phase, has a paramount influence on the final product quality.

### Kinetic Analysis:

The four-step kinetic model is done for description of dynamic measurements with 5, 10 and 20/min.

RCS Simulation



### Simulation of RCS (Rate Controlled Sintering):

With too slow reaction rate the production process will be long and therefore expensive. With the fast reaction rate the microcracks will be created and the quality will be low. The current task is find optimal temperature program for fast sintering with high quality. Such optimal temperature should produce constant sintering rate.

On the picture is the predicted temperature program for the constant length change of 0.1%/min.

The software can make calculation of thermal endurance of the sample and calculate the expected time for isothermal conditions which is necessary to get given value of conversion.

*Additional information about Netzsch Thermokinetics can be found on [www.therm-soft.com](http://www.therm-soft.com)*