Polymerization Technology – Laboratory Course

Determination of Kinetic and Thermodynamic Data of an Initiator Dissociation Reaction by Differential Scanning Calorimetry (DSC)

Subject

Determination of the kinetic and thermodynamic data of the dissociation of V50-initiator (2,”’ – Azobis-(2-amidinopropane)hydrochloride) in water.

Theory

General

In general, thermal analysis is the determination of substance properties in dependence on temperature. Thermodynamic data (heat capacity, phase transitions, enthalpies) and kinetic data can be determined by methods of thermal analysis. The greatest advantage of thermal analysis is the output of much information from small samples of measured substance and easy handling. The most common methods are Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC).

General principles

In a Differential Scanning Calorimeter, the sample and a reference are symmetrically placed in an oven in steel or aluminum capsules. In the state of thermal equilibrium, oven sample and reference have the same temperature. When a change of heat capacity, phase transition or reaction occurs, the equilibrium is disturbed. The sample temperature is higher (exothermic event) or lower (endothermic event) than the reference. This temperature difference is compensated by a heater and the required heat flow is detected.

$$\Delta Q = -K \cdot \Delta T \quad \text{(I)}$$

The constant $K$ has to be determined by calibration. The difference of heat flows to the sample and the reference are given by

$$\Delta \dot{Q} = (\dot{Q}_S - \dot{Q}_R) + (C_{p,MS} - C_{p,MR}) \cdot \beta \quad \text{(II)}$$

where $\dot{Q}_S$ is the heat flow to the sample, $\dot{Q}_R$ is the heat flow to the reference, $C_{p,MS}$ is the heat capacity of the sample measuring system, $C_{p,MR}$ is the heat capacity of the reference measuring system and $\beta$ is the heating rate $\frac{dT}{dt}$.

As can be seen from the previous equation, not only the heat capacities of the sample and the reference itself are important, but also the small difference of the heat capacities of the measuring systems (sample holder etc.). This contribution becomes more and more important with an increasing heating rate but it can be corrected by the software and be neglected in the following equations.
The heat flow in the sample is given by

$$ \dot{Q}_S = C_{p,S} \frac{dT_S}{dt} + \dot{Q}_{chem} \quad \text{(III)} $$

where $C_{p,S}$ is the heat capacity of the sample and $\dot{Q}_{chem}$ is the heat flow by chemical reaction.

For the inert reference, the heat flow is given by

$$ \dot{Q}_R = C_{p,R} \frac{dT_R}{dt} = C_{p,R} \cdot \beta \quad \text{(IV)} $$

where $C_{p,R}$ is the heat capacity of the reference.

We obtain

$$ \Delta \dot{Q} = (\dot{Q}_S - \dot{Q}_R) = C_{p,S} \frac{dT_S}{dt} + \dot{Q}_{chem} - C_{p,R} \cdot \beta \quad \text{(V)} $$

During a reaction $\frac{dT_S}{dt}$ is not identical with $\beta$ and this unknown parameter must be eliminated. We consider that there is a heat flow resistance $R_{MS}$ between the sample measuring/heating system at temperature $T_{MS}$ and the sample, which is at temperature $T_S$

$$ \Delta \dot{Q} = \frac{(T_{MS} - T_S)}{R_{MS}} \quad \text{(VI)} $$

The term $\frac{dT_S}{dt}$ can be eliminated by differentiation the previous equation after the time. With the approximation $\frac{dT_{MP}}{dt} = \beta$ we obtain

$$ \Delta \dot{Q} = \dot{Q}_{chem} + \left(C_{p,S} - C_{p,R}\right) \cdot \beta - C_{p,S} \cdot R_{MS} \cdot \frac{d\Delta \dot{Q}}{dt} \quad \text{(VII)} $$

$$ \Delta \dot{Q} = \dot{Q}_{chem} + \Delta C_{p} \cdot \beta - \tau \cdot \frac{d\Delta \dot{Q}}{dt} \quad \text{(VIII)} $$

The detected signal contains three contributions. At first, there is the heat flow from the reaction $\dot{Q}_{chem}$. Secondly, there is a term which is dependent on the difference of the heat capacities of the sample and the reference. The third contribution is influenced by the so called time constant $\tau = C_{p,S} \cdot R_{MS}$ of the measuring system and the slope of the measured signal. This third term reflects the time lag between the chemical heat flow and the “reaction” of the compensation heater.

The DSC 6 calorimeter, that is used here, works with an more simple principle: It doesn’t compensate temperature differences but only detects them and calculated the heat flow.

**Determination of kinetic data**

The correlations between reaction enthalpy $\Delta H$, conversion $X$ and rate of conversion $\frac{dX}{dt}$ are given by

$$ X(t) = \frac{\Delta H(t)}{\Delta H} = \frac{\int_{t_0}^{t \text{end}} \dot{Q}_{chem} \, dt}{\int_{t_0}^{t \text{end}} \dot{Q}_{chem} \, dt} \quad \text{(IX)} $$
\[
\frac{dX}{dt}(t) = \frac{\dot{Q}_{\text{chem}}(t)}{\int_{t_0}^{t_{\text{end}}} \dot{Q}_{\text{chem}} \, dt} \quad (IX)
\]

where \(t_0\) and \(t_{\text{end}}\) are the time of the beginning and of the end of the measured heat flow peak (integration limits), \(\Delta H(t)\) is the reaction enthalpy at time \(t\) (partial peak area) and \(\Delta H\) is the complete enthalpy of the reaction (complete peak area).

The rate of reaction related to the component A (reactant) is assumed to follow the rate law

\[
\frac{dc_A}{dt} = -k(T) \cdot c_A^n \quad (X)
\]

And the conversion is given by

\[
X = 1 - \frac{c_A}{c_{A,0}} \quad (XI)
\]

For the concentration and the reaction rate we get the following relations between reaction and conversion

\[
c_A = c_{A,0} - X \cdot c_{A,0} \quad (XII)
\]

\[
\frac{dc_A}{dt} = -c_{A,0} \cdot \frac{dX}{dt} \quad (XIII)
\]

Combining equations (XII) and (XIII) with (X) results in the equation for the conversion rate

\[
\frac{dX}{dt} = k(T) \cdot c_{A,0}^{n-1} (1 - X)^n \quad (XIV)
\]

The rate constant \(k(T)\) is described by the Arrhenius equation with the Arrhenius factor \(k_\infty\) and the activation energy \(E_A\)

\[
k(T) = k_\infty \exp \left( -\frac{E_A}{R \cdot T} \right) \quad (XV)
\]

Thus the rate of a reaction of \(n\)th order is expressed by

\[
\frac{dX}{dt} = k_\infty \exp \left( -\frac{E_A}{R \cdot T} \right) \cdot c_{A,0}^{n-1} (1 - X)^n \quad (XVI)
\]

For data analysis the conversion \(X\) and the differential quotient \(\frac{dX}{dt}\) can be calculated from the measured heat flow. The temperature can be kept constant (isothermal measurement) or varied, e.g., from a lower to a higher temperature with a rate \(\frac{dT}{dt}\) (non-isothermal measurement). The reaction order \(n\), the activation energy \(E_A\) and the Arrhenius constant \(k_\infty\) have to be calculated by a procedure which is described in the chapter analysis.
Experimental

First, three DSC steel capsules has to be prepared. Each consists of three parts: the capsule, a O-ring and a cap. The O-ring has to be inserted into the cap.

To prepare a 10 wt% solution of V50 (2,2’-Azobis-(2-aminsopropane)hydrochloride) in water, 0.1g V50 is weighed and diluted in 10.0 g of water. Note the exact masses! 25 µl of this solution are given in three steel capsules, which are closed by caps with seals using the “self-made” press. Two of the samples are stored in the freezer to avoid decomposition. The last one is put in the auto sampler of the DSC.

In this reaction nitrogen is set free. Therefore, steel capsules are used which are stable against a pressure up to 24 bar, whereas aluminum capsules only resists pressures up to 2 bar. Calculate the expected increase of pressure! Why we can’t use the cheaper aluminum capsules?

a) Nonisothermal measurements
The nonisothermal experiments are performed by using three different heating rates (5, 3 and 1 K/min). For each run, a method for the DSC has to be programmed. The following data are required:
- Sample name
- Filename of the result file
- Initial temperature
- Step information: Isothermal / Temperature scan, hold time / temperature rate and target temperature in case of temperature scan
- End condition

The first run should be the fastest with a temperature rate of 5 K/min to get an idea at which temperature the reaction starts. Therefore, a temperature range of 30 to 200°C should be chosen. In addition, each measurement should start with a one minute isothermal step. 10 minutes before the measurement is finished, the new sample should take out of the freezer
To save time, the experiments with 1 and 3 K/min should be performed in an adjusted temperature range. But pay attention to peak shifting: Be sure to have enough “place” leftwards the peak!
The samples should put in the DSC via the auto sampler to avoid damaging the machine.

!!! Don’t touch the auto sampler !!!

b) Isothermal measurements

In respect to the limited time in lab course, the isothermal measurements are already done. The data is given by the assistant.

The specific DSC files have to be converted into ASCII-files in order to read them on your computers. Per measurement, two files should be created, heat rate as function of temperature and heat rate as function of time. The procedure will be explained by your assistant.

Analysis

The analysis should be done with help of a spreadsheet program (e.g. Excel, OpenOffice, Calc, gnumeric).

1) Open file in your spreadsheet program:
The text files can mostly be imported by copy and paste them in your spreadsheet program. The text files have a point as decimal separator. In some cases you have to replace it by your regional setting decimal separator.

2) Subtracting of $\Delta C_p \cdot \beta - \tau \cdot \frac{d\dot{Q}}{dt}$:
Before you can calculate, you have to subtract the heat rate which is used to hold or increase temperature of the system in order to get $\dot{Q}_{chem}$ by equation (VIII). To do this, it is useful to plot the curves as a function of temperature or time and create regression functions (polynomial 2nd order) of points before and after the reaction peak (Figure 2).

![Figure 2: Calculation of the baseline](image)

With help of the regression curve equations, it should be able to calculate $\dot{Q}_{chem}$.
3) Calculate the conversions as function of time by equation (1):
   To form the integrals, summation method, trapezoid method or software can be used.
4) Calculation of the change of conversion with time
5) Transforming nonisothermal curves into isothermal curves:
   A table (Table 1) should be created in order to collect rate of conversions at same
   conversions and different temperatures from the three curves.

<table>
<thead>
<tr>
<th>Conversion X [1]:</th>
<th>Temp 1 [K]:</th>
<th>Rate 1 [1/s]:</th>
<th>Temp 2 [K]:</th>
<th>Rate 2 [1/s]:</th>
<th>Temp 3 [K]:</th>
<th>Rate 3 [1/s]:</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,1</td>
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<td>0,2</td>
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</tr>
</tbody>
</table>

With help of this table and equation (XVII) 3x8 quotients \( Q_{xy} \) can be calculated:

\[
Q_{xy} = \left( \frac{\frac{dX}{dt}}{\frac{dX}{dt}} \right)_{T_{y},X} = \exp \left( \frac{E}{R} \left( \frac{1}{T_{x}} - \frac{1}{T_{y}} \right) \right) \quad (XVII)
\]

In addition 24 values of \( \frac{E}{R} \) and the average can be calculated.
Now the nonisothermal measuring curves are transformed into isothermal curves. This is done by calculating an average temperature from all temperatures of the points measured. With the estimated value of \( \frac{E}{R} \) the differential quotients at the average temperature are calculated by

\[
\left( \frac{dX}{dt} \right)_{T, X} = \left( \frac{dX}{dt} \right)_{T, X} \cdot \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T} \right) \right) \quad (XVIII)
\]

In the ideal case we get three identical (calculated) isothermal curves from three different nonisothermal measuring curves.

6) Calculation of the order and rate constant of the average temperature:
The three isothermal \( \frac{dX}{dt} \) versus X curves can be fitted with the equation (XVI) to obtain the order of reaction n and the rate constant

7) Calculation of the activation energy and Arrhenius-factor:
If we assume a reaction of first order, the data analysis can easily be done in case of isothermal measurements. For a first order reaction, the kinetics is given by

\[
\frac{dX}{dt} = k_\infty \cdot \exp \left( \frac{-E}{RT} \right) \cdot \left( 1 - X \right) \quad (XIX)
\]

The solution of the differential equation is

\[
X = 1 - \exp \left( -k(T) \right) \quad (XX)
\]
\[ \frac{dx}{dt} = k(T) \cdot \exp(-k(T) \cdot t) \quad \text{(XXI)} \]

The measured curves can be fitted with equation (XXI) to get the rate constant \( k(T) \) for temperature \( T \) (in case of isothermal measurement). From the three obtained \( k(T)/T \) pairs from three measurements, an Arrhenius plot can be made to get the values for \( E_A \) and \( k_\infty \).

**Report**

1. Estimate the molar enthalpy, the order of reaction, the activation energy and the Arrhenius constant of the dissociation reaction of V50 initiator. Compare with literature data!

2. Compare the data obtained from the isothermal and the nonisothermal method!

**Literature**