# Polymerization Technology – Laboratory

Thermal Degradation of Polymers

Reactions where the degree of polymerization of polymers decreases without changing the chemical constitution of the monomers are called degradation reactions. There are two different mechanisms of degradation of polymers: depolymerization and statistical fragmentation of chains.
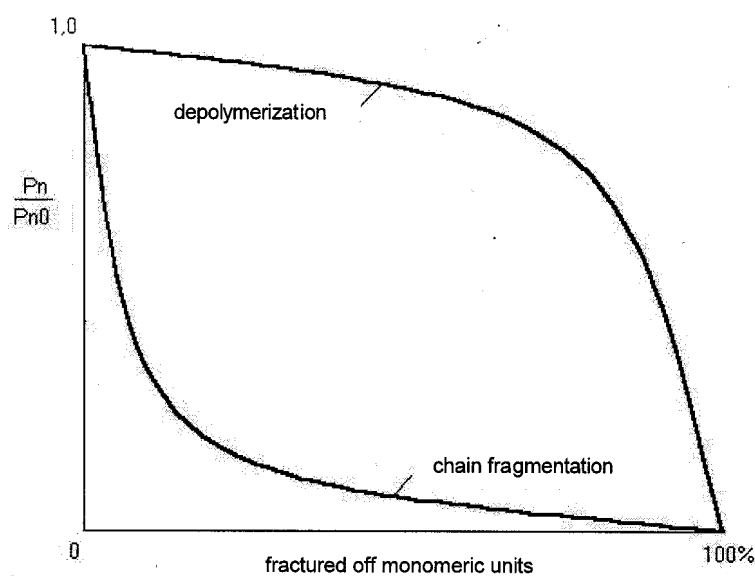
Figure 1: *Degree of polymerization changing with the amount of fractured off monomeric units for two different degradation mechanisms: fragmentation and depolymerization*

Chain fragmentation

Polymers that don´t depolymerize, like polyethylene, generally decompose by thermal stress in smaller fragments. These fragments break again in smaller fragments and so on.

The degree of polymerization decreases without formation of free monomeric units but only chain fragments (Figure 1). The statistical fragmentation can be initiated by chemical, thermal or mechanical activation or by radiation.

The kinetics of polymer degradation can be described by the degree of fragmentation S of the molecular chains. S is the fraction of broken bonds of a macromolecule with an infinite degree of polymerization. For $P_n = \infty$ is $S = 0$ and S is defined as

$$S = \frac{1}{P_n} \tag{1}$$

If all bonds that can be be broken have the same reactivity, independent of the length of the chain and their position in the chain, the fragmentation is a statistical phenomenon. Under constant reaction conditions the change of the degree of fragmentation with time can be described as follows

$$\frac{dS}{dt} = k_s (1 - S) \qquad\qquad k_s = \text{rate constant of fragmentation} \qquad\qquad (2)$$

If S_0 is the degree of fragmentation of the original polymer and S_t is the degree of fragmentation at the time t, we obtain by integration

$$\ln \frac{(1 - S_0)}{(1 - S_t)} = k_s t \qquad\qquad (3)$$

With equation (1) follows:

$$\ln \left(1 - \frac{1}{P_{n,0}} \right) - \ln \left(1 - \frac{1}{P_{n,t}} \right) = k_s t \qquad\qquad (4)$$

The degrees of polymerization of the original polymer $P_{n,0}$ and of the partially degraded polymer $P_{n,t}$ are much higher than 1, and so we can approximate

$$\frac{1}{P_{n,t}} = \frac{1}{P_{n,0}} + k_s t \qquad\qquad (5)$$

or

$$\frac{1}{P_{w,t}} = \frac{1}{P_{w,0}} + \frac{k_s}{D} t \qquad\qquad (6)$$

$$\text{with} \quad D = \frac{M_w}{M_n} \qquad P_n = \frac{M_n}{M_0} \qquad P_w = \frac{M_w}{M_0}$$

If statistical degradation occurs the size of the fragments is described by a Schulz Flory distribution with $D = 2$ after only a few degradation steps.

Depolymerization

The mechanism of depolymerization can occur under the same conditions (high temperature) as the statistical fragmentation. In this mechanism monomeric units split off from the end of the polymeric chain. This is the reverse mechanism of the polymerization. Active polymers can be depolymerized until the equilibrium between monomer and polymer at a given temperature is reached (in a closed reaction system).

Statistical fragmentation and depolymerization of polymers often occur simultaneously (e.g. polystyrene). In this case equation (5) must be extended to

$$\frac{1-x_m}{P_{n,t}} = \frac{1}{P_{n,0}} + k_s t \tag{7}$$

$$\frac{1-x_m}{P_{w,t}} = \frac{1}{P_{w,0}} + \frac{k_s}{D} t \tag{8}$$

x_m is the molar fraction of the monomer that is split off by depolymerization. It grows linearly with the reaction time. For PMMA it was found to be (Ulbricht):

$$x_m = 8 \cdot 10^{-7} \, s^{-1} \cdot t$$

Molecular weight and viscosity of a polymer melt

Independently from the mechanism of degradation, the viscosity h_0 of the melt can be determined from the torque (T) and the rotation per minute (n) of the kneading machine

$$\boldsymbol{h}_0 \approx \boldsymbol{h}_{eff} = K \cdot \frac{T}{n} \tag{9}$$

The constant K was determined for this equipment to be 132.5 m^{-3}. If the shear rate of the machine is low, the effective viscosity should be identical to the zero viscosity of the polymer. Additionally it is known that the viscosity of polymer melts is proportional to the weight average of the molecular mass M_w according to the following relation

$$\boldsymbol{h} = c \cdot M_w^{3,4} \tag{10}$$

From eq. (9) and (10) we get the following relation for the time-dependent average of the molecular mass:

$$M_{w,t} = M_{w,0} \cdot \left(\frac{T_t}{T_0}\right)^{1/3,4} \tag{11}$$

T_0 = *measured torque in the original polymer melt at the beginning of the measurement* (t=0)
T_t = *torque at time t*
$M_{w,0}$ = *molecular mass at the beginning of the measuremt* (t=0)

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Experimental

The kneading machine has to be filled with the polymer when the desired temperature is reached (attention: high temperature). The measurement is started immediately at 60 rotations per minute (constant rotation). A time dependent torque is measured (ordinate skaling is set at 25 Nm).
After the measurement the instrument has to be cleaned thoroughly.

Data analysis and report

Unfortunately, there is no possibility to save data as ASCII file, so that the data has to be read from the monitor. 15 to 20 data points per measurement are sufficient.
Please calculate following data in their dependence on time:
Viscosity, weight average of molar mass and average degree of polymerization.
Create a diagram of reciprocal degree of polymerization versus time and fit equation (6) or equation (8) (when PMMA is used) to the data.
Discuss the method and possible errors.

Polymer properties

Polyhydroxybutyric acid: V22 $M_n = 1.27 \cdot 10^5$ g/mol $M_w = 2.75 \cdot 10^5$ g/mol

                              V27 $M_n = 1.61 \cdot 10^5$ g/mol $M_w = 2.88 \cdot 10^5$ g/mol

Polymethylmethacrylate: $M_n = $ g/mol $M_w = $ g/mol

Polyethylene: $M_n = $ g/mol $M_w = $ g/mol

Polystyrene: $M_n = $ g/mol $M_w = $ g/mol

Literature

- Joachim Ulbricht, Grundlagen der Synthese von Polymeren (2. Auflage), Hüthig & Wepf, Basel, 1992 (German)

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