4 DEFORMATION OPTIONS OF POLYMER MOLECULES

Polymer molecules can be regarded as chains from flexible segments (Kuhn segments) that are entangled with each other. They have three ways to deform: bending of the chain segments, rotation of the chain segments and reptation of the entire molecule.

4.1 BENDING OF CHAIN SEGMENTS

The chain segments (Kuhn segments) in a polymer molecule will bend a little bit when a load is applied. This results in a small deformation of the polymer molecule. The polymer feels stiff and its elasticity modulus is high.

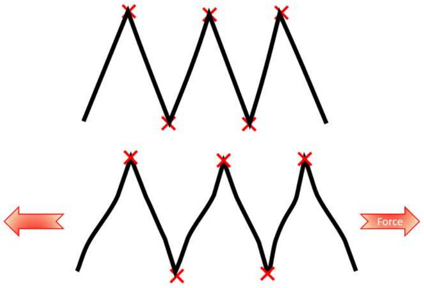

Figure 15: Bending of chain segments results in a small deformation. The relative position of the molecules does not change.

4.2 ROTATION OF CHAIN SEGMENTS

Due to the thermal vibrations of the atoms the chain segments (Kuhn segments) in a polymer molecule can rotate in any direction. This allows the molecule to change its shape under load. The rotations of the chain segments make a polymer flexible. The polymer feels elastic and its elasticity modulus is low.

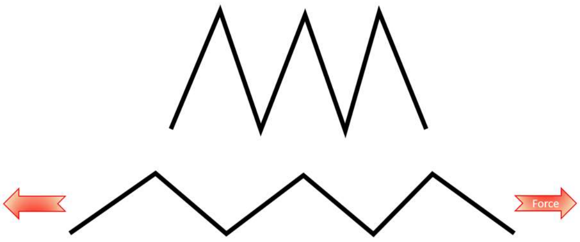

Figure 16: Rotation of chain segments results in a large deformation. The relative position of the molecules does not change.

The time needed for these rotations, the **rotation time**, is strongly temperature dependent. At low temperatures the rotation time is long and at high temperatures the rotation time is short. At a sufficiently high temperature the Kuhn segments have a rotation time of, for example, 0.001 second. Now the polymer molecules easily change their shape under a force. The polymer is flexible now. On the other hand, at low temperature the rotation time can be as high as 1 million seconds. The polymer behaves as a rigid (stiff) solid now.

We humans experience the polymer as flexible when the rotation time is less than 1 second. The polymer feels as a rubbery substance. We experience the polymer as stiff when the rotation frequency is much higher than 1 second. The polymer now feels as a rigid glassy substance. The temperature at which the rotation time is 1 second is the glass transition temperature.

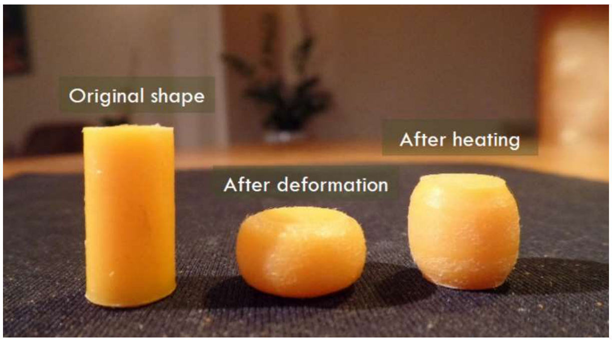

Figure 17: Below the glass temperature a polymer can be deformed but will not forget its original shape.

Rotation of the chain segments allow for large deformations in the polymer molecule. However, the position of each molecule relative to others does not change. Due to this, a polymer deformed by a force will regain its original shape when heated close to the glass transition temperature.

4.3 REPTATION OF POLYMER MOLECULES

Due to the wriggling motions of all the rotation Kuhn segments the entire polymer molecule may shift its position a little bit. The surrounding molecules will limit this shift to a displacement along the axis of the molecule. Other displacements are not possible. The polymer molecule moves as a snake along its axis through the other molecules. This way of motion is called **reptation**.

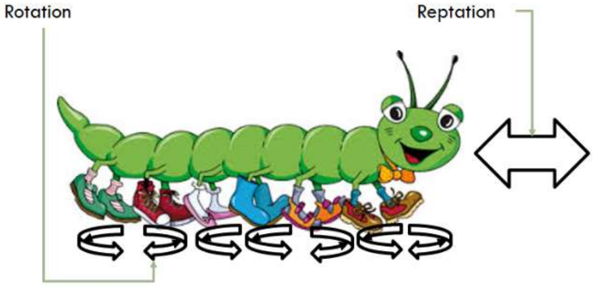

Figure 18: Reptation is caused by the random rotation of the Kuhn segments.

Compared to rotation the reptation is a relatively slow process. Due to the random nature of the rotations that counteract each other a single shift over the length of one Kuhn segment may take very many rotations.

After some time, the polymer molecule will have reptated over its entire length. It has moved into an entirely new position compared to the surrounding molecules. The time that this process takes is called the **reptation time**. At times longer than the reptation time the polymer behaves as a fluid because the position of the molecules changes continuously. Contrary to the rotation of the Kuhn segments the reptation makes the polymer to forget its original shape.

We humans experience a polymer as a fluid when the reptation time is less than 1 second. In case that the reptation time is higher than 1 second then we experience the polymer as a rubber. The temperature at which the reptation time is 1 second is the **rubber-melt transition temperature**.

4.4 KUHN SEGMENT ROTATION TIME

4.4.1 Rotation above the glass transition temperature

Segments of the polymer molecules rotate at a certain frequency causing the molecules to reptate through each other. The rotations in the polymer molecules occur at a time dictated by thermal activation. The energy barrier E_{rot} that must be passed is dependent on temperature:

Equation 9

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{E_{rot}(T)}{kT}\right)$$

In Equation 9 $\theta_{rot,0}$ is the rotation time at infinitely high temperatures and will be of the order of magnitude of 10^{-13} s.

Just like any other material polymer molecules also tend to rearrange themselves into crystalline structures when the temperature is sufficiently low. Due to their disordered nature however, polymer molecules will have difficulties in forming such crystalline structures, if they can at all. Some polymers like polyethylene are at best partially crystalline below the melting temperature; many polymers show no crystallinity at all.

Yet all polymers, whether they are partially crystalline or not, do experience an attractive potential U to crystallize. This causes clusters of polymer segments that move simultaneously. Such clusters are called cooperatively rearranging regions (CRR's). The nett result is that segmental rotation of one molecule is copied by neighbouring molecules into a cooperative action. In this way, local crystalline structures are formed on a sub-molecular scale.

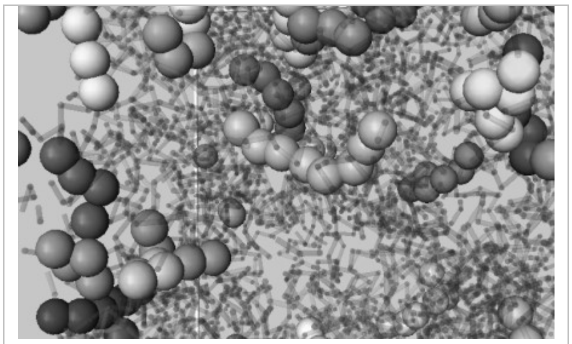

Figure 19: Graphical illustration of CRR's in the polymer.

Upon further cooling the volume continues to decrease as if the material is still a liquid. However, the level of cooperativity continues to increase. More and more polymer segments are coupled into larger groups that act together in the same way. The effective activation energy (E_{rot}) for such co-ordinated movements increases linearly with the number of cooperating segments (z_0).

Equation 10

$$E_{rot} = z_0 E_0$$

E_0 can be regarded as the energy barrier for rotation of a single repeat unit. A Kuhn segment consists of c_∞ repeat units. Therefor the minimum activation energy for the rotation of a Kuhn segment is $c_\infty E_0$. Also the minimum level of the number of cooperating segments z in a CRR will be c_∞.

The fraction of polymer segments p_β which have a thermal energy higher than the attractive potential is given by:

Equation 11

$$p_\beta = \exp\left(-\frac{U}{kT}\right)$$

This polymer fraction is relatively flexible because their mobility is not hindered (not cooperative). We call this fraction the β-phase and this phase can also be considered as a melt. The other fraction consists of cooperatively moving polymer segments that are strongly hindering each other. We call this fraction the α-phase. This phase can be considered as being formed from crystallites on a sub-molecular scale.

At the crystalline melting temperature T_m the probability for a segment to leave the CRR is just as large as the probability to enter the CRR: $p_\beta = ½$. We then find for the attractive potential U:

Equation 12

$$p_\beta = \exp\left(-\frac{U}{kT_m}\right) = \frac{1}{2} \Rightarrow U = kT_m \ln(2)$$

We then find for the fraction of the β-phase:

Equation 13

$$p_\beta = 2^{-T_m/T}$$

The CRR's in the α-phase are separated from each other by the flexible β-phase with a thickness of at least one segment. The α-phase and the β-phase, at a temperature above the glass transition temperature, are in a dynamic equilibrium with each other. Depending on the local thermal energy segments in the β-phase can change into the α-phase and vice versa.

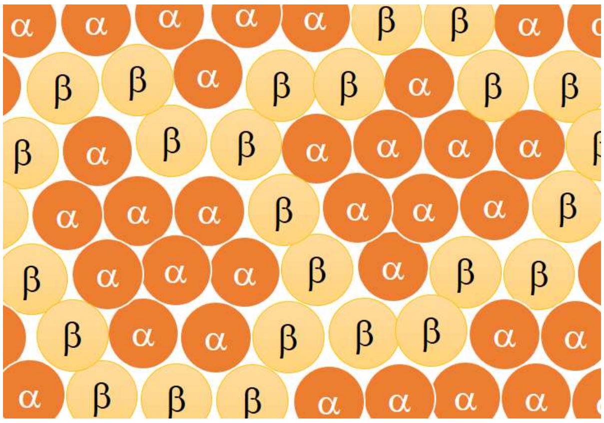

Figure 20: Schematic representation of the α-phase and the β-phase. The CRR's in the α-phase are separated by a one segment thick layer of β-phase.

The number of cooperating segments in a CRR is estimated by means of volume considerations. Let us assume that the shape of the CRR's is approximately spherical and that each CRR is surrounded by a layer of the β-phase with a thickness of half a segment. If the volume of one segment is V_0 then we can write for the volume of the α-phase V_α and the β-phase V_β:

Equation 14

$$V_\alpha = z_0 V_0 \text{ and } V_\beta = \frac{3}{2} z_0^{2/3} V_0$$

The fraction of polymer segments p_β in the β-phase is equal to the volume fraction of the β-phase:

Equation 15

$$p_\beta = \frac{V_\beta}{V_\alpha + V_\beta} = \frac{1}{\frac{2}{3} z_0^{1/3} + 1}$$

It then follows for the number of segments in a CRR:

Equation 16

$$z_0 = \left(\frac{3 - 3p_\beta}{2p_\beta} \right)^3 \text{ with } p_\beta = 2^{-T_m/T}$$

This equation only holds for $z_0 \geq 2$ (or $p_\beta \leq 0.54$) because a CRR must have at least two coupled segments.

The rotation time is now described with:

Equation 17

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{z_0 E_0}{kT} \right) \text{ with } z_0 = \left(\frac{3 - 3p_\beta}{2p_\beta} \right)^3 \text{ and } p_\beta = 2^{-T_m/T}$$

The value of E_0 can be calculated from the glass transition temperature. At T_g the rotation time is, by definition, 1 s. It then follows for E_0 using Equation 17:

Equation 18

$$E_0 = -\frac{kT_g \ln(\theta_{rot,0})}{z_0(T_g)}$$

A graphical representation of Equation 17 is shown in Figure 21 for PVC with $\theta_{rot,0} = 10^{-13}$ s, $T_m = 513$ K and $T_g = 358$ K. E_0 was determined to be 8.9 x 10^{-21} J.

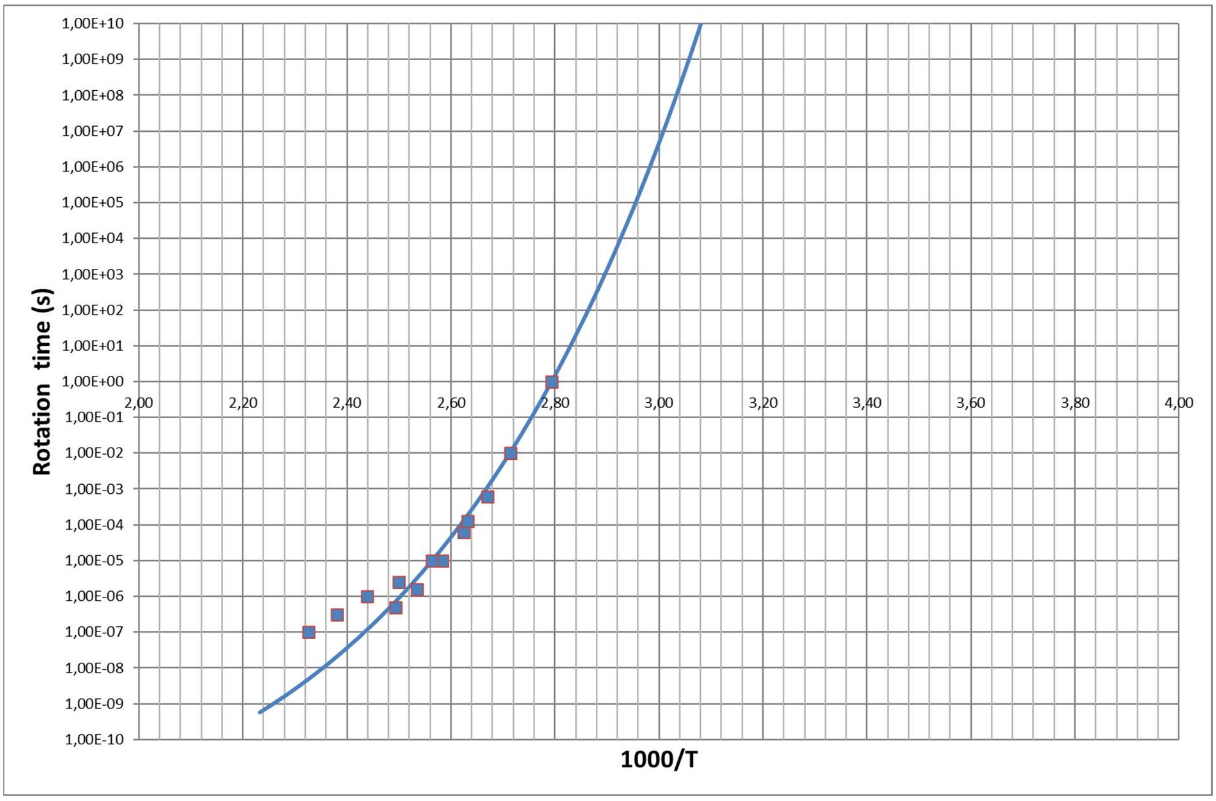

Figure 21: Segmental rotation times for PVC. Dots measured data. Line calculated according to Equation 17 with with $\theta_{rot,0}$ = 10^{-13} s, T_m = 513 K and T_g = 358 K. E_0 was determined to be 8.9 x 10^{-21} J.

4.5 CHAIN REPTATION TIME

4.5.1 General

Chain reptation, the axial movement of the polymer molecules, requires the combined motion of many chain segments. That means that reptation is virtually impossible at temperatures below the glass transition temperature. Also, in a limited region above the glass transition temperature where the frequency of the segment rotation is above 1 s^{-1} reptation is still difficult.

In the melt phase the polymer molecules are flexible: their chain segments can make many rotations in a short time. The macromolecules are also able to slide into other positions by means of reptation. This allows for large plastic deformations of the material: it is a fluid with elastic properties.

4.5.2 Sliding of macromolecules through tubes

Due to all surrounding macromolecules, it is impossible for a single polymer molecule to move freely in any direction. The macromolecule must “slide” along its own axis, in a kind of a tube formed by the other molecules. Driven by thermal energy each polymer chain can diffuse via a snake-like motion known as reptation. The macromolecule makes forward and backward jumps in a random way. The movement is to be considered as a one-dimensional random walk.

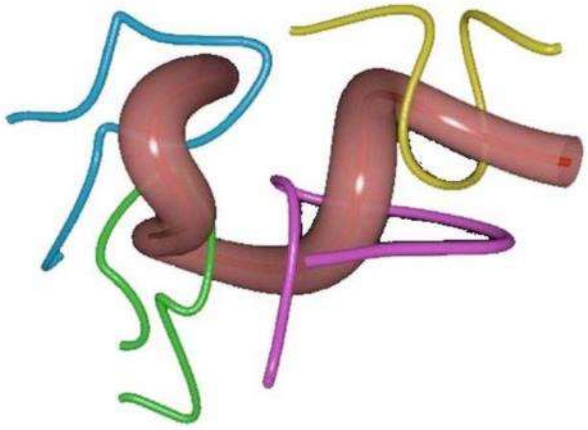

Figure 22: Polymer chain diffuses through tube.

4.5.3 Reptation time

The diffusion of the macromolecule through the matrix is caused by the uncorrelated displacements of the Kuhn pairs. Suppose that we have a fictive molecule that consists of 1 Kuhn segment. It will make steps with a size l_K randomly backwards and forwards (+ and -) during θ_{rot} seconds. Another molecule that consists of 2 Kuhn segments has 4 different step configurations (++, +-, -+ and --). Only 2 of these configurations will result in a displacement with size b. A single step forwards or backwards will therefor take 2 θ_{rot} seconds. A macromolecule with N_K Kuhn segments will reptate randomly backwards and forwards with step size l_K during a time of $N_K\theta_{rot}$ seconds.

The reptation time is the time needed for the macromolecule to diffuse over N_K Kuhn segments:

Equation 19

$$\theta_{rep} = N_K^2 N_K \theta_{rot} = N_K^3 \theta_{rot}$$

According to Equation 19 the reptation time strongly increases with temperature and it is proportional to the third power of the number of Kuhn segments in the macromolecule (N_K) or the molecular weight (m_w). Investigations have shown that the reptation time increases even faster: it increases with the molecular weight to the power 3.5:

Equation 20

$$\theta_{rep} = N_K^{3.5} \theta_{rot}$$

The reptation time is thus directly proportional to the rotation time. All temperature dependant effects of the rotation time will be duplicated in the reptation time:

Equation 21

$$\theta_{rot} = N_K^{3.5} \theta_{rot,0}\, exp\left(\frac{z_0 E_0}{kT}\right) \text{ with } z_0 = \left(\frac{3-3p_\beta}{2p_\beta}\right)^3 \text{ and } p_\beta = 2^{-T_m/T}$$