4 The Intrinsic Viscosity

4.1 The Dilute Solution

The number of parameters that have influence on the flow behavior of a polymer solution is, as will be shown in the upcoming chapters, enormous and makes it difficult to interpret the viscosimetric measurements. For this reason, viscosimetric measurements are carried out with dilute sample solutions to minimize the interactions of the single polymer molecules. In this case, only the interactions between the polymer and the solvent are determined. The dilute state of solution is shown in Fig. 4.1.

The polymer molecules are isolated from each other in solution. They take on the statistically most likely conformation and form a coil. The dimension of this coil in dilute solution is what affects the viscous properties of a polymer solution. Despite of the regional isolation between the coils, as shown in Fig. 4.1, there are interactions that take effect during the flow process. These interactions are only prevented when the state of the so-called ideal dilute solution is reached. In this case, the polymer concentration $c \to 0$ and the single polymer molecule only interacts with the solvent. The following description for the determination of the intrinsic viscosity is based on this idealized state of solution.

4.2 The Ideal Viscosity Correlation by Einstein

The viscosity enhancing properties of a polymer coil can be described via a Taylor-series:

$$\eta_{sp} = B_1 \cdot \phi + B_2 \cdot \phi^2 + B_3 \cdot \phi^3 + \ldots$$  \hspace{1cm} (4.1)

Fig. 4.1. Schematic view of a dilute polymer solution. The concentration is below the critical concentration $c'$ at which the solution volume is totally filled with polymer coils. Although the polymer coils are separated from each other, intermolecular interactions can still occur in a flow field.
Here the fraction of the polymer in solution is given by the volume fraction $\phi$:

$$\phi = \frac{V_{\text{polymer}}}{V_{\text{solution}}}$$  \hspace{1cm} (4.2)

Fortunately, all higher powers in Eq. \((4.1)\) can be disregarded for an ideal state of dilution! According to Einstein, the polymer coils are assumed to be perfectly inelastic and behave like hard spheres. Therefore, the following simple (and experimentally confirmed) relationship is obtained:

$$\eta_{\text{sp}} = 2.5 \cdot \phi$$  \hspace{1cm} (4.3)

The volume of the polymer coils $V_{\text{polymer}}$ can be described via the ratio of the mass $m_{\text{polymer}}$ of the polymer to its density $\rho_{\text{equ}}$. This density $\rho_{\text{equ}}$ does not correspond with the density in the dry state, but with the density of the polymer in solution, where solvent molecules surround the polymer chain:

$$\phi = \frac{V_{\text{polymer}}}{V_{\text{solution}}} = \frac{m_{\text{polymer}}}{\rho_{\text{equ}}} = \frac{c}{V_{\text{solution}} \rho_{\text{equ}}}$$  \hspace{1cm} (4.4)

With this, the specific viscosity is

$$\eta_{\text{sp}} = 2.5 \cdot \frac{c}{\rho_{\text{equ}}}$$  \hspace{1cm} (4.5)

The specific viscosity, introduced in Chap. 2 still depends on the concentration according to Eq. \((4.5)\). In order to obtain the true viscosity enhancing properties of a polymer, the reduced viscosity $\eta_{\text{red}}$ is introduced:

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{c} = \frac{2.5}{\rho_{\text{equ}}}$$  \hspace{1cm} (4.6)

This reduced viscosity only depends on a polymer specific property, its density in solution.

The unit of the reduced viscosity is defined via the used concentration unit, which is usually [g ml$^{-1}$] for viscosimetric measurements. With this, the unit for the reduced viscosity is [ml g$^{-1}$].

However, the reduced viscosity is also not totally independent of the concentration. Even though viscosimetric measurements are performed in the range of dilute solutions (below the critical concentration $c^*$, where the single polymer coils start to interpenetrate), small polymer interactions (that are decreasing with a decreasing concentration) have to be considered. The true viscosity enhancing properties of a polymer is therefore the reduced viscosity extrapolated to $c \to 0$:

$$[\eta] = \lim_{c \to 0} \eta_{\text{red}}$$  \hspace{1cm} (4.7)