Summary

Because of their significant visco-elastic properties polymers in aqueous solutions have a high relevance in industrial applications. Methylcellulose (E 460) and κ-carrageenan (E 407), which were investigated in this dissertation, are characterised by thermic induced sol-gel transition. The methylcellulose is in a sol-state at room temperature and is used as thickening agent and stabiliser, because of the viscosity increasing effect. With *rising* temperature these cellulose ethers form gel structures, and are therefore used as texture creators. The κ-carrageenans, which are in the sol-state at high temperatures, form gels when the temperature is *decreased*. Due to the fact that so far the desired visco-elastic properties are adjusted only empirically, the aim of this work was to describe their visco-elastic properties with molecular models.

Since the visco-elastic properties of polymer solutions are decisively influenced by the molar mass, the molar mass distribution, the chemical structure and the amount of accompanying substances, these polysaccharides were firstly investigated with structural analysis methods. The ues of atomic absorption spectroscopy (AAS) and ion chromatography (IC) quantifies the percentage of extraneous electrolytes. Furthermore, the degree of substitution (DS) of the methylcellulose samples was determinated by nuclear magnetic resonance (NMR) spectroscopy to lie between 1.8 and 2.1. In addition to this, the percentage of other carrageenan modification in the κ-carrageenan samples was evaluated by this method (κ- / ι-ratio from 100 % / 0 % to 44 % / 56 %).

In addition, the intrinsic viscosity $[\eta]$, the molar mass distribution and the radius of gyration R_G of the methylcellulose was determined by viscosimetry, size exclusion chromatography (SEC) coupled with multi angle laser light scattering (MALLS) and the differential refractive index (DRI). The formulation of structure-property relationships of the single molecule offers the possibility to obtain a relation between these molecular parameters. For methylcellulose in 0.1 M sodium nitrate at 25 °C the following $[\eta]$-M- and R_G-M-relationships were established.

$$[\eta] = 3{,}05 \cdot 10^{-2} \cdot M_w^{0{,}81} \qquad\qquad R_G = 5{,}17 \cdot 10^{-2} \cdot M_w^{0{,}57}$$

Because of the aggregation tendency of κ-carrageenans at room temperature these macromolecules could only be investigated by viscosimetry, and can therefore only be characterised by the intrinsic viscosity $[\eta]$.

For the different technical applications of methylcellulose, the viscosity yield is an important parameter. Rheo-mechanically detected shear experiments were carried out to analyse the thickening properties. In addition to the zero-shear viscosity η_0 at low shear rates, the onset of a power-law region with a slope n was detected at a critical shear rate $\dot{\gamma}_{crit}$ (reciprocal value of the longest relaxation time λ_0). These viscous parameters could be modelled by η_0-M_w-c-relationship or by η_0-c-$[\eta]$, λ_0-c-$[\eta]$ and n-c-$[\eta]$ relationships. The structure-property relationships of the shear flow for different concentrations and molar masses of methylcellulose in 0.1 M sodium nitrate at 25 °C are given below.

$$\eta_0 = 8{,}91 \cdot 10^{-4} \cdot \left(c \cdot [\eta] + 0{,}35 \cdot \left(c \cdot [\eta] \right)^2 + 2{,}97 \cdot 10^{-2} \cdot \left(c \cdot [\eta] \right)^{4{,}31} + 1 \right)$$

$$\lambda_0 = \frac{3{,}16 \cdot 10^{-10} \cdot \left(\left(c \cdot [\eta] \right)^2 + 0{,}35 \cdot \left(c \cdot [\eta] \right)^3 + 2{,}97 \cdot 10^{-2} \cdot \left(c \cdot [\eta] \right)^{5{,}31} \right)}{c^{2{,}27}} \qquad n = -0{,}818 + 0{,}84 \cdot 10^{0{,}026 \cdot c \cdot [\eta]}$$

Besides the viscous characteristics, macromolecules in solution are distinguished by elastic properties. Since the elasticity in form of the first normal stress difference N_1 could not be detected for all methylcellulose samples in the rheo-mechanical shear flow, this material function was calculated from the rheo-optical data by using the stress-optical rule.

For the investigation of the sol-gel transition of methylcellulose, temperature-sensitive rheo-mechanical oscillation experiments in the linear visco-elastic range were used. After a pre-gelation zone, an increase of the storage modulus G' was detected. In this temperature area of 50 °C to 60 °C the values of the storage modulus G' exceed the values of the loss modulus G''. The temperature, where the cross-over of the two modulus was detected, was defined as the gelation temperature T_{Gel}. To describe the gel structure, frequency-dependent oscillation experiments were performed at 85 °C. The storage modulus G'_{Gel}, which was frequency-independent at this temperature, was used to describe the stability of the gels. The dependence of the values of T_{Gel} and G'_{Gel} on the concentration and the molar mass of the methylcellulose samples could be acquired by new structure-property relationships of the gelation, which are listed below for the methylcellulose in 0.1 M sodium nitrate.

$$T_{Gel} = 35{,}77 \cdot \left(\frac{c}{\sqrt[3]{[\eta]}} \right)^{-0{,}07} \qquad\qquad G'_{Gel} = 2{,}25 \cdot 10^5 \cdot \left(c \cdot \sqrt[3]{[\eta]} \right)^{2{,}53}$$

To describe the characteristic in the pre-gelation zone, rheo-optical shear experiments were performed. These measurements show already at room temperature (25 °C) the presence of aggregated structures, whose material functions are dominated at high shear rates by the orientation process of the polymer segments. The sigmoidal curve of the orientation can either be explained by finitely stretchable aggregates or a break-up of these aggregates. With rising temperature the dominance of the characteristics of the aggregates increased.

To verify the validity of the structure-property relationship of the gelation process, its general form was used to describe the gelation of κ-carrageenan. In this investigation the different potassium concentrations and the different ι-carrageenan fractions show a dominat effect on the characteristics of the gelation. The temperature of the gelation T_{Gel} could be modelled by including the potassium concentration $c_{[Kalium]}$ in the equation. The gel stability G'_{Gel} of the κ-carrageenans, which contained ι-carrageenan fractions, was below the stability of the pure κ-carrageenans and could not be described by the structure-property relationship of the gel stability. For high concentration these material function converge, so that the equations, which are shown below, describe all κ-carrageenan samples at high concentrations.

$$T_{Gel} = 209{,}04 \cdot \left(\frac{c \cdot c_{[Kalium]}}{\sqrt[3]{[\eta]}} \right)^{0{,}16} \qquad\qquad G'_{Gel} = 7{,}42 \cdot 10^5 \cdot \left(c \cdot \sqrt[3]{[\eta]} \right)^{1{,}56}$$