

New ways to characterize the gelation process of biopolymers

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ABSTRACT

Taking κ -carrageen as an example, this contribution shows that by means of rheo-optical methods, it is possible to characterize the polymer's specific solution properties, which influence the solution structure at different concentrations, as well as its gelation process.

INTRODUCTION

Due to their thickening, jelling, binding, stabilizing and therefore structure forming abilities, biopolymers are widely used as ingredients in food stuff. This especially counts for polysaccharides – on their own or in combination with hydrocolloids. Quantitative characterization of the gelation process of, for example, κ -carrageen can help to improve food processing. Generally speaking, a complete rheo-mechanical characterization can only be achieved by applying steady shear flow, oscillation and uniaxial elongational flow, see Fig. 1. Rheo-mechanical investigations can provide a wide range of information for food processing. The information thus obtained applies to the sample volume as a whole¹.

In addition, rheo-optical investigations that analyse the flow birefringence and flow dichroism can be used to draw conclusions about the mobility and orientation of the polymer as a function of the shear rate (for details see ^{2,3,4} and references cited therein). It is possible to characterize the dynamic behaviour of local structures (polymer segments and polymer aggregates), determine intermolecular and intramolecular interactions, and detect changes in the solution structure.

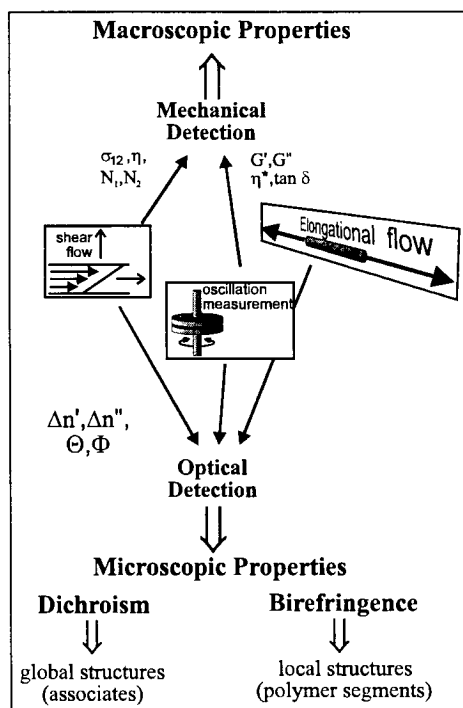


Figure 1. Mechanical and optical detection of rheological material functions for a comprehensive characterization of polymer solutions

κ -carrageen, which has various applications in food industry, as a thickener, an additive or a stabilizer for puddings, dressing and beverages, shows strong jelling properties at concentrations above 1 % (w/w) and temperatures lower than 25° C.

A kinetically controlled helix-coil-transition is assumed to be the reason for the gelation behaviour⁵, at which aggregated structures are built up by formation of helical dimers⁶. Investigations of viscosity in dependence on temperature show that at going below a critical temperature, a drastic increase of viscosity is detected⁷. The critical temperature itself is a function of the applied concentration, i.e. with increasing concentration the transition temperature rises. The number of entanglements for this thermoreversible gel formation depends on temperature and on the dissociation energy of the entanglements⁸. The dissociation energy for κ -carrageen broken up in an autoclave was determined to be $\Delta H = -74$ kJ/mol.

While detailed investigations on the reversibility of gelation and on the dependence on concentration of loss and storage moduli in the jellified state have been carried out previously⁷, the rheologically detectable molecular changes in the solution structure for an increase in concentration in the not jellified state still have to be determined. Therefore, investigations in stationary shear field at 323 K, i.e. above the temperature of gel formation, have been performed for different concentrations ($c = 0.5, 1, 2\%$ (w/w)). The gel formation temperatures have been found to be 298 K for $c = 0.5\%$ (w/w), 305 K for $c = 1.0\%$, and 313 K for $c = 2.0\%$. Below these temperatures, gellification occurs. From a concentration of 1% (w/w) onwards, one therefore gets cut resistant gels at room temperature.

It was the aim of these investigations, to detect the interactions leading to gellification already prior to the formation of a gel.

RESULTS AND DISCUSSION

Fig. 2 shows the flow birefringence, normalized over concentration (left y-axis) and the orientation angle determined by means of birefringence (right y-axis).

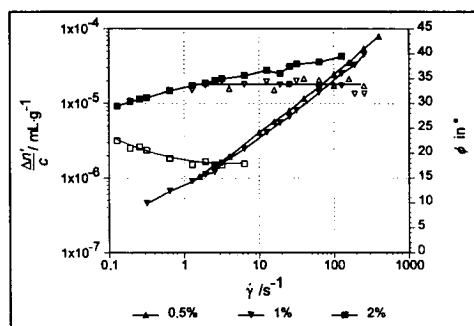


Figure 2. Reduced flow birefringence $\Delta n'/c$ (solid symbols) and orientation angle ϕ (hollow symbols) as functions of shear rate $\dot{\gamma}$ for κ -carrageen (in aqueous solution; $T = 323$ K)

While such a normalization is possible for many different other polymers (e.g. sodium carboxymethylcellulose or waxy maize starch⁹), κ -carrageen does not show ideal behaviour. At concentrations up to 1% (w/w) the curves are superimposable, i.e. an increase of concentration by factor 2 causes an increase of birefringence by factor 2 as well. The higher concentrated solution deviates from this principle and exhibits distinctly higher values for birefringence at low shear rates. At higher shear rates the curves approximate. The higher concentration of $c = 2\%$ (w/w) therefore shows a different slope, i.e. there is a different shear sensitivity of the molecules.

These results indicate that if a critical concentration is exceeded, differences in the solution structure arise (for details on the five solution states see¹⁰). These differences are not detectable only by means of rheomechanics. Although - analogous behaviour of optical and mechanical measurable variables assumed - the superimposition of the curves normalized over concentration of samples of $c = 0.5$ and 1% (w/w) would correspond to a slope of one in double logarithmically scaled $\eta_{sp}-c \cdot [\eta]$ - or $\eta_0 \cdot c \cdot M_w$ diagrams, the strongly enhanced birefringence for $c = 2\%$ (w/w) can not be explained by a transition from the diluted to the concentrated state. In this case one would expect a slope of 3.4 at the highest in an $\eta_{sp}-c \cdot [\eta]$ diagram. But the optical values determined for κ -carrageen correspond to a slope of 6, which shows that a transition

from a diluted to a concentrated solution can not be the only cause for the high birefringence observed. This high birefringence could rather be caused by a helix-coil transition. Moreover, intermolecular interactions could also be the reason. Independent on the nature of the interactions, these investigations demonstrate that intermolecular interactions, which influence the solution structure, already occur prior to the gel formation and above the temperature and concentration of gellification.

This assumption is confirmed by the orientation angles of solutions of different concentrations. An orientation angle, ϕ , of 45° means that the polymer segments are statistically disordered in the solution, while an orientation angle of 0° indicates complete alignment of the polymer segments in shear direction.

While the solutions of $c = 0.5$ and 1% (w/w) show identical orientation angles, exhibiting high values and being independent on shear rate, for concentrations of $c = 2\%$ (w/w) distinctly smaller angles – meaning stronger alignment – were detected (Fig. 2). This stronger alignment can only be caused by intermolecular interactions, confirming the thesis above.

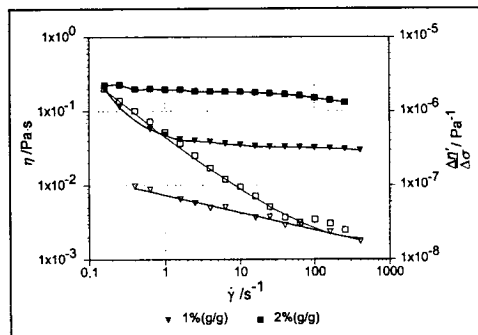


Figure 3. Viscosity, η , (solid symbols) and stress-optical coefficient, C , (hollow symbols) as functions of shear rate, $\dot{\gamma}$, for κ -carrageen at different concentrations (in aqueous solution; $T = 323\text{ K}$)

Fig. 3 shows the shear viscosity, η , and the stress-optical coefficient, C , as functions of shear rate. Above a shear rate of $\dot{\gamma} = 1\text{ s}^{-1}$, viscosity is nearly constant. The increase of

shear stress at rising shear rate is therefore higher than the increase of the birefringence, $\Delta n'$. This is confirmed by the stress-optical coefficient, C , which strongly decreases with increasing shear rate. Therefore, the stress-optical rule¹¹ can not be applied here. The mechanical properties are not only determined by the properties of the polymer segments, which are detected by the aid of flow birefringence, but also by other parts of solution, e.g. aggregated or helical portions, which can not be described by the stress-optical rule. As κ -carrageen does not exhibit any flow dichroism, no statements on the multi phase state of the solution can be made.

REFERENCES

- Eidam, D., Kulicke, W.-M., Kuhn, K., Stute, R. (1995), "Formation of maize starch gels selectively influenced by the addition of hydrocolloids", *starch/stärke* **47**, 378-384
- Reinhardt, U. T., Meyer de Groot, E. L., Fuller, G. G., Kulicke, W.-M. (1995), „Rheo-optical characterization (flow-birefringence and flow-dichroism) of the Tobacco Mosaic Virus“, *Macromol. Chem. Phys.* **196**, 63-74
- Kulicke, W.-M., Arendt, O. (1997), "Rheo-optical investigation of biopolymer solutions and gels", *Appl. Rheol.* **7**, 12-18
- Kulicke, W.-M., Reinhardt, U., Arendt, O. (1998), "Rheo-mechanical and rheo-optical investigations of locust bean gum/ κ -carrageenan mixtures", *Macromol. Rapid Commun.*, in print
- Rees, D. A., Steele, I. W., Williamson, F. B. (1969), "Conformational analysis of polysaccharides III", *J. Polym. Sci. C* **28**, 261-276
- Rochas, C., Rinaudo, M. (1984), "Mechanism of gel formation in κ -carrageenan", *Biopolymers* **23**, 735-745
- Kramer, R. (1990), *Ph.D. thesis*, University of Hamburg, p. 111

8. Elridge, J. E., Ferry, J. D. (1954), "Cross-linking process in gelatine gels III", *J. Phys. Chem.* **58**, 992-996

9. Kulicke, W.-M., unpublished results

10. Kulicke, W.-M., Griebel, T., Bouldin, M. (1991), "Description and forecast of rheological characteristics of semi-dilute polymer solutions as a function of the molecular weight, concentration and solvent quality", *Polymer News* **16**, 39-48.

11. Janeschitz-Kriegl, H. (1969), "Flow birefringence of elasto-viscous polymer systems", *Adv. Polym. Sci.* **6**, 170-318.