RHEO-OPTICAL AND RHEO-MECHANICAL CHARACTERIZATION OF THE VISCOELASTIC PROPERTIES AND SHEAR-INDUCED ORIENTATION OF HYDROCOLLOIDS

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SYNOPSIS

In addition to rheo-mechanical shear and oscillation measurements, recent years have also seen the parallel determination of rheo-optical material functions, such as flow birefringence and flow dichroism, used in order to investigate macroscopic viscoelastic flow behaviour at a molecular level. Apart from determining these moduli, which are proportional to rheo-mechanical parameters, it was also possible to determine the orientation of polymer segments and aggregated structures. In particular, it became possible to explain aggregation behaviour during the sol-gel transition and during temperature-induced phase separation on a molecular level. Investigations centred mainly on polysaccharides relevant to applications in the food industry. In addition to *native polysaccharides* (maize starch, waxy maize starch, waxy rice starch, potato starch, locust bean gum, guar, carrageenan, β-glucan) and mixtures of these, investigations also included *chemically modified celluloses* (CMC, HPMC, HPC) and *fermentation polymers* (xanthan, schizophyllan). Particular consideration was given here to the dependence of the viscoelastic properties on concentration, molar mass, molar mass distribution, degree of substitution, solvent quality and temperature. The overriding aim was to establish structure-property relationships by correlating the rheo-mechanical and rheo-optical material functions with data from polymer analysis.

1 INTRODUCTION

As renewable raw materials, polysaccharides today play a major role as alternatives to fossil raw materials due to both their generally non-toxic nature and the constantly rising global demand for energy and raw materials. It is especially in the food industry that native polysaccharides, chemically modified celluloses and fermentation polymers are used as additives to selectively achieve a desired properties profile for a product [1]. The applications for polysaccharides here include use as thickeners, thixotropic agents, flow and texture enhancers [2], as well as stabilizers and emulsifiers [3], as water-binding agents for improving the freeze-thaw stability and preventing synaeresis and retrogradation, as a gelation agent and as dietetic substitutes [4]. However, the addition of a polymer to acquire a desired properties profile results in an increase of the variable parameters as now – in addition to the usual influential factor of concentration – the molar mass, the molar mass distribution, the substitution pattern and resulting conformation in the selected solvent also have to be taken into account. This is made more difficult by the fact that many of the polysaccharides employed in solution tend to form aggregates, which, while being desirable in special applications, does, however, cause problems in establishing a selected properties profile. To date great effort has often been expended on empirically determining the amount of substance that needs to be added, and for mixtures of polymer additives this quantity has often been heavily dependent upon chance.

By using rheological shear and oscillation measurements, it is possible to determine the viscoelastic properties of a system quantitatively, as a function of the many influential parameters. The overriding aim here was to establish structure-property relationships for a polymer in a solvent system from the viscoelastic material functions correlated with data from polymer analysis [5]. These structure-property relationships make it possible to quantitatively predict the viscoelastic properties as a function of the molecular parameters [6], [7],[17], [22], [27].

In the case of mixtures of polysaccharide additives and in systems subject to a change in the material

functions over time (aggregation, micelle formation and gelation), the establishment of structure-property relationships for the individual components in the sol state is not sufficient to enable the properties profile to be adjusted. For this reason, this report aims to show how, with the aid of rheo-mechanical and rheo-optical methods, new rheological material functions (flow birefringence, $\Delta n'$, and flow dichroism, $\Delta n''$, together with the accompanying orientations ϕ and θ) can be obtained, which extend beyond the structure-property relationships. These new functions then enable the interactions of polysaccharides to be detected at the molecular level. Another aim during this work will be to show the extent to which molecular interactions of dual polysaccharide mixtures (maize starch [8], waxy maize starch [9], [10], waxy rice starch [11], potato starch [12], locust bean gum [13], guar [8], carrageenan [8], [9], xanthan [9], [10] and CMC [14], [15]) have an influence on the macroscopic flow behaviour. Furthermore, an attempt will be made to describe the sol-gel formation behaviour (carrageenan [16], β-glucan [17], [18]) and the formation of aggregates (CMC [19], HPMC [20], [21], HPC [22], [23] and xanthan [24], [25], [26], [27]) at a molecular level and to employ this in explaining the change in the macroscopic material functions over time.

2 EXPERIMENTAL

The rheo-mechanical measurements were performed on commercially available rheometers of the following types: RFS-8500 and ARES (Rheometrics, Inc., Piscataway, NJ, USA), UDS 200 (Paar/Physica Messtechnik GmbH, Stuttgart, Germany) and CS 50 (Bohlin Reologi AB, Lund, Sweden).
Rheo-optical stationary shear measurements were performed on a measuring apparatus of our own construction with a Couette geometry. An optical measuring path integrated into a commercial rheometer was used for dynamic measurements. A detailed description of this method is given in references [28], [29].

3 RESULTS AND DISCUSSION

The description of rheo-mechanical material functions by means of empirical structure-property relationships is illustrated in detail by the ideal, coiled system of polystyrene/toluene [5]. For polysaccharides, too, the following structure-property relationships were established (Table 1):

Table 1 *Structure-property relationships for aqueous polysaccharide solutions*

CMC:
$$\eta_0[Pa \cdot s] = 8.91 \cdot 10^{-4} + 1.30 \cdot 10^{-5} \cdot c \cdot M_w^{0.9} + 5.33 \cdot 10^{-8} \cdot c^2 \cdot M_w^{1.8} + 4.60 \cdot 10^{-15} \cdot c^{4.34} \cdot M_w^{3.91}$$

HPC:
$$\eta_0[Pa \cdot s] = 8.91 \cdot 10^{-4} + 8.91 \cdot 10^{-4} \cdot c \cdot [\eta] + 6.1123 \cdot 10^{-4} \cdot (c \cdot [\eta])^2 + 1.28 \cdot 10^{-4} \cdot (c \cdot [\eta])^{4.24}$$

Schizophyllan:
$$\eta_0[Pa \cdot s] = 8.91 \cdot 10^{-4} + 8.91 \cdot 10^{-4} \cdot c \cdot [\eta] + 3.74 \cdot 10^{-4} \cdot (c \cdot [\eta])^2 + 3.65 \cdot 10^{-7} \cdot (c \cdot [\eta])^{5.03}$$

Xanthan:
$$\eta_0[Pa \cdot s] = 8.91 \cdot 10^{-4} + 8.91 \cdot 10^{-4} \cdot c \cdot [\eta] + 5.08 \cdot 10^{-4} \cdot (c \cdot [\eta])^2 + 1.34 \cdot 10^{-4} \cdot (c \cdot [\eta])^{3.50}$$

(1,3)(1,4)-β-glucan:
$$\eta_0[Pa \cdot s] = 8.91 \cdot 10^{-4} + 5.38 \cdot 10^{-5} \cdot c \cdot M_w^{0.71} + 2.28 \cdot 10^{-6} \cdot c^2 \cdot M_w^{1.42} + 2.41 \cdot 10^{-15} \cdot c^{5.18} \cdot M_w^{3.68}$$

In the case of systems that form aggregates it is often not possible to indicate the exact molar mass, and this is substituted by the Staudinger index, [η]. For solutions with binary mixtures of substances, these material functions cannot be obtained additively from the structure-property relationships of the individual components. Intermolecular interactions result in a change in the solution structure, which leads to drastic changes in the macroscopic flow behaviour.
In Fig. 1 it can be seen from the example of the mixed system of waxy maize starch (WMS) / κ-carrageenan that the viscosity, η, of the mixture is distinctly larger than the sum of the individual systems. With the aid of birefringence and dichroism measurements (Fig. 2 and Fig. 3) more precise conclusions can be drawn at the molecular level on the nature of the interactions.
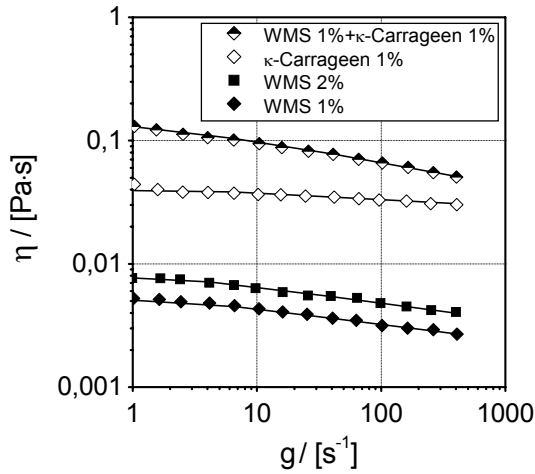
Fig. 1 *Flow curves of waxy maize starch (WMS) and κ-carrageenan (T = 298 K)*

As can be seen in Fig. 2, it is exclusively the interaction of the carrageenan with the waxy maize starch that leads to a considerable increase in the birefringence, $\Delta n'$, which is approximately proportional to the shear stress, τ_{21}.
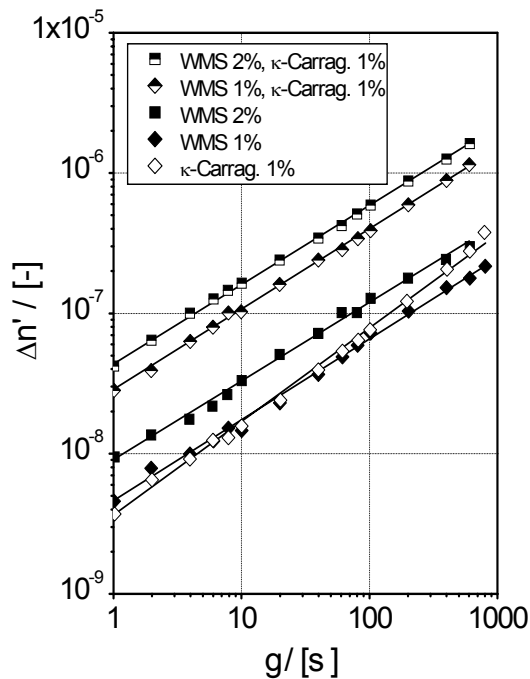
Fig. 2 *Flow birefringence, $\Delta n'$, of waxy maize starch (WMS) and κ-Carrageenan versus shear rate, , (T = 298 K)*

On the other hand, increasing the waxy maize starch component causes only a slight increase in the birefringence, $\Delta n'$, in both the pure waxy maize starch solution and the mixture. As expected, this can be attributed to the higher particle density resulting from the increase in concentration. In this case no change occurs in the solution structure. Further indications of a change in the solution structure can be seen from the dichroism measurements (Fig. 3), which represent a measure for the size of the aggregate component.
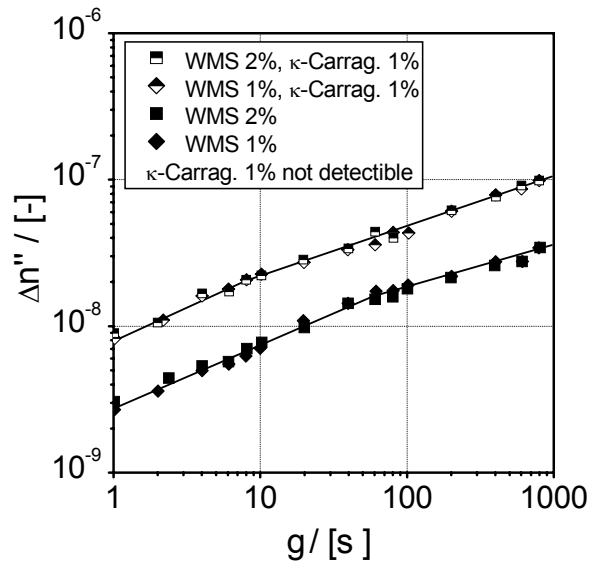

Fig. 3 *Flow dichroism, $\Delta n''$, of the mixed system of waxy maize starch (WMS) and κ-Carrageenan versus shear rate (T = 298 K)*

Accordingly, the solution structure of the aggregates is not sensitive to changes in concentration of the waxy maize starch; the change in dichroism, $\Delta n''$, during this process is negligible. The addition of κ-carrageenan results in a sharp increase of the dichroism, $\Delta n''$, and hence to a rise in the size of aggregates or the aggregate component. This can be largely attributed to the increasing intermolecular interactions. In contrast, κ-carrageenan alone only forms such small aggregates that these could not be determined via the dichroism.

The altered solution structures can also be detected in systems in which the macroscopic flow behaviour reacts only very slightly to a change in the solution composition. Fig. 4 shows the flow curves for the mixed system of locust bean gum (LBG) / κ-carrageenan. Here the overall

concentration of 5% (w/w) remained unchanged, only the ratio of the two components to one another was varied.
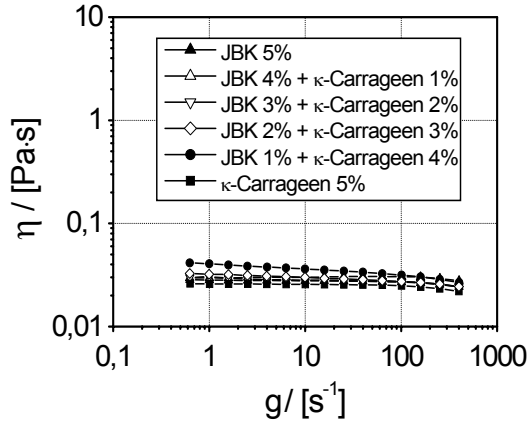
Fig. 4 *Flow curves of locust bean gum (LBG) and κ-carrageenan for different concentration ratios (T = 298 K)*

During this process, the viscosity of the Newtonian flow region remains almost constant; only when the concentration ratio of locust bean gum (LBG) / κ-carrageenan was 1:4 was it possible to observe a slight increase in viscosity. A distinct increase in the birefringence, Δn', for the concentration ratio of 1:4 can be seen in the birefringence measurements (Fig. 5), and this is also visible even at a ratio of 2:3. This can be attributed to increased intermolecular interactions between the components of the mixture. In addition, form birefringence is superimposed on the intrinsic birefringence signal for the 1:4 ratio in the lower shear range, which is only balanced out by the purely intrinsic birefingence beyond a shear rate of $= 100$ s^{-1}. This behaviour is typical of aggregated superstructures that are no longer deformed within the shear field but are only degraded. However, the aggregates in this system are still so small that by using dichroism, Δn'', it was only possible to detect a signal at the lower measuring limit for the mixture ratio of locust bean gum (LBG) / κ-carrageenan of 1:4.
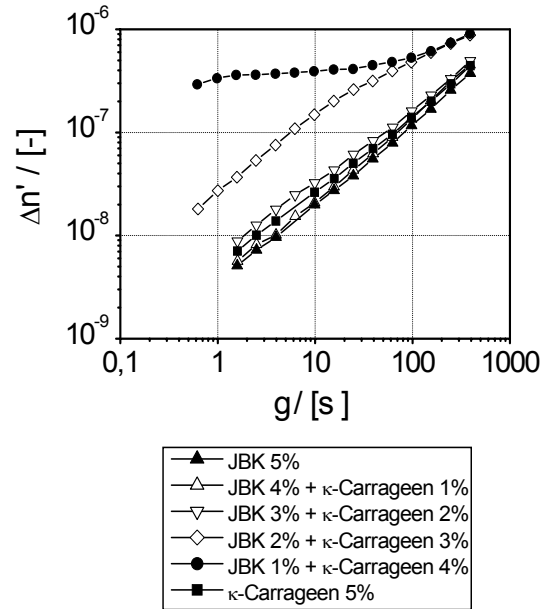
Fig. 5 *Flow birefringence, Δn', of the mixed system of locust bean gum (LBG) and κ-carrageenan (T = 298 K)*

A change in the solution structure can also be recognized from the orientation angle, ϕ, of the birefringence (Fig. 6), which is primarily determined by the rotary diffusion coefficient, D_R, of the detected structures.
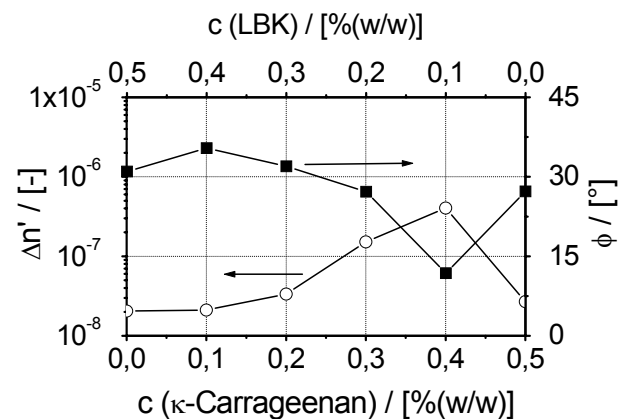
Fig. 6 *Flow birefringence, Δn', and the corresponding orientation angle, ϕ, for the mixture system of locust bean gum (LBG) and κ-carrageenan at a shear rate of $= 10$ s^{-1} (T = 298 K)*

If the viscosity, η, is approximately constant, the sharp decrease in the orientation angle, ϕ, in the Newtonian flow region can be attributed to an increased shape component due to aggregate formation, in an analogous manner to the rise in birefringence, $\Delta n'$.

In many polysaccharides, increasing the concentration, c, above a critical value leads to spontaneous gelation. The observable material functions then change additionally with time until they have achieved a stationary state. The intermolecular interactions of binary mixture systems can also be employed in order to achieve a desired processing and properties profile in the systems considered here. In Fig. 7 the storage moduli, G', which are a measure of the elastic components in a system, are plotted as a function of time for mixtures of maize starch (YMS) with various hydrocolloids. The gelation rate can be described by the increment of elasticity, I_E,

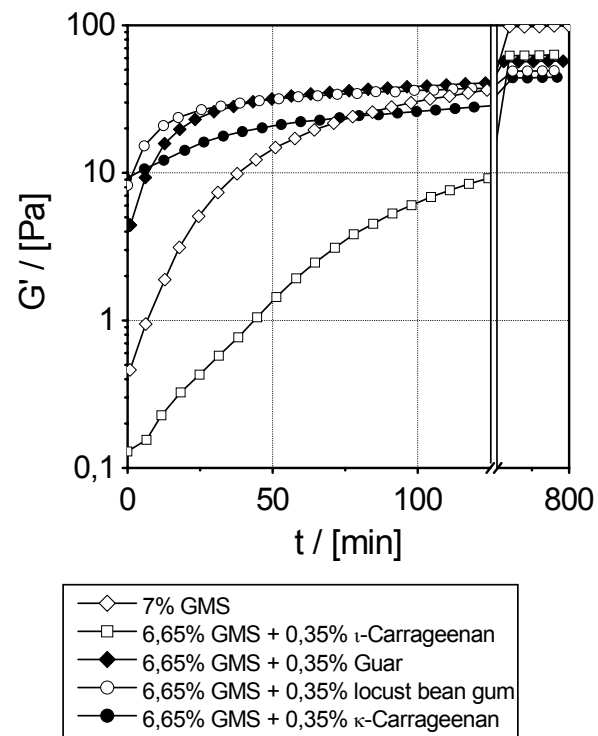$$I_E = \left(\frac{d \log G'}{dt} \right)_{max}$$

which corresponds to the maximum gradient of the change in storage modulus with time [18].

Table 2 *Comparison of the gel stiffness and gelation rate for various mixtures of maize starch (YMS) with hydrocolloids (6.65% YMS+0.35% hydrocolloid)*

| G' [Pa] (after 800min)	$G'/G'(YMS)$ [%] (after 800 min)	I_E [h^{-1}]
Pure maize starch (YMS)		
98	100	4.41
YMS + guar		
58	59	10.1
YMS + locust bean gum		
48	49	8.72
YMS + κ-carrageenan		
44	45	0.72
YMS + ι-carrageenan		
63	64	1.83
YMS + xanthan		
-	83	-
YMS + CMC		
-	50	-

As can be seen from Table 2, the gelation rate of pure maize starch can be both accelerated and retarded by the addition of different polysaccharides. Adding the galactomannans guar and locust bean gum results in an increase in the gelation rate, adding the alginates ι-carrageenan and κ-carrageenan reduces the gelation rate. However, adding κ-carrageenan leads to an increase in the storage modulus from the very beginning. The *gel stiffness*, expressed as the quotient of the storage modulus of the pure maize starch and of the mixture after complete gelation, decreases in all the mixtures, but is nevertheless dependent upon the intermolecular interactions.

Legend:
- 7% GMS
- 6,65% GMS + 0,35% ι-Carrageenan
- 6,65% GMS + 0,35% Guar
- 6,65% GMS + 0,35% locust bean gum
- 6,65% GMS + 0,35% κ-Carrageenan

Fig. 7 *Storage modulus, G', as a function of the time for various mixtures of maize starch (YMS) with hydrocolloids ($\omega = 1$ rad/s, $\gamma = 5$ %, T = 298 K)*

The causes for the occurrence of spontaneous gelation and the influence of molecular parameters were investigated in more detail on aqueous solutions of (1,3)(1,4)-β-glucan. Ultrasonic degradation made it possible to produce an homologous series of differing molar masses, the gelation rates of which were determined at

different concentrations. As can be seen in Fig. 8, the gelation rate in the form of the elasticity increment, I_E, decreases with increasing molar mass, M_W. This contradicts the previous assumption that a higher molar mass leads to more extensive intermolecular interactions. Instead, the higher chain mobility of smaller molar masses seems to result in an improved contact rate between the molecules and hence increases the gelation rate. This assumption is supported by the fact that the samples with higher polydispersity, i.e. a higher proportion of short chains, also gel more quickly. The increase in gelation rate with rising concentration is in keeping with expectations.
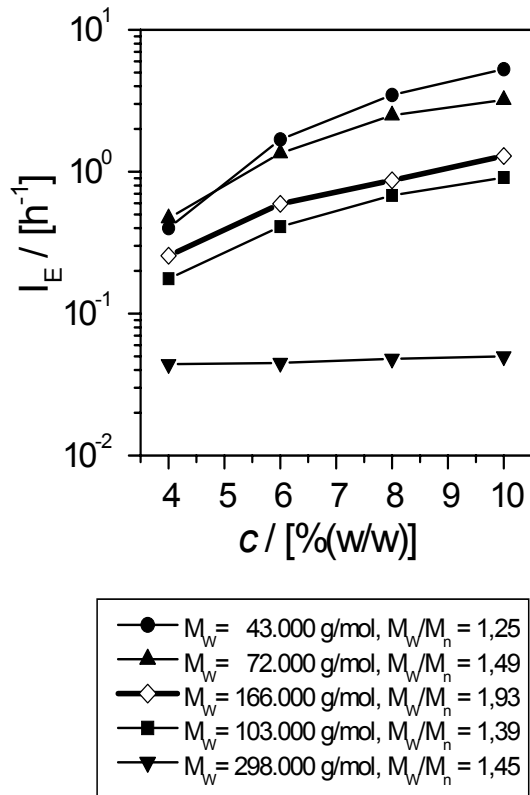
Fig. 8 *Gelation rate in the form of the elasticity increment of (1,3)(1,4)-β-glucan for various molar masses and concentrations (T = 298 K)*

The reason for the occurrence of spontaneous gelation from an initially stable sol state was investigated in more detail by means of rheo-optics. The (1,3)(1,4)-β-glucan investigated in Fig. 9 exists in the sol state at room temperature.

The induction period prior to the onset of spontaneous gelation is 5 h.
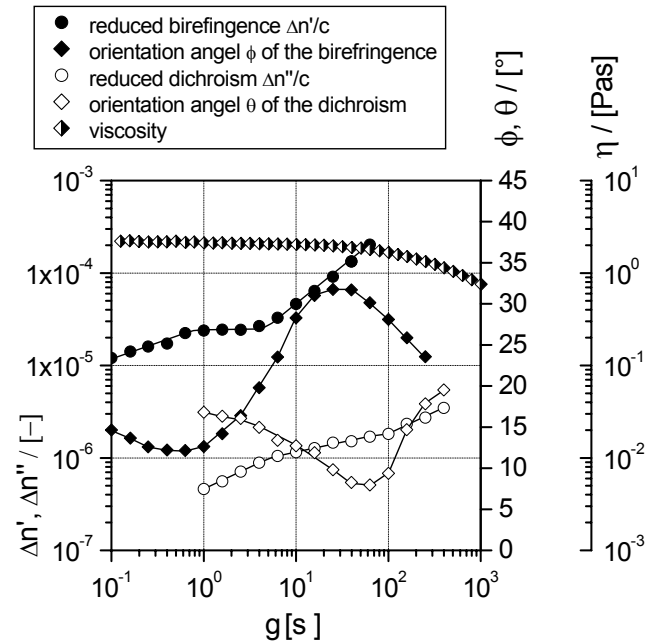
Fig. 9 *Flow birefringence, Δn', and flow dichroism, Δn'', of a (1,3)(1,4)-β-glucan solution (4% (w/w)) with a molar mass of M_W = 298000 g/mol in the sol state (T = 298 K)*

Measurements were taken in the sol state. Nevertheless, here too a dichroism, Δn'', was measured which shows that already aggregated structures are present in the sol state and that these can serve as nuclei for spontaneous gelation. As a result of the orientation angle, θ, these superstructures are shear-stable up to a shear rate of = 50 s^{-1}, and are then reversibly degraded. The birefringence, Δn', exhibits a high form component in the lower shear-rate range, which is also an indication of this superstructure, as is the early onset of the orientation of the birefringence in the lower shear range. However, from a shear rate of = 10 s^{-1} the intrinsic component of the birefringence is superimposed upon this form component. The intrinsic birefringence represents the deformation and orientation of the individual segments. As it can be seen from the rheo-optic measurements, the spontaneous gelation is induced by small, shear stable aggregates that are present even in the sol state.

4 LIST OF ABBREVIATIONS

c   concentration
CMC   carboxymethyl cellulose
$G^{'}$ storage modulus
YMS   (yellow) maize starch
HPC   hydroxypropyl cellulose
HPMC hydroxypropylmethyl cellulose
LBG   locust bean gum
M_w weight-average molar mass
M_n number-average molar mass
$\Delta n^{'}$ flow birefringence
$\Delta n^{''}$ flow dichroism
T   temperature
WMS   waxy maize starch
ϕ orientation angle of the birefringence
θ orientation angle of the dichroism
         shear rate
η shear viscosity
η_0 zero-shear viscosity
$[\eta]$ Staudinger index
τ_{21} shear stress
4   List of abbreviations

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