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Rheological studies of barley (1→3)(1→4)-β-glucan in concentrated solution: mechanistic and kinetic investigation of the gel formation

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Abstract

The gelation of concentrated barley (1→3)(1→4)-β-glucan solutions was investigated. The gelation rate was quantified by a novel parameter called the elasticity increment I_E, accessible via oscillatory time experiments. Decreasing molar mass and increasing concentration proved to raise the gelation rate. Despite a very similar plateau storage modulus G'_p of the final gels for a given concentration, the mechanical stability increases with increasing molar mass. Oat β-glucan and lichenan, both (1→3)(1→4)-β-glucans, are also able to form solid gels. The turbidity, syneresis, melting temperature of the gels and the gelation rate increase in the order oat β-glucan, barley β-glucan and lichenan, indicating an increasing extent of the junction zones. Examination of the fine structure revealed the most regular chain structure for lichenan, with cellotriose units linked by β-(1→3) bonds as the main structural feature. From this it was deduced that sections of consecutive cellotriose units constitute the cross-links. A gelation model based on sporadic nucleation similar to crystallization of polymer melts is proposed.

Keywords: (1→3)(1→4)-β-D-glucan; Oat; Barley; Lichenan; Gelation; Rheology

1. Introduction

Gelation of polysaccharides is a common phenomenon and is widely used for achieving a desired texture in foods such as jellies, aspics, tarts, and puddings. Starch, carrageenans and pectins and some others [1,2] are very common in the food industry. Pectin with a low degree of esterification requires bivalent ions for gel formation; highly esterified pectin forms a gel when it competes for solvent with sugar [1,3]. ι-Carrageenan gels consist of isolated double helices. κ-Carrageenan achieves a higher degree of organization: the double helices additionally join to form extended associates [2–4]. Gel-forming polysaccharides must have a moderately irregular structure that allows partial but not overall association, which would cause precipitation or insolubility.

(1→3)(1→4)-β-glucan is a cell-wall polysaccharide present in barley, oats and in small amounts in some other cereals. Another source of this type with both β-(1→3) and

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β-(1→4) linkages in the linear chain is lichenan found in Iceland Moss. Differences in the linkage arrangement compared with the cereal glucans have been reported [5–7], though the (1→3) : (1→4) ratio is similar (about 3:7) [6]. The β-(1→3) linkages always occur in isolation and interrupt the regular cellulose-like structure in a random fashion [8,9]. This irregularity makes (1→3)(1→4)-β-glucans water soluble.

In the brewing process barley β-glucan tends to form gels which block the filter media in the final beer filtration. A high content of dissolved solids in the wort [10], high alcohol content [10,11], low temperatures [12] and shear forces [12–14] promote gel formation. Barleys with high β-glucan content or low germinability, improper malting, unmalted barley adjuncts in the mash and unsuitable mashing programs also raise the gelation tendency [15–17]. However, the total amount of β-glucan in wort or beer does not correlate with filtration problems [12,18]. Two forms of β-glucans seem to exist: troublesome high-molar-mass β-glucans and unimportant low-molar-mass glucans [19,20].

In the literature, no investigations were found that dealt with the mechanistic aspects of the gelation of (1→3)(1→4)-β-glucans nor with the formation of solid gels. It seems to be accepted that longer blocks of contiguous β-(1→4)-linkages in the barley β-glucan associate in a cellulose-like manner and serve as junction zones [15,17,21], but this has not been proved. An alternative proposal [22] is that insolubility is caused by sequences of structural regularity, involving both (1→3) and (1→4) linkages.

In an earlier, related publication rheological aspects of barley β-glucan in the sol state were described [23]. It was demonstrated that β-glucan in solution exists in two states: molecularly disperse with normal viscoelastic flow behaviour and as an infinite network structure. The gel proved to be completely thermoreversible. In this article rheological investigations of concentrated solutions of different molar mass and concentration are used to gain an insight into the mechanism and kinetics of the gelation of (1→3)(1→4)-β-glucans.

2. Materials and methods

Samples and sample preparation.—The characteristics of the β-glucan samples used in this work are listed in Table 1. All the glucan samples were commercially available (Megazyme, Bray, Ireland). BG50 and OG40 were degraded by sonication, for details see [23]. ι-Carrageenan (No. 22045) and agarose (No. 05066) were purchased from Fluka (Neu-Ulm, Germany). κ-Carrageenan was a technical product provided by Diamalt (Munich, Germany) and gelatin was a culinary product.

The samples were dissolved in water (including 3 mmol L^{-1} sodium azide to prevent microbial contamination) as described in [23].

Gel discs were prepared between two steel plates with a cylindrical cavity (40 mm ∅, 1 mm height). The plates were heated to 80 °C and the hot polymer solution filled in the cavity. Then the top plate was quickly screwed to the bottom plate, cooled to the required temperature and stored until gelation was complete.

Determination of molar mass, polydispersity, intrinsic viscosities, protein and glucose content.—All macromolecular and analytical data were obtained as described in [23].

Rheological experiments.—Oscillatory measurements were carried out with a Rheometrics Fluids Spectrometer (RFS 8500, Rheometric Scientific, Bensheim, Germany). For temperature sweeps and gel-disruption experiments a Bohlin CS 50 stress rheometer equipped with an air-cooled Peltier heating element (Bohlin, Mühlacker, Germany) was employed. The rheometers were equipped with cone-plate tools for measuring fluids and with plate-plate tools for measuring gel discs in temperature sweeps (heating rate 1 K min^{-1}). The measurements were carried out at 25 °C, unless otherwise noted.

Gel-disruption experiments.—For quantification of the gel strength a rheological tool was manufactured equipped with engraved teeth both in the bottom and the top plate (15 mm ∅). The gap was kept small (0.5 mm) compared to the tooth height (1.5 mm). The sample was transferred to the tool as a sol and covered with paraffin oil to prevent evaporation of solvent. After complete gelation of the

sample a stress ramp was applied until the gel broke.

Enzymatic degradation of β-glucans with lichenase.—The samples (25 mg) were completely dissolved in phosphate buffer (5 mL, 0.05 M, pH 6.5) in a boiling water bath. After conditioning at 40 °C, lichenase (EC 3.2.1.73, Megazyme) in phosphate buffer was added (0.5 mL, 10 U) and the reaction mixture gently stirred. After 1 h, lichenase addition (0.35 mL, 7 U) was repeated and a further 30 min later the solution was boiled for 5 min. A white precipitate was removed by centrifugation at 10,000*g* and the supernatant lyophilized. The white powder was then redissolved in 0.1 M NaOH and injected into an anion exchange chromatograph (AEC) or redissolved in water and injected into a size-exclusion chromatograph (SEC).

Quantitative analysis of β-glucan oligomers.—The oligomers released by lichenase were qualitatively determined by anion-exchange chromatography (AEC) on a Dionex chromatography system (CarboPac PA1 column) with pulsed amperometric detection on gold electrodes (Dionex, Idstein, Germany) with 0.1 M NaOH as eluent A and 0.1 NaOAc in 0.1 M NaOH as eluent B. The column was run with a solvent gradient from A:B = 95:5 (20 min) to 70:30 (10 min) and back to 95:5 (15 min) during the 45 minute elution cycle.

The quantitative analysis of the main peaks was carried out on a preparative size-exclusion chromatograph (SEC) column (HW 40, Toso Haas, Stuttgart, Germany) with deionized water as eluent. The concentration was detected with a differential refractive index detector (RI 2000 F, Schambeck, Bad Honnef, Germany) connected to a plotter. The peak areas were integrated with a planimeter.

Turbidity measurements.—The transmissions of polymer solutions and gels were ascertained with a UV–Vis spectrophotometer (V-530, Jasco, Bünde, Germany) at a wavelength of 600 nm. The solutions were freshly prepared, placed into semi-micro disposable cuvettes and sealed to prevent solvent evapo-

Table 1
Characteristics of the used samples[a]

Code	Origin	M_w (10^3 g mol^{-1})	M_n (10^3 g mol^{-1})	M_w/M_n	$[\eta]$ (cm^3 g^{-1})
Barley glucans					
BG300	Megazyme	300	205	1.5	460
BG165	Megazyme	165	85	1.9	255
BG100	Megazyme	100	75	1.3	210
BG70	sonicated BG100	70	50	1.4	170
BG50	sonicated BG165	40	30	1.3	115
BGBlend1	BG300:BG50 = 25:75	110	50	2.2	200
BGBlend2	BG300:BG50 = 50:50	175	65	2.7	290
BGBlend3	BG300:BG50 = 75:25	240	100	2.4	380
Oat glucans					
OG220	Megazyme	220	150	1.5	335
OG40	sonicated OG220	40	30	1.3	n.d.
Lichenan					
LN55	Megazyme	55	30	1.8	n.d.
ι-, κ-*Carrageenan*, *agarose*					
ι-Carra	Diamalt (tech. sample)	180	80	2.3	n.d.
κ-Carra	Fluka	190	125	1.5	n.d.
Aga	Fluka	n.d.	n.d.	n.d.	n.d.
Gelatin					
Gelat.	culinary product	n.d.	n.d.	n.d.	n.d.

[a] M_w = weight-average molar mass, M_n = number-average molar mass, M_w/M_n = polydispersity, $[\eta]$ = intrinsic viscosity. The accuracy of the molar mass determination is ± 5% and of the intrinsic viscosities ± 3%, respectively.

ration. The transmission measurements were carried out in the sol state and subsequently repeated until a constant value was obtained, usually after a number of days.

3. Results and discussion

Rheological time measurements of barley β-glucan solutions.—As already reported in Ref. [23], freshly prepared barley β-glucan solutions do not exhibit any evidence of associated structures, they behave as typical molecularly disperse systems. However, after an induction period the β-glucan sol begins to adopt gel properties. In the end the viscoelastic fluid has turned to an elastic solid. A gel is rheologically characterized by a storage modulus nearly independent of the angular frequency G'_p (plateau modulus) and a loss modulus G'' at least one decade below G'_p [24]. The complex dynamic viscosity $|\eta^*|$ has a slope of about −1 on a double-logarithmic plot against angular frequency.

The most suitable material function for pursuing sol–gel transformations is the storage modulus, G', accessible via rheological oscillatory time experiments. The logarithm of G' as a function of time generally proved to be sigmoidally shaped for barley β-glucans but differs with concentration and molar mass. The slope of log $G'(t)$ at the turning point (maximum slope obtained at 1% deformation and 10 rad s^{-1}) was chosen as a measure of gelation rate (Eq. (1)). We have named it the elasticity increment I_E. Its dimension is reciprocal time. It indicates the number of decades G' increases at maximum per time unit.

$$I_E = \left(\frac{d \log G'}{d t}\right)_{max} \quad (1)$$

Fig. 1 shows the different shapes of log $G'(t)$ curves for three molar masses in 10% (w/w) concentration at 25 °C. The turning points and the related I_E values differing in the orders of magnitude are also shown. A high I_E value reflects rapid gelation. Despite the different appearance of the curves they obey the same rules. As shown in Fig. 2, the I_E values of a set of samples with both varying molar masses and concentrations at 25 °C can be

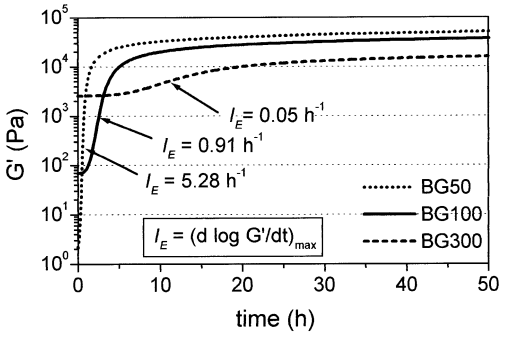

Fig. 1. Storage modulus G' as a function of time for barley β-glucan samples of different molar mass in 10% (w/w), and the elasticity increment (I_E) values as a measure of gelation rate.

standardized by scaling factors with excellent agreement when the turning point is set as the reference point. However, a standardization was impossible for temperature variation (data not shown). The former indicates an identical reaction pattern despite different gelation rates and the latter altered kinetics for temperature variation.

Influence of molar mass, concentration and polydispersity on gelation rate.—The elasticity increments I_E were measured for a set of barley β-glucan sample solutions differing in molar mass and concentration (Fig. 3). Two trends are obvious: the gelation rate declines with decreasing concentration and increasing molar mass. The concentration determines the segment density in solution and hence the probability of contact between the coils which is a basic requirement for three-dimensional network formation. The molar mass influence can be explained by the higher mobility of

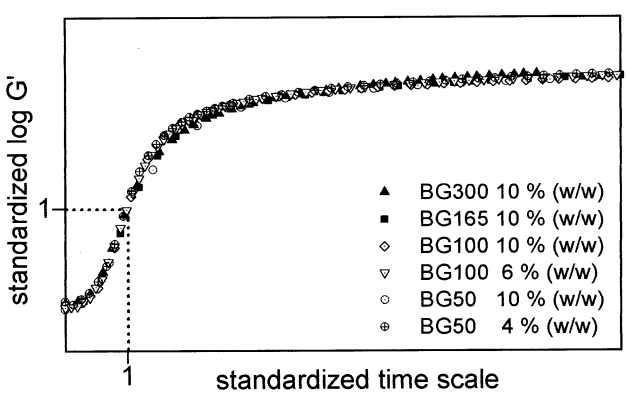

Fig. 2. Plot of standardized storage modulus $G'(t)$ curves of barley β-glucan solutions of different molar mass and concentration at 25 °C.

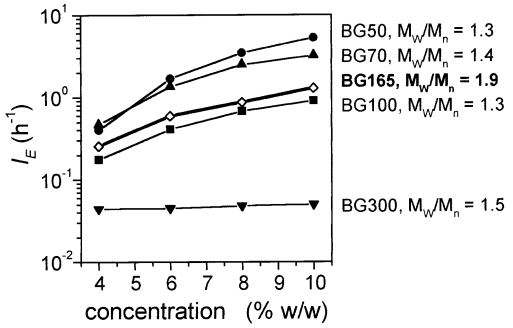

Fig. 3. Elasticity increment (I_E) values as a measure of gelation rate for barley β-glucan solutions of varying molar mass and concentration.

shorter chains. A similar explanation was given in [25] for association behaviour of low-molar-mass oat β-glucan. So the combination of mobility and segment density in solution determines the gelation rate.

Although the trend of increasing gelation rate with decreasing molar mass is obvious, a closer look at Fig. 3 reveals higher I_E values for the BG165 sample than for BG100. The broad polydispersity of BG165 ($M_w/M_n = 1.9$) is in contrast with the narrow $M_w/M_n = 1.3$–1.5 for the other samples. To verify the polydispersity influence on gelation rate of barley β-glucan, three blends from BG50 and BG300 with broad polydispersities ($M_w/M_n = 2.2$–2.7) were mixed (BGBlend1, 2, 3) and the I_E measured for 10% (w/w) solutions. A strong influence of the polydispersity is detected both for log I_E (log M_w) and log I_E(log [η]) (Fig. 4). The broadly dispersed samples exhibit higher gelation rates than the narrowly dispersed samples. In contrast, a good linear correlation ($r = -0.985$) independent of the polydispersity is only found for log I_E (log M_n) according to the following equation: $\log I_E = 14.8 - 3.03 \log M_n$. This function allows the prediction of the gelation rate of an unknown barley β-glucan sample in 10% (w/w) aqueous solution at 25 °C simply via M_n. A possible explanation for the good correlation of M_n with I_E might be that M_n emphasizes the low molecular tail of the molar mass distribution, which mainly promotes the gelation rate. In contrast, both M_w and [η] are strongly influenced by the high molecular tail.

Plateau modulus G'_p of barley β-glucan gels.—A gel is typified by its nearly frequency-independent storage modulus (plateau modulus) G'_p, which is associated with the number of cross-links in the network structure (Eq. (2)).

$$G'_p = \frac{cRT}{M_e} \tag{2}$$

where c = concentration, R = gas constant, T = absolute temperature, M_e = molar mass between two cross-links.

The larger G'_p is, the smaller will be the entanglement molar mass, i.e., the higher the cross-link density. The cross-link density determines the rigidity of the gel. G'_p is predominantly dependent on the concentration and not on the molar mass, which on the other hand strongly influences the zero shear viscosity of the sol (Fig. 5). But decreasing molar mass reduces the mechanical stress that is required for disrupting the gel [2,26]. The results are summarized in Table 2. To improve gel strength, it is more effective to increase the concentration than the molar mass. In comparison to other common gelling agents, e.g., gelatin, ι- and κ-carrageenan, the barley β-glucan gels are in the medium range of gel strength. The different role of molar mass on G'_p and on gel strength is reasonable because the segment density determines the network

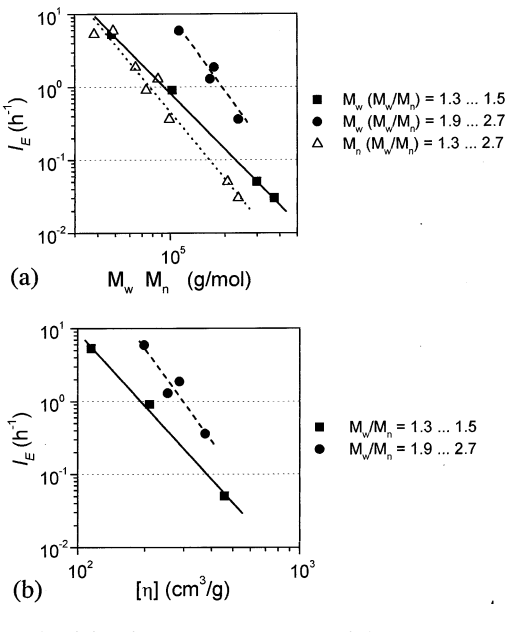

Fig. 4. Elasticity increment I_E vs. weight-average M_w and number-average molar masses M_n (a) and intrinsic viscosities [η] (b) of several barley β-glucan samples in 10% (w/w) of narrow (1.3–1.5) and broad (1.9–2.7) polydispersities M_w/M_n.

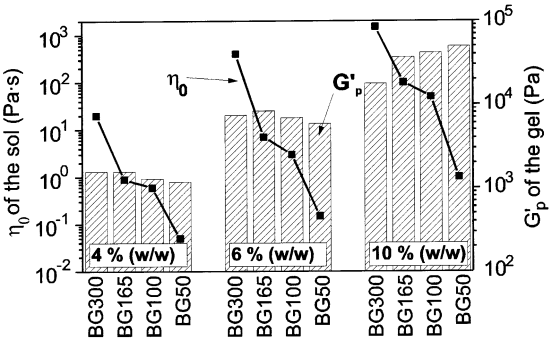

Fig. 5. Zero shear viscosities η_0 (lines) of barley β-glucan samples in the sol state and the plateau moduli G'_p of the resulting gels (columns).

structure. The thermoreversible gels are joined by weak hydrogen bonds. These are easily disrupted compared to covalent bonds. With increasing molar mass and concentration the number of cross-links per chain increase, so that the disruption resistances of the single bonds are added.

Gels from lichenan and oat β-glucan compared to gels from barley β-glucan.—The ^{13}C NMR spectra of barley β-glucan, oat β-glucan and lichenan are very similar (spectra not shown). Slight differences are attributed to a different linkage arrangement [6] despite similar (1→3):(1→4)-ratios (barley: 30:70, oat: 29:71, lichenan: 28:72). Heat-prepared oat β-glucan and lichenan solutions also yielded gels similar to barley β-glucan but with some remarkable differences concerning turbidity, gel melting temperature and gelation rate.

Table 2
Plateau moduli G'_p of the gelatinized samples and gel strength values (standardized on BG50) for barley β-glucan samples and references

Sample code	Concentration (% w/w)	G'_p (Pa)	Rel. gel strength
BG50	6	6000	1
BG100	6	7000	1.5
BG165	6	8500	1.9
BG300	6	7500	3
BG100	4	1300	0.5
BG100	8	18000	3.6
BG100	10	42000	5.5
Gelatin	6	400	0.6
ι-Carrageenan	6	1000	0.6
κ-Carrageenan	6	70000	7.4
Agarose	6	120000	16

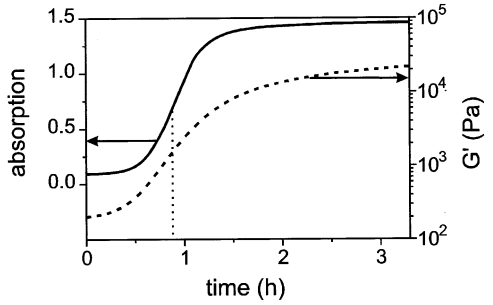

Fig. 6. Synchronous changes of storage modulus G' and the absorption (turbidity) during gelation of barley β-glucan.

(a) Turbidity. Two types of gels can be distinguished: clear, compliant and turbid, rigid gels. Whether a gel is turbid or clear depends on the size of the junction zones. Junction zones with a similar magnitude to the wavelength of visible light (>0.1 μm) cause scattering. The gelatin network is joined by isolated triple helices [2] and hence is clear. κ-Carrageenan gels are turbid because the double helices associate to extended junction zones [4].

The turbidity increases synchronously with G' during gelation of (1→3)(1→4)-β-glucans (Fig. 6). Accordingly, increase of storage modulus and turbidity are different indicators for the growing network. (1→3)(1→4)-β-glucan gels are very turbid compared to other gels. The turbidities of the different gels are listed in Table 3. Lichenan and barley β-glucan are the most turbid, oat β-glucan is, like agarose and κ-carrageenan, rather opaque, whereas ι-carrageenan and gelatin are clear like water. Accordingly, the size of the junction zones decreases in this order.

Table 3
Increase of turbidity during gelation of various samples in 6% (w/w), expressed as relative transmission T_{rel} (transmission of the sol divided by transmission of the gel)

Sample code	T_{rel}
LN55	65
BG300	28
OG220	2.6
Agarose	2.1
κ-Carrageenan	1.9
ι-Carrageenan	1.1
Gelatin	1.05

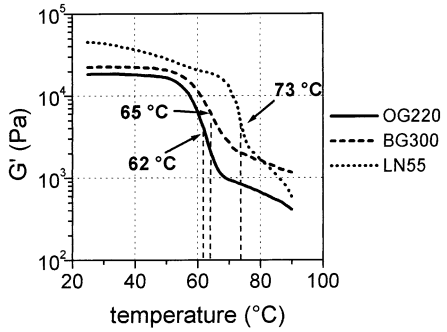

Fig. 7. Gel melting (step in storage modulus G'-curve) of oat β-glucan (OG220), barley β-glucan (BG300) and lichenan (LN55) in 10% (w/w).

(b) Melting temperature. In Fig. 7 the storage moduli G' of the three β-glucans in temperature ramps are compared. A step in the $G'(T)$ graph indicates gel remelting. The gels do not exhibit a melting point but a melting range over 10 °C, which is independent of the heating rate (0.5–5 K min^{-1}). The turning point of the $G'(T)$ graph was chosen as melting temperature. The melting temperatures are independent of the molar mass and decrease in the order lichenan (73 °C), barley β-glucan (65 °C) and oat β-glucan (62 °C) (Table 4). Similar to the melting points of crystallites, which increase with increasing size owing to the free surface energy, a high melting point of structurally similar gels hints at a larger extension of the junction zones [2,27].

(c) Gelation rate. The I_E values for the three β-glucans differ in orders of magnitude, despite very similar M_n. For direct comparison the samples LN55 ($M_n = 30{,}000$ g mol^{-1}), BG50 ($M_n = 30{,}000$ g mol^{-1}) and OG40 ($M_n = 30{,}000$ g mol^{-1}) were chosen. The I_E were > 50, 5.3 and 0.86 h^{-1}, respectively.

Table 4
Melting temperatures of gelatinized samples obtained with rheological temperature sweeps

Sample code	Concentration (% w/w)	Melting temperature (°C)
BG300	10	65
BG165	10	65
BG100	10	65
OG220	10	62
LN55	10	73
Gelatin	10	32
ι-Carrageenan	4	40
κ-Carrageenan	4	72
Agarose	4	78

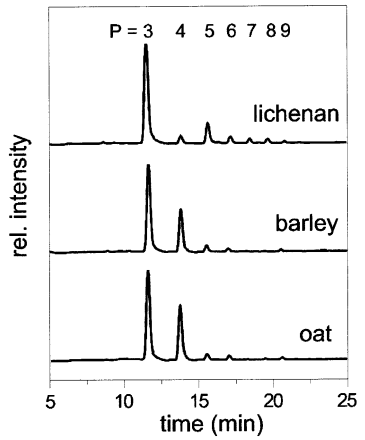

Fig. 8. Elution profiles of oligosaccharides with degrees of polymerization P 3–7 released by lichenase from lichenan, barley β-glucan and oat β-glucan.

Lichenan gelatinized at such a speed that the resolution limit of our method was exceeded.

The reason for the strikingly different behaviour must be based on the structural diversity of the three β-glucans. Analysis of the fine structure of (1→3)(1→4)-β-glucans can be achieved by enzymatic degradation with lichenase (EC 3.2.1.73), which selectively hydrolyses the (1→4) linkages subsequent to a (1→3) linkage [28]. About 5% (w/w) of the oligomers released by lichenase are insoluble because they have a degree of polymerization, $P > 7$ [7,29]. Analysis of these cellulose-like oligomers is described in Ref. [7]. Barley and oat β-glucan have a similar oligomer distribution above P 7 with P 9 as the major component. Lichenan contains only traces of oligomers above P 7. The explanation of the association via cellulose-like sequences is therefore not satisfactory. The distribution of the soluble oligomers (mainly P 3, 4 and 5) is easily accessible via size-exclusion or anion-exchange chromatography. The elution profiles of the examined β-glucans proved to be unique like fingerprints. In Fig. 8 the oligomer distribution of lichenan, barley and oat β-glucan is shown. It is obvious that mainly trimers are released from lichenan and from the cereal glucans tetramers too. This is in general agreement with previous anlyses [5–7,30]. Accordingly, lichenan has the most and oat β-glucan

Table 5
The quantitative ratios of the lichenase-released oligomers with a degree of polymerization $P = 3, 4$ and 5[a]

Sample code	P_3:P_4:P_5	M_n (g mol^{-1})	I_E (h^{-1})
LN55	23:1:2.5	30 000	>50
BG50	2.5:1:0.12	30 000	5.3
OG40	1.9:1:0.08	30 000	0.86

[a] Additionally listed are the number-average molar masses M_n and the related elasticity increments I_E (10% (w/w), 25 °C).

the least regular chain structure. Table 5 summarizes the experimental data. With these findings a new model of the gelation mechanism of (1→3)(1→4)-β-glucans can be drawn. The main structural feature of these glucans is the cellotriose unit, (1→3)-linked to the next cello-oligomer. Assuming that consecutive cellotriose units are responsible for association, lichenan has the best conditions to quickly form extended junction zones, because most of the chain sections fit together. The oat β-glucan structure is less regular so that suitable sections are rare and shorter and hence gelation is much slower. In Fig. 9 the common (a) and our (b) association model are drawn. It was found earlier that the amount of ammonium sulphate necessary for precipitation of barley β-glucans from aqueous solution

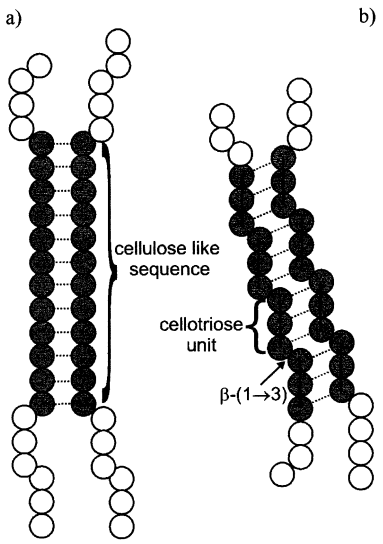

Fig. 9. Chain interactions in (1→3)(1→4)-β-glucan leading to gels. According to the common model, sequences of consecutive (1→4)-linkages stick together (a). The authors propose association of consecutive celltriose units linked by β-(1→3) bonds, which probably forms a helical structure (b).

correlated with the regularity of the chain: the fractions precipitated at low ammonium sulphate concentrations (fairly soluble) contained more cellotriosyl units than the readily soluble fractions [22]. Indeed solubility and gel forming tendency should be contrary.

The fact that lichenan and barley β-glucan gels have large junction zones points at a strong affinity of the regular cellotriose sections to each other. This causes a pronounced phase separation into polymer rich and polymer poor regions, i.e., the mesh width is big and hence the water retention is weak. Indeed the lichenan and barley β-glucan gels reveal syneresis.

Kinetic aspects of (1→3)(1→4)-*β-glucan gel formation.*—The long induction period, the strong increase and the approach to a limit value of the storage modulus (Figs. 1 and 2) are reminiscent of crystallization kinetics according to the Avrami equation (Eq. (3))

$$x = 1 - \exp(-kt^n) \quad (3)$$

where x = fraction of crystallized material, k = constant, n = Avrami exponent. In the latter quantity both the dimension r of the growing crystallites ($r = 1$ for rods, 2 for discs, 3 for spheres) and the kind of nucleation s ($s = 0$ for predetermined and 1 for sporadic nucleation) is reflected ($n = r + s$). Predetermined nucleation means that the nuclei are already present in the polymer melt and develop at once on cooling the polymer to the temperature of crystallization (e.g., in starch solutions [31]); sporadic nucleation means that the nuclei arise in the supercooled melt and the number of nuclei increases linearly with time. For $n > 1$ the graph of Eq. (3) becomes sigmoidal, similar to the $G'(t)$ curves. It must be emphasized that the junction zones of β-glucans are not crystalline in the narrow sense, as it was impossible to detect a melting peak with DSC, indicating a very weak bonding energy which is unusual for crystallites. They are better described as well-ordered domains. But the kinetics of polymer melt crystallization and β-glucan gel formation are comparable.

According to the findings in Ref. [23] there is no indication of association in heat-prepared β-glucan solutions. Hence sporadic nucleation must be considered. The pronounced

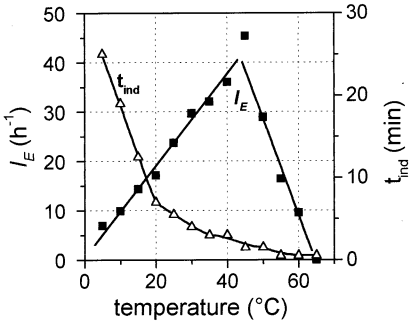

Fig. 10. The elasticity increment I_E and the duration of the induction period t_{ind} for temperatures in the range 5–65 °C for the sample BG50.

turbidity points at junction zones of spatial extension, so that the Avrami exponent n should be 3 or 4. Experimental verification of n cannot be obtained from $G'(t)$ because it is not a quantitative measure of the fraction of well-ordered material.

Another parallel is the temperature dependence of crystallite growth rate from polymer melts compared with that from the elasticity increment I_E of the β-glucan gels. In polymer melts sporadic nucleus formation is zero above the melting point and first increases with supercooling. Further lowering of the temperature diminishes molecular motion and at the glass temperature nucleus formation again is zero [32]. A similar maximum behaviour is observed for β-glucan gelation rate with varying temperature (Fig. 10). A pronounced maximum of the gelation rate occurs at 45 °C, whereas the duration of the induction period decreases steadily with increasing temperature. The melting point of the gel is analogous to the melting point of the polymer and the freezing point of water is analogous to the glass temperature.

The growth rate of spherulites of blends from isotactic and atactic polypropylene decreases with increasing portion of the atactic species acting as impurity [32]. Similarly the shortage of structural elements capable of association (cellotriose units) in oat β-glucan can be regarded as 'impure' polymer in contrast to lichenan which is short of impurities causing a high gelation rate.

It can be summarized that the gelation of (1→3)(1→4)-β-glucans can be described in terms of a sporadic nucleation mechanism similar to crystallization kinetics from polymer melts. In order to gain insight into the molecular structure of the junction zones, further investigations are necessary, possibly employing scattering techniques, for example.

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