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ORIGINAL CONTRIBUTION

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Continuous swelling pressure equilibria of the system κ-carrageenan/water

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Dedicated to Prof. Dr. Ronald Koningsveld on the occasion of his 70th birthday

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Abstract The deformation of κ-carrageenan/water gels in a centrifugal field leading to a continuous equilibrium is described. These gels form three-dimensional physical networks. The concentration gradient and the movement of the meniscus gel/solvent during the change of the concentration in the gel phase is measured with a Schlieren optical system of an analytical ultracentrifuge. The gel is considered to be a binary elastic mixture of crosslinked polymer and solvent and is assumed to remain isotropic during the deformation. The concentration dependence of the swelling pressure in the concentration range between the maximum swollen gel and that at the cell bottom can be obtained in a single equilibrium experiment. For the evaluation of the experiments, the weight fraction of the polymer in the maximum swollen gel has been determined separately by a gravimetric method.

By means of the swelling pressure-concentration curves the thermodynamic properties of the investigated κ-carrageenan/water gels can be calculated. The system can be described semi-empirically with a slightly modified Flory–Huggins equation with an interaction parameter χ_w in the weight fraction scale, which depends linearly on the concentration. The dependence of the static shear modulus G on the polymer concentration follows the scaling theory of De Gennes.

Key words Gel – deformation – ultracentrifugal field – discontinuous/continuous equilibrium – swelling pressure – Flory/Huggins equation

Introduction

During recent years crosslinked systems swollen in water gained more and more industrial importance. Many of them show the characteristics of thermoreversible gelation, others are known as superabsorbers.

The linear polysaccharide κ-carrageenan, which is produced from seaweeds, belongs to this group of gelling polymers if their concentration is above that critical for gel formation. Like other gelling polysaccharides, the polymer molecules of κ-carrageenan consist of sequences which are able to associate and others which are not. The primary structure of κ-carrageenan is an alternating sequence of 1,3-linked-D-galactose-4-sulphate and 1,4-linked-3,6-anhydro-D-galactose. The 3,6-anhydro-D-galactose unit is responsible for the partly helical tertiary structure which enables gelation, probably following a mechanism described by Rees [1]. There are cations necessary for the compensation of the negative charges. The crosslinking of κ-carrageenan is strongly affected by the type of counterions present because the association of the helices to the

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three dimensional network takes place under the participation of these cations. The stability of the network is dependent on the kind of cations [2]. K^+, Cs^+ and Rb^+ are more effective than Li^+, Na^+ or $N(CH_3)_4^+$. This follows the so-called Hofmeister series for cations. In the case here, we have potassium ions.

The properties of κ-carrageenan are utilized in the food industry as well as in manufacturing paint and cosmetics. A potential application for κ-carrageenan may be the substitute of agar-gels in microbiological laboratory cultures.

The links in the system κ-carrageenan/water are of physical nature. They break off on raising the temperature as soon as the melting point of the gel is passed over and reform if the gel is cooled down again.

Further information about the structure of the network can be obtained by investigating the swelling pressure equilibria. The swelling pressure of a gel, which can be considered as an osmotically active pressure in an open system, is related to the density of the crosslinks and other molecular parameters [3–11]. An analytical ultracentrifuge equipped with a multiplace rotor is suited for the measurement of swelling pressure-concentration curves because it is possible to obtain the curves of several samples under the same conditions in only one single equilibrium run. In comparison with other methods it is therefore possible to save much time.

Results of the thermodynamic and statistical theories for a binary gel

In this paper we only consider gels consisting of a time independent crosslinked polymer structure and a swelling agent.

A gel in an external field under isothermal conditions is a continuous system which is determined by the gradient of the potential of this external field. As a consequence of this, a continuous equilibrium with a radial concentration gradient inside the gel is obtained as soon as the ultracentrifugal equilibrium of sedimentation and diffusion is reached. To cause a movement of the phase boundary gel/vapor, which is called gel surface, a minimum value of angular velocity has to be passed. The lowest polymer concentration at the gel surface corresponds to the concentration in the maximum swollen sample. As soon as this concentration is reached at the meniscus gel/vapor, the gel starts to settle [7, 10]. Solvent is excluded and the meniscus gel/solvent begins to move in the direction of the cell bottom until the swelling pressure equilibrium is reached. The swelling pressure equation (1) which describes the dependence of the swelling pressure on the radial distance under isothermal conditions can be obtained under the following assumptions [7, 10]:

a) The gel is a binary mixture.
b) The gel remains isotropic during the deformation.
c) Real equilibria are achieved: the swelling equilibrium at the meniscus gel/solvent and the continuous equilibrium inside the gel phase.
d) The volume of the gel can be calculated from the volumes of the pure components.

$$\Pi_s = \omega^2 \int_{r_m^{g/s}}^{r} \frac{\rho_2}{\tilde{V}_1 \rho_1}(1 - \tilde{V}_2 \rho) r \, dr \, . \tag{1}$$

The quantities in Eq. (1), which was named the generalized Svedberg–Pedersen equation, are: Π_s the swelling pressure, ω the angular velocity, $\tilde{V}_i$ the partial specific volume of component i in the gel, ρ_i the local partial density of component i inside the gel, which is defined by $\rho_i \equiv m_i / V_{\text{total}}$, ρ the density of the gel given by $\rho = \sum_{i=1}^{2} \rho_i$, r the radial distance from the axis of rotation to the position in the gel. The index m is the meniscus and the phase boundary g/s means gel/solvent. The component indices are $i = 1$ for the solvent and $i = 2$ for the polymer.

The partial specific volumes of the components are obtained by density measurements of the gels in dependence on the polymer concentration [11]. During the sedimentation run the local concentration inside the gel can be determined from the Schlieren patterns. If the gels are too turbid it is possible to calculate the concentration gradient by means of the mass balance [8, 9]. The weight fraction of the polymer in the maximum swollen gel, $w_{2,s}$, has to be known for the calculation of the concentration profile by use of the mass conservation and has therefore to be determined separately, for example, by a gravimetric method.

For highly swollen gels, where the mass fraction of the solvent is much higher than the mass fraction of the polymer and so the partial density of the polymer is much lower than that of the solvent, we pave $\rho_2 \ll \rho_1$ and therefore $\tilde{V}_1 \rho_1 \approx 1$, $\tilde{V}_2 \approx \tilde{V}_{02}$ and $\rho \approx \rho_{01}$. By these approximations the Svedberg–Pedersen relation is obtained:

$$\Pi_s = \omega^2 \int_{r_m^{g/s}}^{r} \rho_2 (1 - \tilde{V}_{02} \rho_{01}) r \, dr \, . \tag{2}$$

$\tilde{V}_{02}$ is the specific volume of the pure polymer and ρ_{01} is the density of the pure solvent.

The expression in the round brackets of Eq. (2) is the buoyancy term that may vanish in some systems. In this case a setting of the gel does not take place. By applying Eq. (2) it is possible to calculate the swelling pressure dependent on the polymer concentration profile $\rho_2(r)$.

The swelling pressure Π_s inside an incompressible gel is related to the difference of the chemical potentials of the

solvent $\Delta\mu_1$ by [7]:

$$(\Delta\mu_1)_{T,P} \equiv (\mu_1^g - \mu_{01}^s)_{T,P} = -\Pi_s V_1 , \quad (3)$$

where μ_1^g and μ_{01}^s are the chemical potentials of the solvent in the gel and of the pure solvent. V_1 is the partial molar volume of the solvent inside the gel, which may be approximated by the molar volume of the pure solvent $\bar{V}_{01}$ for highly swollen gels.

For a crosslinked polymer nonelectrolyte/solvent system Flory and others derived expressions describing the difference of the chemical potential of the solvent $(\Delta\mu_1)_{T,P}$ [12–16]. The notation of Flory using the mass fraction of the polymer w_2 instead of the volume fraction ϕ_2 reads:

$$(\Delta\mu_1)_{T,P} = RT[\ln(1 - w_2) + w_2 + \chi_w w_2^2 + C_w w_2^{1/3}] . \quad (4)$$

χ_w is the Flory–Huggins interaction parameter in the mass fraction scale containing all enthalpy contributions and also the deviations from the predicted entropy of mixing network chains and solvent. C_w is a parameter characterizing the network where the volume term has been omitted. w_2 is the weight fraction of the polymer inside the gel, R is the universal gas constant and T is the thermodynamic temperature [17].

We use this simple approach, which is considered to be semi-empirical, only because of the following reasons:

1) κ-carrageenan is in reality a polyelectrolyte, where sulphate groups are part of the network chains with potassium ions as counterions. The degree of dissociation of the ionic groups is not known. From the chemical analysis it is known that the concentration of the potassium ions is roughly the same as the concentration of the sulphate groups. The potassium ions are fixed to the sulphate groups of the network chains. No additional salt has been added. Thus the presence of the ionic groups is described by effective values of χ_w and C_w, respectively.

2) The crosslinking is achieved by the aggregation of the helical groups via the potassium ions. Therefore the real structure of the junction points of the physical network is not known. This leads to an effective network term in the mass fraction scale, which up to this moment cannot be reduced to the refined theoretical approaches [18, 19], where the functionality of the junction points, the memory term and the crosslinking density have been considered separately.

3) If the macromolecules are partly helicated we have to expect that the network chains are of the same structure. The conformational details are not yet known so that in reality we have to look for a copolymer structure where rather stiff helical sequences of the macromolecule are alternating with highly flexible ones leading to an entropic change of the chain during the probable coil-helix transition which is not included into the assumptions of the theories mentioned above. If the coiled sequences are very short an energetic contribution may also be expected during the deformation of the network chains.

If there is a better theory at hand, a new evaluation of the measurements may be carried out. But so far the mean functionality of the physical network is not really known. This had lead us to this semi-empirical description. For this reason and the possible polyelectrolyte influence the quantities χ_w and C_w are only semi-empirical parameters. This semi-empirical approach makes sense because other more detailed theories like the approach of the gel as a polyelectrolyte with short chains [20], the treatment of the zipper model [21] or the particle scaled theory [22] may be proved later on.

It has been tried by several authors to linearize Eq. (4) in order to evaluate χ_w and C_w. But in many cases the result was that C_w came out to be negative, which is of no physical sense. Therefore, we admit that the interaction parameter has to be treated as a concentration dependent quantity [4, 8, 10, 23]. This concerns non-ionic gels also [24]. Higher terms in the concentration dependence of χ_w have no significant influence in the concentration range considered. The non-linear regression of the extended form led to the same network constant C_w as the ansatz in Eq. (5) we used. This means the series development of χ_w reads:

$$\chi_w(w_2) = \chi_{w,0} + \chi_{w,1} w_2 . \quad (5)$$

If the dependence of the swelling pressure on the polymer concentration w_2 is known from the measurements, it is possible to calculate the interaction parameters $\chi_{w,0}$, $\chi_{w,1}$ and the network constant C_w by means of a non-linear numerical iteration, e.g., due to the Gauss–Jordan procedure. The Young modules E may be obtained from the network constant:

$$E = \frac{RTC_w w_2^{1/3}}{V_{01}} . \quad (6)$$

For rubberelastic materials showing a Poisson ratio of about 0.5, the shear modulus G is approximately one-third of the Young modulus E [25]:

$$G \approx E/3 . \quad (7)$$

Furthermore, the number average molar mass of the chain segments between two junctions of the network $\bar{M}_c$ can be calculated under the assumption that the chain ends are attached to the network [8, 10]:

$$\bar{M}_c = \frac{(1 - 2/f) \cdot (w_2^0)^{2/3} \cdot M_1}{C_w} , \quad (8)$$

where f is the functionality of the junction points, w_2^0 the initial mass fraction of the polymer, and M_1 the molar mass of the solvent.

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Experimental

The fine powdered κ-carrageenan, which was investigated, included 11.3% by weight water. The potassium content was determined to be 10% by weight. After weighing the κ-carrageenan powder and the distilled water, 0.15 ml of a methanol solution containing 5% by weight chlorophenol was added per gram of dry substance to avoid bacterial attack. The samples were stored in a refrigerator at about 10 °C for 1 day to swell. Depending on the polymer concentration, it took 1 to 5 days to homogenize the samples at 80 °C while stirring. Higher temperatures led to a decomposition of the polymer. The polymer concentrations of the prepared gels were in the range of 1–5% by weight. The high turbidity of the gels in the upper concentration ranges would not allow the determination of the thermodynamic properties by means of an analytical ultracentrifuge. The lower concentration limit was set by the critical concentration of the polymer for gel formation.

It has been tried to remove the so-called soluble parts from the gels by dialysis in hydrochloric acid with a concentration of 0.01 mol/l. The gels swelled greatly and finally became sols. After the dialysis these sols were freeze-dried, but it was not possible to prepare gels again from the resulting substance. So the soluble parts were left in the gels because it was known from other experiments that the amount of soluble parts was very low, see results and discussion below.

To avoid adhesion of the κ-carrageenan gels to the walls and the windows of the ultracentrifuge cells, the surfaces of these parts were treated with Teflon spray or covered with a thin film of highly viscous silicone oil before mounting the cell. The cells were filled with about 0.4 ml of the hot κ-carrageenan solution. After cooling down to room temperature, the cells were annealed for 4 days at 10 °C in an apparatus developed by Cölfen [4, 26]. The sectors of the centerpieces were turned in such a position that the gravitational field acted in the same direction as the later generated centrifugal field.

Four days before the run was started, the evacuated centrifuge was conditioned at the temperature of 10 °C which was the chosen temperature for the later measurements. After the equilibrium run was started, the Schlieren patterns were drawn once or twice a day, depending on the degree of movement of the meniscus. If the patterns did not change for 2 days the equilibrium was considered to be achieved. Then the rotational speed was elevated by 4000 to 6000 RPM until the meniscus gel/solvent had clearly moved further in the direction of the cell bottom. At that moment the speed was lowered to the former selected value. The reswelling of the gel could now be observed until the equilibrium position of the meniscus gel/solvent was reached again, but this time from the opposite direction. The run could be stopped afterwards.

It is necessary to examine the relationship between the density of the gels and the concentration of the polymer to evaluate the results from the runs. The densities of gelling systems cannot be determined directly by means of an oscillating tube [3, 27]. Therefore pycnometers were used. It was not possible to fill the pycnometers completely with the samples without bubbles because of the high viscosity of the κ-carrageenan solutions even at 80 °C. For that reason the densities were measured by displacement of silicone oil where only the bottom of the measuring vessel was covered by a bubble-free gel [4, 10, 28].

The mass fraction of the polymer in the maximum swollen sample has to be known as a further quantity to calculate the swelling pressure-concentration curves. Small gel pieces of known mass were allowed to swell in a large amount of distilled water. For every initial concentration 12 samples are measured to observe the swelling behavior over a time interval of 12 days. The swollen gel pieces were poured out on a stainless steel sieve. The adhering water was absorbed by tissues placed below the sieve before the pieces were weighted in closed glass vessels.

Results and discussion

Continuous swelling pressure equilibria

After the experiment was started, different stages during swelling and deswelling could be obtained by means of the Schlieren optical system. The menisci and the concentration gradients were drawn after different time intervals.

Figure 1 shows different stages of an experiment with a κ-carrageenan gel with an initial concentration of 2.95% by weight. The rotational speed reached from zero was about 30 000 RPM (revolutions per minute).

First, there is only the gel phase between the bottom of the cell (r_b) and the meniscus gel/vapour ($r_m^{g/v}$) (a). After a short while a concentration gradient can be detected within this phase. As soon as water is excluded because of the sedimentation of the meniscus of the gel two menisci can be observed (b). These are the meniscus solvent/vapor ($r_m^{s/v}$) and the meniscus gel/solvent ($r_m^{g/s}$). The latter moves increasingly more in the direction of the cell bottom until the continuous swelling equilibrium is reached (c). If there is a concentration gradient in the sol, too, it is caused by small amounts of soluble parts which are not incorporated in the network. The meniscus solvent/vapor should keep its position during the run to treat the system of gel and solvent as being incompressible and additive in the volumes of its pure components as it is required in the theory.

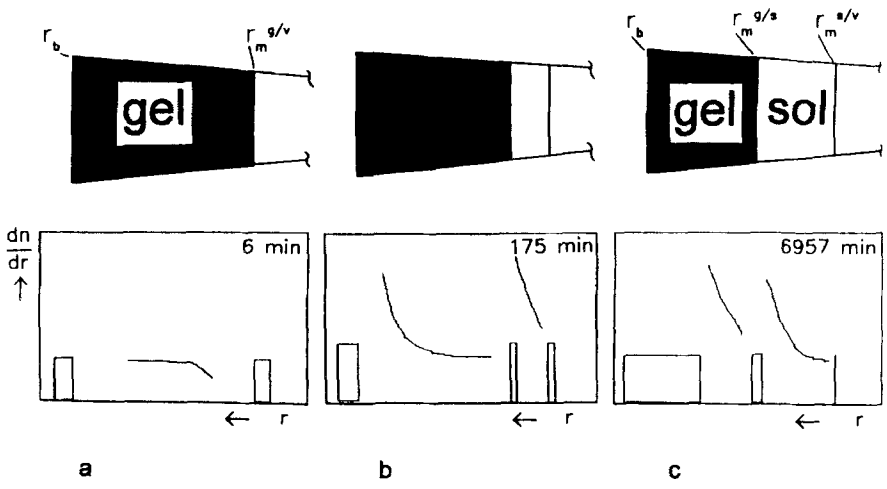

Fig. 1 Different stages of the deswelling of a gel in an analytical ultracentrifuge with the corresponding Schlieren patterns (n = refractive index, r = distance to axis of rotation)

It is not possible to fill all cells with the original solutions to the same height. In order to compare the movements of the meniscus gel/solvent, Holtus defined the relative deformation r^* (3, 6, 9]. Its definition is:

$$r^* = \frac{r_m^{g/s} - r_m^{g/v}}{r_b - r_m^{g/v}} \quad (9)$$

The value of r^* is a normalized variation of the distance and is between 0 and 1 because $r_m^{g/v} < r_m^{g/s} < r_b$. Values between 0.4 and 0.6 were reached at 26000 and 30000 RPM at 10 °C for the κ-carrageenan gels. According to the expectation a higher rotational speed led to a stronger and faster deformation for the same initial gel concentration. The same rotational speed led to stronger and faster deswelling for low concentrated gels compared with higher concentrated gels.

For the evaluation of the swelling pressure measurements by means of an analytical ultracentrifuge it is necessary to show that the results are true swelling pressure equilibria. Therefore it is appropriate to use the principle of pathway independence of the equilibrium values [3, 4, 6, 9]. Leaving all other conditions constant it should be possible to reach the equilibrium position of the meniscus gel/solvent from two different initial positions: On the one hand, by increasing the rotational speed which leads to the deswelling of the possibly maximum swollen gel, on the other hand by decreasing a higher rotational speed to the chosen one, whereby a swelling up to the equilibrium position may be obtained.

The relative deformation of the gel as a function of time for the example of an 1.75% κ-carrageenan gel is shown in Fig. 2. The lower curve is obtained by accelerating the rotor from 0 to 26000 RPM. The upper curve is achieved after taking a higher rotational speed to force an additional movement of the meniscus. At that moment the

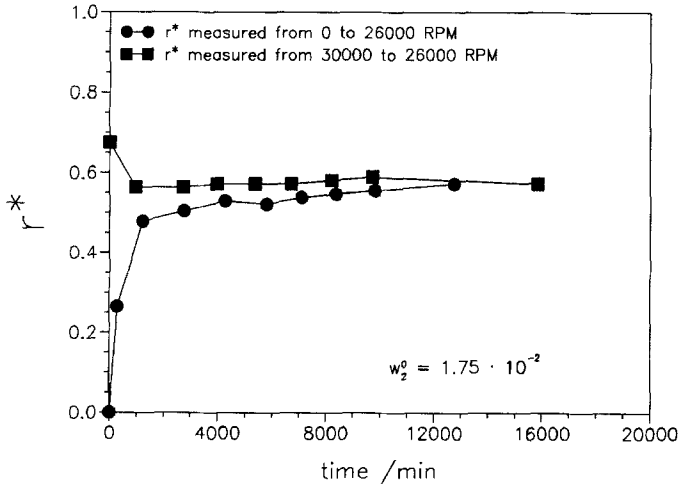

Fig. 2 Relative deformation of the meniscus dependent on time. The upper curve had been measured after an elevated rotational speed was taken for a short time (w_2^0 = initial weight fraction of the polymer)

initial speed of 26000 RPM is chosen again and the gel begins to reswell until the former volume has been reached.

As shown in the example continuous swelling pressure equilibria have been proved in this way for all other κ-carrageenan/water gels with different polymer concentrations [11]. But that is not the case if the equilibria have also been reached at the higher rotational speed in the presence of the soluble parts of the polymer. After decreasing the speed to the initial one again, the reswelling of the gel does not take place in the required extent. The former volume of the gel cannot be obtained again in this case. It has been observed that irreversible deformations occur above a critical value of acceleration. This corresponds to

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a characterization of DeGennes, where the gels are strong at a low centrifugal field and weak at higher fields [29].

An explanation for this non-equilibrium behavior can be given in the action of the soluble parts which have been detected in all samples. If the rotational speed is increased, first the sedimentation of the gel and afterwards that of the soluble parts within the solvent takes place. Within the gel phase the sedimentation of soluble parts is possible if they are able to move freely in the network. Waiting at the elevated rotational speed until the meniscus has reached its final position, the continuous swelling pressure equilibrium is superimposed by the sedimentation-diffusion equilibrium of the soluble parts. The activity of the solvent is changed which may lead to the higher deswelling of the gel at the same swelling pressure in a quasi binary representation (Fig. 7, which will be discussed later on). After lowering the speed to the initial one, the back diffusion of the soluble parts takes place very slowly. The gradients of the polymer in the sol and in the gel phase remain nearly unchanged and correspond mainly to the equilibrium at the higher rotational speed. These gradients influence the swelling pressure as has been shown schematically [30]. Therefore, the gel is not able to regain its initial volume in the time allowed experimentally.

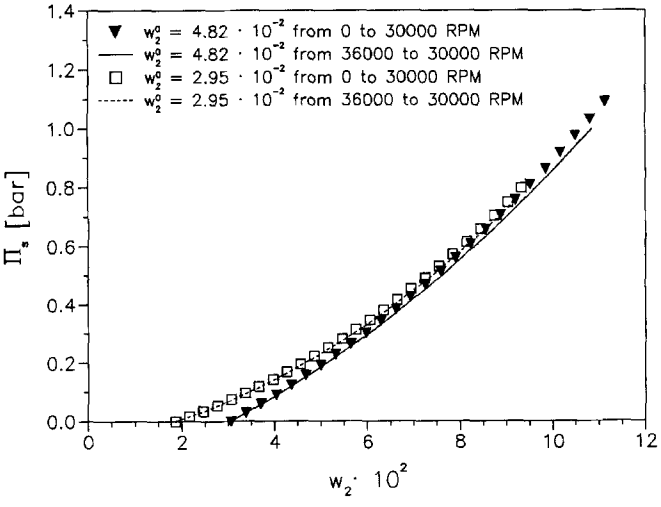
A second reason for the pathway dependence may be that the soluble parts are able to associate reversibly at concentrations which are high enough. As a concentration gradient of the network polymer and the soluble lower molecular part is given – due to the sedimentation of both – we may expect that an equilibrium association is favored at increased values of r. The soluble parts may either react with the free bounding sites of the network or of the associated low molecular material. In both cases this will lead to a trapping of the originally soluble part in regions of higher polymer concentration. If the association can be described like a chemical reaction leading to an equilibrium, the back diffusion is probably a very slow process caused by the superposition of this equilibrium and the sedimentation–diffusion equilibrium of the gel and the soluble parts. As a third possibility, we may envisage that the junction points or zones are of partial crystalline nature. In this case the gel is a multiphase system consisting of amorphous and crystalline phases. We know that the latter have to be of a critical size to be able to grow further. But this growth occurs inside the gel. Every crystal which acts as a junction point or nodule is surrounded by a highly concentrated amorphous phase and not the pure solvent. Therefore, it is not likely that these gels dissolve if the partial crystalline junction zones are stable. The only possibility of dissolution is at the surface in contact with the pure solvent. We expect anisotropic gels with a crosslinking density depending on r if soluble parts are incorporated in the network by this mechanism. This irreversible process is called aggregation.

By waiting at the higher speed only for a short time – about half a day – until the meniscus gel/sol has clearly moved in the direction of the bottom, but not until the new swelling pressure equilibrium corresponding to the higher speed has been obtained, the formation of the sedimentation–diffusion equilibrium is not yet complete. Under these circumstances the soluble parts have no significant influence on the swelling pressure equilibrium. Therefore, the gel is able to reach its initial value after lowering the speed again.

The swelling pressure curves lead to identical results. In Fig. 3 two curves for different polymer concentrations in the gel – once measured from zero, once from higher speeds – are represented. The superimposition of the curves shows the path independence of the equilibrium in the range of accuracy of the measurements. In this experiment the rotational speed was increased only for a short time as described above.

The other possibility is to wait until the meniscus gel/solvent no longer moves at the higher rotational speed, which means that the swelling pressure equilibrium which corresponds to that speed has been obtained. Under these conditions the swelling pressure-concentration curves, measured after lowering the rotational speed to the initial one again, do not cover those which were measured by increasing the speed from zero to the chosen speed. The curve which had been received from the direction of the higher speeds is displaced to higher polymer concentrations. By the sedimentation of the soluble parts the men-

Fig. 3 Evidence for real equilibria by means of swelling pressure curves (Π_s = swelling pressure, w_2 = weight fraction of the polymer, w_2^0 = initial weight fraction of the polymer); (see text)



tioned irreversible increase of the polymer concentration may occur.

The applied forces lead to high deformations of the gels. Therefore the network structure might become unstable and phenomena combined with a regrouping of the junction points could appear. Another possibility for the observed irreversible behavior could be caused by the high strength of the gels. Friction of the network chains may prevent the gel from reswelling to the former extent.

The swelling pressure-concentration curves for a single gel concentration measured at different rotational speeds coincide totally below a critical value of $r\omega^2$. The only difference is that the swelling pressure curve corresponding to the higher speed covers a wider range of concentrations. This is caused by the higher effective centrifugal field which leads to a stronger deswelling of the gel. Therefore the maximum of the swelling pressure at the bottom of the cell is increased. By means of the superimposition of the curves it becomes obvious that the swelling pressure equilibria are real equilibria.

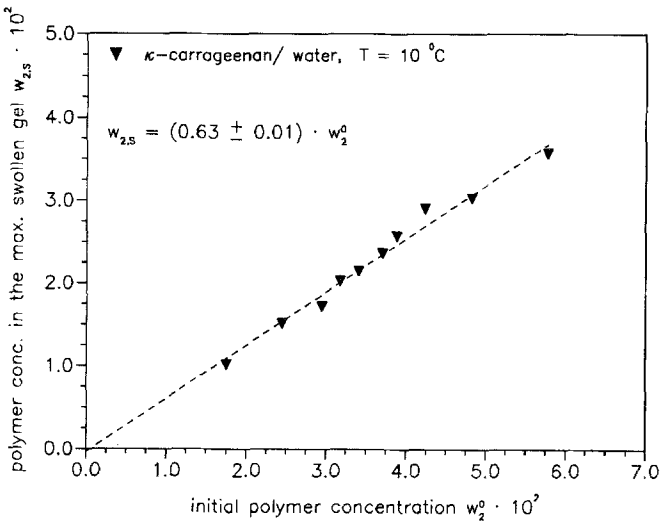


Fig. 4 Dependence of the saturation concentration $w_{2,s}$ on the initial concentration w_2^0 of the gels

Additional measurements

The course of the locally dependent density of the gel $\rho(r)$ has to be known besides other parameters for the evaluation of the ultracentrifugal measurements. The course of the polymer concentration within a transparent gel phase can be determined from the Schlieren patterns. If the relation between concentration and density is known it is possible to calculate $\rho(r)$. Within the investigated range of concentration (1 to 5% by weight) the volume of the mixture composes additively of the volumes of the pure components. The specific volume of the mixture as a function of the weight fraction of the polymer w_2 can be described by: $\tilde{V} = \rho^{-1} = 1.0001 - 0.4662 \cdot w_2$ [11].

The concentration at saturation $w_{2,s}$ within the maximum swollen sample has to be determined to calculate the swelling pressure-concentration curves in the case that there is a movement of the gel meniscus. This concentration is present at the meniscus gel/solvent and indicates the point of intersection of the swelling pressure-concentration curve with the axis of concentration at zero swelling pressure.

By plotting the obtained values of $w_{2,s}$ versus the initial concentrations w_2^0 of the corresponding samples, a straight line through the origin of the coordinate system is obtained as represented in Fig. 4. The value $w_{2,s}$ obtained by free swelling of the sample in water is always lower than the corresponding value w_2^0. This shows that no syneresis occurs.

The mass degree of free swelling Q_m of the gel is defined by [10]:

$$Q_m = \frac{m_1 + m_2}{m_2} = \frac{1}{w_2}, \tag{10}$$

for $w_2 = w_{2,s}$, we have $Q_m = Q_{m,s}$.

From the slope of the line in Fig. 4 we obtain $(w_2^0/w_{2,s}) = 1.575$ in the investigated range of concentration. The concentration $w_{2,s}$ is only dependent on the initial concentration w_2^0 at constant values of temperature and pressure. This dependence will be discussed by the application of the slightly extended semi-empirical Flory/Huggins equation (see Eq. (4)).

The interaction parameter is supposed to be dependent linearly on the concentration (see Eq. (5)). Some calculations have been made assuming a higher concentration dependence. But it turned out that there is no significant influence on the magnitude of the network term. Therefore, it is not necessary to introduce further terms in the series development of χ_w. In the state of swelling equilibrium with $w_2 = w_{2,s}$, Eqs. (3) and (4) read:

$$\Delta\mu_1 = 0$$

This leads to:

$$\ln(1 - w_{2,s}) + w_{2,s} + \chi_{w,0} w_{2,s}^2 + \chi_{w,1} w_{2,s}^3 + C_w w_{2,s}^{1/3} = 0 . \tag{11}$$

Series expansion of the logarithmic term, neglect of the third term of the series and introduction of $Q_{m,s}$ gives a result of Flory derived for the volume degree of swelling [31].

$$\frac{(0.5 - \chi_{w,0})}{C_w} = w_{2,s}^{-5/3} = Q_{m,s}^{5/3} . \quad (12)$$

The parameter C_w in the weight fraction scale is related to other network characterizing parameters in the following way:

$$C_w = A \eta_w \frac{1}{z_{w,eff}} . \quad (13)$$

A is the functionality or structure factor given by $A = 1 - 2/f$, where f is the functionality of the junction points describing the average of the number of chains belonging to a junction point. It has been introduced by Graessly and Staverman in order to consider the fluctuations of the junction points in a phantom network where the chains are allowed to intersect freely during their motions [15, 19]. By introducing w_2 instead of the volume fraction the quantity $z_{w,eff}$ is the ratio of the mean molar mass of the network chains M_c and the molar mass of the solvent M_1 and is inversely proportional to the crosslinking density which is the number of network chains per volume of the solvent free polymer [32].

Although the description of the physically crosslinked polyelectrolyte κ-carrageenan by Eq. (13) is only semi-empirical, some remarks have to be made concerning the so-called memory term η which according to Tobolsky [33] has been introduced by:

$$\eta = \frac{\overline{r_d^2}}{\overline{r_0^2}} , \quad (14)$$

where $\overline{r_d^2}$ is the mean square end-to-end distance of the network chains in the dry network and $\overline{r_0^2}$ the mean square end-to-end distance of the free chains in the reference state prior to crosslinking. It should be mentioned that the dry network is assumed to be in the rubber elastic state, to which this value has be to extrapolated if the polymer is in reality in the glassy state. As the network is built up from a physical aggregation of the network chains in solution – probably in the helicated form [34] – we first have to consider the change of $(\overline{r_0^2})_{coil}$ in the coiled state to $(\overline{r_0^2})_{p.-hel.}$ in the partly helicated state prior to crosslinking, if a solution is cooled from 80 °C to room temperature. This leads to $\overline{r_0^2} = (\overline{r_0^2})_{p.-hel.}$. Afterwards the network is formed by aggregation of the partly helicated sequences. If the volume degree of swelling during crosslinking is given by Q_c, where the corresponding mean square end-to-end distance is given by $\overline{r_c^2}$, we have for an affine deformation of the junction points [18]:

$$\eta = \frac{\overline{r_d^2}}{(\overline{r_0^2})_{p.-hel.}} = \frac{\overline{r_d^2}}{\overline{r_c^2}} \cdot \frac{\overline{r_c^2}}{(\overline{r_0^2})_{p.-hel.}} = \frac{1}{Q_c^{2/3}} \cdot \frac{\overline{r_c^2}}{(\overline{r_0^2})_{p.-hel.}} \quad (15)$$

Changing to the mass degree of swelling, this gives us with Eq. (10) for $w_2 = w_2^0$ and $Q_c = Q_{m,c} = (w_2^0)^{-1}$:

$$\eta_w = (w_2^0)^{2/3} \cdot \frac{\overline{r_c^2}}{(\overline{r_0^2})_{p.-hel.}} \quad (16)$$

The ratio $\overline{r_c^2}/(\overline{r_0^2})_{p.-hel.}$ considers the changes of the end-to-end distance of the partly helicated chains during the crosslinking. If during this process neither chain extensions nor chain contractions will occur, this ratio is assumed to be unity. Furthermore, it can be said that η_w is mainly influenced by w_2^0 where the crosslinking took place. These considerations are only valid for an endlinking of the partly helicated chains. Therefore the real situation will be given by $[\overline{r_c^2}/(\overline{r_0^2})_{p.-hel.}] \leqslant 1$ which gives a further argument for the semi-empirical treatment.

Because of the masked repeating structure of the polymer chain [35], which tells us that the comonomer units are not completely of the same structure, we may deduce that the chain is only partially helicated. This resembles in the easiest case to a free chain with the alternation of a flexible element of length, l_i, and stiff element of length, l_j, stemming from the helices. The calculation of the mean square end-to-end distance – following the deduction of Flory [31] – results in:

$$(\overline{r^2})_{p.-hel.} = \frac{N}{2}(1 + k^2) l_i^2 \quad \text{with } |\vec{l}_j| = k|\vec{l}_i| \quad (17)$$

For $|\vec{l}_j| = |\vec{l}_i|$ or $k = 1$ the well known relation of a freely jointed chain is obtained. If the helical sequences are larger by factor $k = 20$ the mean square end-to-end distance increases strongly to nearly 200-fold of the mean square end-to-end distance before the helix formation. But if the chains contain many of the alternating copolymer units they may be considered as Gaussian chains, because the interlinking of l_i- and l_j-segments can be considered as being highly flexible. As soon as $(\overline{r^2})^{1/2}$ comes close to the contour length of the chain ($k \to N$) we have to consider for this stiff chain the failure of the theory of entropy elasticity.

Insertion of these relations in Eq. (12) leads to:

$$w_{2,s} = \left[\frac{z_{w,eff} \cdot (0.5 - \chi_{w,0})}{A}\right]^{-3/5} \cdot (w_2^0)^{2/5} . \quad (18a)$$

According to Eq. (18a), the proportionality between $w_{2,s}$ and w_2^0, which was found experimentally, can only be explained if the following relation is valid:

$$\frac{z_{w,eff} \cdot (0.5 - \chi_{w,0})}{A} = k_1 \cdot \frac{1}{w_2^0} . \quad (18b)$$

Taking $\chi_{w,0}$ as being constant (which is nearly fulfilled; see

Fig. 8), this leads to:

$$\frac{z_{w,\mathrm{eff}}}{A} = k_2 \cdot \frac{1}{w_2^0}, \tag{18c}$$

where k_1, k_2 are constants [11].

With the definition of $z_{w,\mathrm{eff}}$ (see above) and the validity of Eqs. (18), it follows that the molar mass between two junction points of the network $\bar{M}_c$ is expected to be proportional to $(w_2^0)^{-1}$. Taking the corresponding values from Table 1, it is demonstrated in Fig. 5 that the logarithm of the network constant C_w versus the logarithm of the initial polymer concentration w_2^0 gives a straight line with a slope of 1.92 and a regression coefficient of 0.997, telling us that $C_w \sim (w_2^0)^{1.92}$ holds. This is clearly at variance with the predicted value of 1 following the theory of Flory. Even if the correction term for a non perfect endlinking $(1-2\,M_c/M)$ is introduced [31] this discrepancy is not explained. This will be treated in the last section. The experimentally obtained value for the critical concentration of gel formation at a temperature of 10 °C is about 1% b.wt. of the polymer.

The course of the ratio of mass swelling degrees Q_m and Q_m^0 dependent on time is shown in Fig. 6 by the example of a gel containing 3.41% polymer. The corresponding curves of other polymer concentrations of the gel nearly superimpose with this one. It is astonishing that the saturation value of swelling is already reached after only 1 day. The paths of diffusion, which are given by the dimensions of the gel pieces, are very small (about 0.1 to 0.2 cm). This may be the reason for the short diffusion times. The interaction parameter identifies water as a good solvent for κ-carrageenan. The fast process of swelling is caused by a high diffusion coefficient [36, 37]. In contrast to the gelatine gels, which were investigated by Cölfen [8, 10], the κ-carrageenan gels did not show any tendency of dissolution even in long lasting measurements (up to 4 weeks). This means that the course of the relative swelling degree, which had been introduced before, is parallel to the abscissa after the first day of swelling.

Soluble parts

Within all κ-carrageenan gels soluble parts could be observed in the form of concentration gradients in the solution phase at high rotational speeds. One possible reason for their appearance can be found in the preparation procedure of the κ-carrageenan. The seaweeds are washed under quite alkaline conditions at high temperatures. This may cause a partial decomposition of the chains and probably the formation of low molecular parts. The critical mass degree for gel formation $w_{2,c}$ is inversely proportional to the weight average molar mass of the chains M_w [38]. Because of the low molar masses and the low concentrations of the "decomposed" chains, they cannot be incorporated into the network. If the gel deswells these parts can be found within the solvent phase or – if permeability is possible – also in the gel phase. Another reason for the appearance of the soluble parts is given by the fact that κ-carrageenan consists of various polysaccharides, some of which, ν-, μ-, λ- and ξ-carrageenan, do not possess the capability of gelation. The composition of carrageenan as well as the distribution of the molar masses is strongly dependent on the season of harvest.

For the evaluation of the Schlieren patterns the soluble parts are not taken into account because their concentration is too low. The soluble parts were extracted from the

Fig. 5 Plot of the logarithm of the network term C_w versus the logarithm of the initial weight fraction of the polymer w_2^0 of the system κ-carrageenan/water

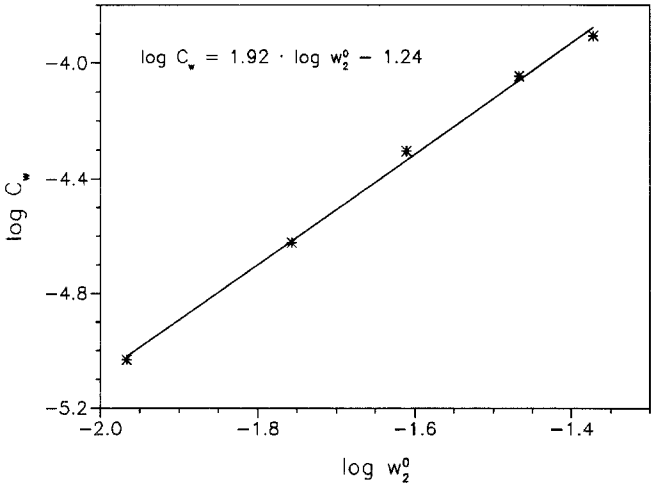
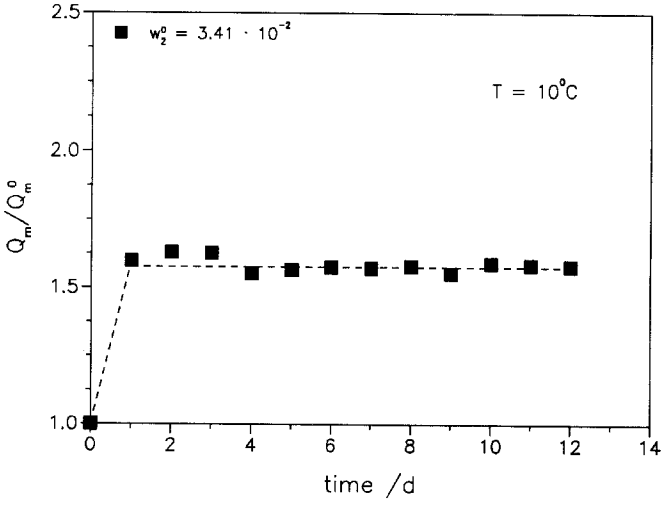


Fig. 6 Course of the relative swelling degree Q_m/Q_m^0 dependent on time



gel by the exertion of pressure on the gel in a special apparatus. For the highest concentration of the polymer in the gel (5%) the amount of soluble parts was 0.028% and for the lowest polymer concentration it was 0.056% b.wt. referring to the mass of the gel. This means that the amount is negligibly low. Attempts have been made to remove these soluble parts by dialysis. After dialysis and freeze-drying the substances were not able to form gels again. Probably this occurs as a result of the exchange of the potassium ions by hydrogen ions during the process of dialysis. But the potassium ions are necessary for the aggregation of the helices to form three-dimensional networks and therefore these very few soluble parts are left within the gels.

Besides the gradients of the soluble parts, double peaks within the solvent phase near the meniscus gel/solvent could be detected in higher concentrated κ-carrageenan-gels. The double peaks become smaller with decreasing polymer concentration. Their appearance is typical of polymer aggregates with an association degree $n \geq 3$ [39, 40]. These polymer clusters are built by secondary valences corresponding to a reversible reaction.

The interaction parameter

The swelling pressure-concentration curves of identical gel concentrations coincide in the whole concentration range for different rotational speeds. The swelling pressure is calculated by integrating over the distance r to the axis of rotation corresponding to Eq. (2). A higher filling level causes a higher swelling pressure at the bottom of the cell. The swelling pressure-concentration curve therefore extends to higher polymer concentrations in comparison with that in the cell with a lower content.

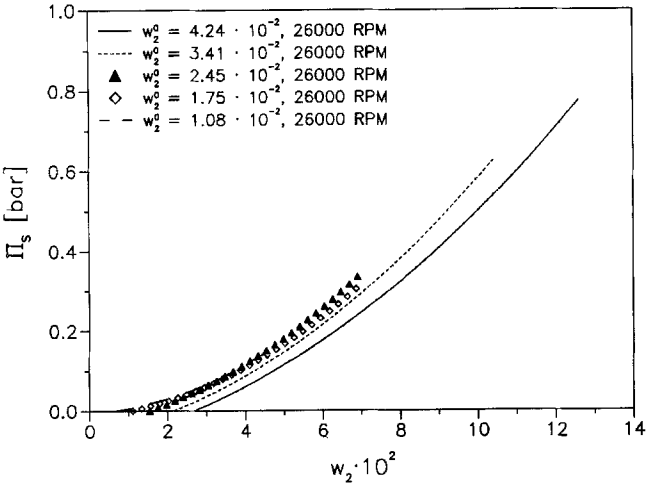
The results of all measurements are well comparable. The method used was extremely sensitive, so that concentration differences of 0.2% by wt. led to different swelling pressure curves. The reproduction of the results is excellent.

By using a multiplace rotor it was possible to investigate several samples simultaneously at identical conditions. In Fig. 7 the course of the swelling pressure curves, measured at 26 000 RPM, for five various concentrations is represented. According to the Flory/Huggins theory for homogeneously swollen networks, we would expect nearly parallel swelling pressure-concentration curves for networks with different crosslinking densities if the χ_w-parameter is assumed to be independent of the concentration [3, 4, 6, 10]. Form Fig. 7 it can be gathered that the swelling pressure curves intersect for gel concentrations below 2.45% b.wt. The swelling pressure-concentration curves which were measured at a rotational speed of 30 000 RPM intersect already below a polymer concentration of 3.88%. This has led to the conclusion that the interaction parameter is a function of the initial polymer concentration. In some polymer/solvent systems it could be shown that the concentration dependence is influenced by the network structure, mainly by the functionality [8, 24].

The network structure is only determined by the initial polymer concentration in the gel at the time of setting. This was already shown experimentally in 1931 by Northrop and Kunitz [41]. The network structure remains unchanged by subsequent drying or swelling. A gel, the concentration of which is changed with respect to the initial polymer concentration by drying or swelling, swells to the same final concentration as a gel of the same original concentration placed directly in water. This leads to the conclusion that C_w and χ_w are determined only by the initial polymer concentration in the gel which is w_2^0. This justifies the concentration dependence of χ_w expressed by Eq. (5) and the equations shown in Fig. 8.

The intersection of the swelling pressure-concentration curves was in the first instance traced back to inhomogenities of the network in the corresponding concentration range [3, 4, 6]. An inhomogeneous network may either consists of short and long chains which are randomly disposed or of chains with the same length which are quite differently distributed in space [17]. These inhomogeneities lead to flatter swelling pressure-concentration curves compared with the homogeneous network because the weaker crosslinked network deswells much easier. But it is evident from our own calculations that it is not correct to describe the system κ-carrageenan/water with an interac-

Fig. 7 Swelling pressure-concentration curves for various initial concentrations w_2^0 of the polymer at 26 000 RPM (Π_s = swelling pressure, w_2 = weight fraction of the polymer)



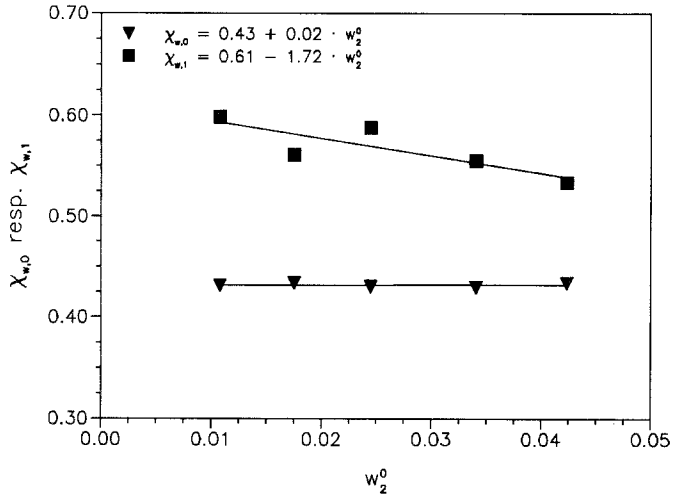


Fig. 8 Dependence of the parameters $\chi_{w,0}$ and $\chi_{w,1}$ on the initial concentration of the polymer within the gel

The values for $\chi_{w,0}$ represented in this figure correspond to an extrapolation of the χ_w- values to the range of infinite dilution. These values have only a formal character for the system gel/solvent and could only be accepted if tensions at the gel surface become effective so that more solvent is taken up by the gel as corresponding to the free swelling equilibrium [10]. Calculating the χ_w-parameters for the maximum swollen gels, the values listed in Table 1 are obtained. They become a little larger with increasing initial polymer concentration.

Table 1 Interaction parameters χ_w for the system κ-carrageenan/water at 10 °C, calculated for the weight fraction of the polymer in the maximum swollen gel $w_{2,s}$ with the $\chi_{w,0}$- and $\chi_{w,1}$-values taken from Fig. 8

$w_2^0 \cdot 10^2$	1.08	1.75	2.45	3.41	4.24
$w_{2,s} \cdot 10^2$	0.69	1.11	1.55	2.16	2.69
$\chi_w(w_{2,s})$	0.435	0.440	0.440	0.442	0.448
$C_w \cdot 10^4$	0.093	0.238	0.496	0.900	1.239

tion parameter independent of the concentration. This would lead to negative network densities if the Gauss–Jordan-iteration is applied for this case. But negative network densities do not make physical sense. The interaction parameter χ_w is on the contrary considered to be dependent on the polymer concentration like it was predicted in newer theories [42]. This might be the reason for the intersection of the curves because the interaction parameter is responsible for the increase of the swelling pressure-concentration curves.

Assuming the course of the partial density of the polymer ρ_2 to be linear within the gel phase, the evaluation of the Schlieren patterns can be realized with Eq. (2) if the relation between concentration and density is known. The interaction parameters $\chi_{w,0}$, $\chi_{w,1}$ and the network constant C_w in Eqs. (4) and (5) can be calculated from the obtained swelling pressure-concentration values by means of a non-linear numerical iteration like, for exmaple, the Gauss–Jordan procedure. In this way the calculation of the network parameters leads to values with physical sense. Therefore it can be assumed that the Flory–Huggins theory with an interaction parameter χ_w depending linearly on the polymer concentration describes the system κ-carrageenan/water correctly at least semi-empirically.

The concentration dependence of $\chi_{w,0}$ and $\chi_{w,1}$ is represented in Fig. 8. Whereas $\chi_{w,0}$ is nearly constant, $\chi_{w,1}$ decreases slightly with increasing polymer concentration. Both curves can be described approximately by regression lines. In this context it has to be recalled that only a small range of concentration was accessible to investigations. The course of the curve for a broader range of concentration cannot be predicted.

Comparable results have been found for the system polystyrene/benzene at 30 °C [43]. The polystyrenes which were investigated were model polymers with linear and star-shaped chemical structures. The structure does not influence the interaction parameter χ_w very much in those polymer/solvent systems at high polymer concentrations. But in the dilute range (up to 10% by vol.) an increase of χ_w can be observed with increasing branching of the polymer. Beyond this concentration limit, which is related to the overlap of polymer coils resp. to a homogeneous distribution of the polymer, the curves converge to a value different from zero. The authors explain this attitude by the fact that benzene – contrary to cyclohexane which was also investigated – is a good solvent for polystyrene. Therefore the expansion of the macromolecule is high which leads to a uniform distribution even at relatively low polymer concentrations. The χ_w-parameters for this system were found in the range of 0.42 to 0.46, far below 0.5, corresponding to the criterion for a not too bad solvent.

An analogous argumentation could be applied to the system κ-carrageenan/water. The determined interaction parameters have the same order of magnitude. Therefore water has to be a good solvent for κ-carrageenan. There is an increase of branching and crosslinking with rising polymer concentration. The interaction parameter grows a little bit in this direction, comparable with the transition linear polystyrene to branched polystyrene in the semi-dilute range of solution. It would be interesting to investigate higher concentrated gels because there also might be a convergence of the χ_w-parameter to a constant value different from zero.

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The network structure

Now it might be asked why the crystallization of the κ-carrageenan-molecules is suppressed. These molecules are copolymers. They are composed of units which are capable to helicate and associate and other units which are not. The latter prevent complete helix formation and crystallization as interrupting units [44]. The resulting partial helication and crystallization is probably the reason for gelation.

The exact manner of how κ-carrageenan-molecules are linked to three-dimensional networks is not yet known. Also, the network functionality f of this sytem is unknown. The values of $\bar{M}_c$ are calculated by means of Eq. (8) (see Table 2) for the lowest integer number which is necessary for the construction of a network, $f = 3$, and the limiting case, $f \to \infty$.

The number of potential junction points increases with increasing polymer concentration. If the concentration of the cations is high enough the network density rises in the same direction by association of the network chains. Roughly a doubling of the polymer concentration and, with it, of the number of precursor chains in the gel, leads to a fourfold increase of the effective crosslinking density.

The molar mass of the primary chains, which are the polymer chains before gelation, is not known. The range of 10^5 to 10^6 g/mol which is often given in literature is very broad and does not allow any further interpretation. With the polymerization degree of 1200 which was estimated by Ebert [45], the calculated molar mass is about 460000 g/mol. The results for $f = 3$ as well as those ones for $f \to \infty$ therefore seem to be physically suitable because all calculated $\bar{M}_c$-values are clearly below this evaluated mean molar mass of the polymer chains. For the validity of these values it has to be assumed that all the chains are integrated in the network with at least two junction points per chain. By means of the Schlieren patterns it is getting obvious that beside the network chains there are soluble parts of very low concentration which are not integrated into the network so that the given values are only useful for a model consideration as has been mentioned.

Table 2 Number average molar masses of the network chains between two junction zones of the network $\bar{M}_c$ for different initial polymer concentrations w_2^0. The molar mass of the primary chain is about 460000 g/mol [45]

$f = 3$					
$w_2^0 \cdot 10^2$	1.08	1.75	2.45	3.41	4.24
$\bar{M}_c$ [g/mol]	31667	16994	10207	7004	5883
$f \to \infty$					
$w_2^0 \cdot 10^2$	1.08	1.75	2.45	3.41	4.24
$\bar{M}_c$ [g/mol]	95000	50983	30620	21012	17649

The shear modulus

In Fig. 9 the dependence of the shear modulus G on the initial polymer concentration w_2^0 is shown in a double logarithmic representation. The obtained results can be described well by a regression line.

The curve of the static shear modulus of the system κ-carrageenan/water could be achieved by means of the ultracentrifugal experiments. For better comparison the results of the experimentally obtained real parts G' of the complex dynamic shear modulus of the system gelatine/water measured at the frequency of 1 Hz in a similar concentration range are also represented. These values are quoted from the literature [46, 47]. Both curves coincide completely concerning the slope and coincide nearly concerning the section through the ordinate. This result seems to be surprising because of the different investigated systems. A theoretical statement for this behavior is given in the scaling approach of De Gennes for gels starting from the so-called c^*-theorem [29]. For a good solvent he determined a law which describes the proportionality of the shear modulus on the polymer concentration in our notation:

$$G \sim T \cdot \rho_2^{2.25} \cdot (v^{3/4} \cdot a^{3/2}) \tag{19}$$

T and ρ_2 have already been introduced, v is an excluded volume parameter, and a a numerical coefficient, dependent on the functionality of the junction points.

It should be mentioned that for small deformations all different relationships for Hookean and neo-Hookean behavior may be linearized, where the difference between

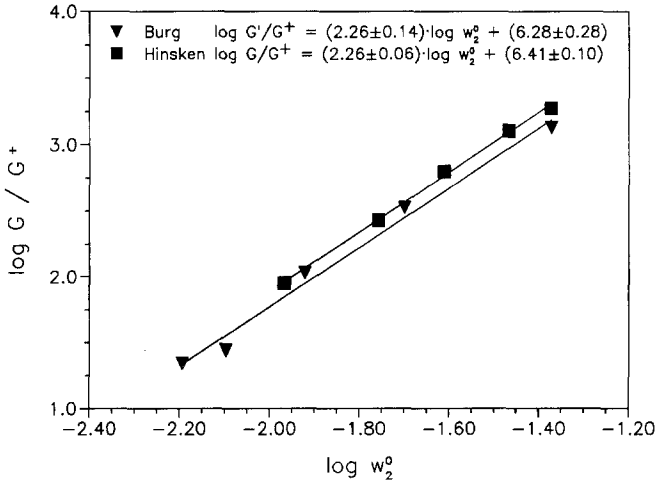

Fig. 9 Static shear modulus G for different initial polymer concentration w_2^0 of the system κ-carrageenan/water resp. real part of the complex dynamic shear modulus G' at a circular frequency of $\omega = 1$ Hz for gelatine/water [46, 47] in double logarithmic representation ($G^+ = [\text{Pa}]$)

Gaussian and neo-Gaussian chains gives only a different proportionality factor in the stress-strain relation.

This law is given for gels near the cross-over concentration c^* between the dilute and semi-dilute range and has been found for a variety of chemically crosslinked systems [48–53]. From our findings, which give an exponent of 2.26, it seems not to be restricted to chemically crosslinked systems but is in a certain sense universal.

This theory shows that the results for the different systems portrayed in Fig. 9 are not really surprising. On the contrary a slope near 2.25 should also be found for other physically gelling systems. Furthermore the influence of the soluble parts during the determination of the shear modulus with the analytical ultracentrifuge seems to be negligible for the investigated system. The values of the shear moduli G follow exactly De Gennes' theory. From these results it can be concluded that the majority of the primary chains became network chains during the process of gelation.

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