Elasticity and swelling behaviour of chemically crosslinked cellulose ethers in aqueous systems*

U. Anbergen and W. Oppermann†
Institute of Physical Chemistry, Technical University Clausthal,
Arnold-Sommerfeld-Strasse 4, 3392 Clausthal-Zellerfeld, FRG
(*Received 22 March 1990; accepted 27 April 1990*)

The mechanical properties and the swelling behaviour of hydrogels based on sodium carboxymethylcellulose and hydroxyethylcellulose were investigated. The gels were prepared by crosslinking the cellulose ethers via divinylsulphone in alkaline solution. The outstanding feature of such materials is their increase of modulus with increasing swelling, which starts already at rather low degrees of swelling (around 10). In this respect, the cellulosic gels are superior to the hydrogels based on acrylic polyelectrolytes currently in use for superabsorbent products. The reason for these properties is seen in the large persistence length of the cellulose backbone, giving rise to non-Gaussian behaviour at much lower chain deformations than with more flexible polymers.

(Keywords: polyelectrolyte gels; superabsorbent polymers; cellulosic materials; swelling; elasticity; non-Gaussian behaviour)

INTRODUCTION

Hydrophilic, slightly crosslinked polymer networks are among the fastest growing products in the chemical industry[1,2]. They are mainly applied as superabsorbents in modern hygiene articles, but potential uses also comprise water storage systems for soil improvement, fluid-retaining materials in food packaging, etc. All these applications are in the consumer products or disposables area.

Presently, the majority of superabsorbents are made from synthetic polymers, essentially acrylics[2]. An investigation on the use of naturally occurring polymers as raw materials for superabsorbents seems appropriate in view of the continuously growing reservation of the public towards fully synthetic products. It is also likely that such products degrade more easily, causing fewer environmental problems that most synthetic substances.

In the present study, the polysaccharides, sodium carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC), were chemically crosslinked. The swelling properties in aqueous salt solutions of different ionic strengths and in pure water were studied, and the elastic properties of the gels were investigated.

Basic requirements for superabsorbents are large fluid uptake and high mechanical strength. These two demands are clearly conflicting, and a suitable compromise needs to be found. A high degree of swelling in aqueous systems is usually achieved by using polyelectrolytes because the mobile counterions present in such gels develop a large swelling pressure[3]. However, the degree of swelling depends considerably on the ionic strength of the fluid to be absorbed. A general theoretical treatment of such systems encounters a lot of difficulties. First, the swelling pressure due to the mobile ions within the gel is difficult to estimate because the ion activity is largely affected by counterion condensation[4,5], the consequences thereof not being quantitatively understood. Secondly, previous investigations have clearly shown that a network theory based on the Gaussian chain-length distribution function is not applicable, particularly at high degrees of swelling and low salt concentrations[6–8]. For a calculation of the free energy of deformation, the finite chain length has to be taken into account. This has significant influence on the swelling properties as well as on the elastic properties of the materials.

Non-Gaussian behaviour of network chains results in an increased modulus of the gels, which is a strongly desirable effect[6]. Polysaccharides exhibit a much higher intrinsic chain stiffness than vinyl polymers like poly(acrylic acid)[9]. Therefore, non-Gaussian effects are expected to appear at fairly low degrees of deformation or swelling, and this could be an essential advantage of such systems. Additionally, polysaccharides are strongly hydrophilic even without containing ionic groups. Thus non-ionic hydrogels may be formed, which exhibit less salt sensitivity than the usually employed ionic systems.

EXPERIMENTAL

Materials

CMC and HEC were received from Fluka Feinchemikalien GmbH. According to the supplier, the CMC has a degree of substitution in the range 0.7–0.85, and was specified as low-viscosity material (90–200 mPa s in 4% aqueous solution). It was employed as the sodium salt. The HEC was of medium viscosity (75–125 mPa s in 2% aqueous solution).

Crosslinking was performed by divinylsulphone in alkaline solution according to the following scheme[10,11]:

---

* Dedicated to Professor Walther Burchard on the occasion of his 60th birthday

† To whom correspondence should be addressed

0032-3861/90/101854-05

$$\begin{gathered}\mathrm{Cell{-}OH} \;+\; \mathrm{CH_2{=}CH{-}SO_2{-}CH{=}CH_2} \;+\; \mathrm{HO{-}Cell}\\ \big\downarrow \mathrm{OH^-}\\ \mathrm{Cell{-}O{-}CH_2{-}CH_2{-}SO_2{-}CH_2{-}CH_2{-}O{-}Cell}\end{gathered}$$

The cellulose ether was dissolved in demineralized water to form a solution of concentration 6–8 wt%. Potassium hydroxide solution (1 M) was added to yield an overall concentration of KOH of 0.02 M. To delay the start of the reaction somewhat, the mixture was cooled to 0°C before divinylsulphone was added. The amount of divinylsulphone employed was varied from 10 to 40 mol m^{-3}. After careful stirring, the solution was filled into cylindrical test tubes, 20 mm in diameter, which were covered with Teflon plugs on both sides, and left at room temperature for 24 h. During this time gelation took place. By measuring the modulus of some of the gels as a function of reaction time, it was assured that the reaction came to completion within this time period. The gels were then taken out of the test tubes and cut to an appropriate length ($\sim$20 mm). Such cylindrically shaped gels were used for the mechanical measurements and for the swelling experiments.

In addition to networks based on either CMC or HEC alone, mixtures of CMC and HEC were used with compositions (by weight) of 25:75, 50:50 and 75:25. A total polymer content of 6 wt% was adjusted in most cases.

Swelling experiments

The samples were immersed in sodium chloride solutions of different concentrations in succession, starting with a high salt concentration of 5 or 10 wt% and going stepwise to less concentrated salt solutions, finally to demineralized water. Equilibration at each concentration was allowed to take place until the weight of the samples had reached a constant value. This took usually several days. Reversibility was checked with a few specimens by bringing them back into a concentrated salt solution after they had attained a much larger degree of swelling in pure water. Typically, the two measurements of the degree of swelling in the concentrated salt solution agreed within 5–10%, which is reasonable in view of the large volume changes occurring (about one order of magnitude).

The degree of swelling was determined simply by weighing the specimens. We define the relative degree of swelling, q_{rel}, as the ratio of the weight of the gel swollen to equilibrium to the weight in the state of network formation. As crosslinking occurred in solution, this already corresponds to a certain degree of swelling, termed q_c, and the total degree of swelling, q_0 (with respect to the dry sample), is given by $q_0 = q_{\mathrm{rel}} q_c$. For simplicity, no density correction was applied.

For some of the modulus measurements, gels of fairly low degree of swelling (below q_c) were prepared by allowing some water to evaporate slowly. Subsequently, the gels were kept in a closed container for several days to restore homogeneity. In these cases the degree of swelling is not an equilibrium quantity.

Mechanical measurements

The shear moduli of the gels were determined by means of a dynamic technique using uniaxial compression of the cylindrical specimens. The sinusoidal vertical movement was achieved by the oscillation of an acoustical diaphragm. The frequency could be adjusted to values between 0.01 and 100 Hz and the amplitude from virtually zero to 0.05 mm. An inductive displacement transducer was employed to register the amplitude and phase of the motion, and the force exerted on the specimen was followed by means of a piezoelectric load cell. Both signals were amplified and then processed by a gain-phase-analyser (Schlumberger type 1253) to obtain the ratio of force and displacement amplitudes as well as the phaseshift between the two signals.

A small static compression (usually around 7–10%) somewhat larger than the amplitude of the dynamic deformation had to be applied to the sample in order to do the measurements. The purpose of this static compression was also to avoid problems due to slightly uneven faces of the cylinders.

The complex shear modulus G^* was calculated according to[6]:

$$G^* = \frac{f^0}{d^0}\,\frac{h}{\pi r^2}\,\frac{1}{1+2\lambda^{-3}}\exp(\mathrm{i}\delta) \qquad (1)$$

Here f^0 denotes the force amplitude, d^0 the displacement amplitude, δ is the phaseshift between force and displacement, h is the height of the undeformed cylinder and r its radius, and λ is the static compression ratio.

The mechanical measurements as well as the swelling experiments were performed at ambient temperature (22°C).

RESULTS AND DISCUSSION

Elastic modulus of the hydrogels in the state of formation

As mentioned in the 'Experimental' section, the complex modulus G^* or its real and imaginary parts (storage modulus G' and loss modulus G'') were measured. The quantity required for an interpretation in terms of network theories, however, is the equilibrium or static modulus, G. To explore under which conditions G' could be equated with G, frequency-dependent measurements were made on some of the gel samples. Typical results are shown in *Figure 1*.

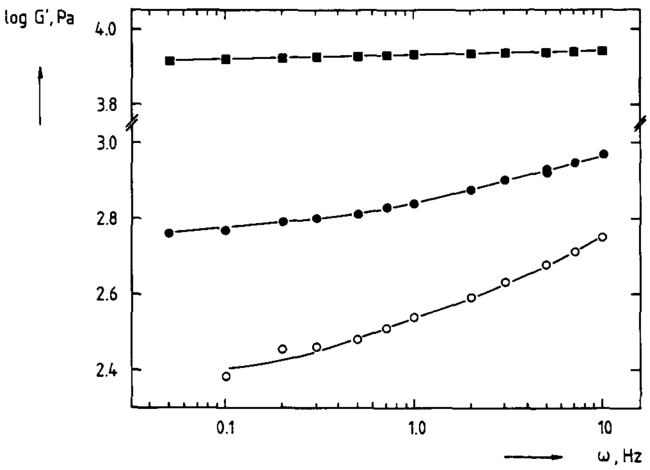

Figure 1 Frequency dependence of the storage modulus of cellulose ether gels, crosslinked and measured at a polymer concentration of 6 wt%: (■) HEC/CMC (50:50), $\nu_c = 77.6$ mol m^{-3}; (●) CMC, $\nu_c = 77.6$ mol m^{-3}; (○) CMC, $\nu_c = 58.2$ mol m^{-3}

If the gels are relatively stiff, i.e. with a storage modulus above 1 kPa, there is no appreciable frequency dependence in the range between 0.1 and 10 Hz. This indicates that in these cases the storage modulus can be used in place of the equilibrium modulus. Further measurements on such gels were usually performed at 5 Hz.

For the weaker gels (mainly pure CMC gels) with moduli in the range 0.3–1 kPa, a perceptible frequency dependence was observed, giving rise to an up to 50% difference between G' (10 Hz) and G' (0.1 Hz) (in extreme cases). Henceforth, the moduli of such gels were measured at 0.1 Hz, because still lower frequencies caused other experimental problems (evaporation of water).

In the following, the moduli measured according to these standards are taken as equilibrium quantities and just termed G, despite the fact that they were obtained by a dynamical method. It is assumed that this procedure does not cause any fundamental errors, but it should be kept in mind that the accuracy of the very small moduli is probably rather poor.

From the amount of divinylsulphone used to prepare the gels, the nominal network density, ν_c, can be calculated. This is a number corresponding to an ideal network where all the crosslinker molecules are incorporated in such a way that they connect elastically effective network chains. Then ν_c would be the molar number of network chains per unit volume. As the crosslinking reaction with divinylsulphone leads to tetrafunctional crosslinks, the nominal network density is just twice the crosslinker concentration employed.

In reality, gels prepared by crosslinking macromolecules in solution often contain a significant amount of network imperfections such as elastically ineffective rings. The number of imperfections is usually higher, the lower the polymer concentration during crosslinking[12]. So it has to be kept in mind that ν_c may not have much physical significance, but it is a useful standard of comparison.

The phantom theory of rubber elasticity predicts the shear modulus G as[13,14]:

$$G=\left(1-\frac{2}{f}\right)\nu RT\frac{\langle r^2\rangle}{\langle r^2\rangle_0} \qquad (2)$$

where f is the functionality of the crosslinks, ν the molar density of network chains, R the gas constant and T the temperature. $\langle r^2\rangle$ is the mean-square end-to-end distance of the chains in the network, and $\langle r^2\rangle_0$ the corresponding quantity for the free, uncrosslinked chains under the same conditions.

Figure 2 shows the shear modulus as a function of nominal network density for gels prepared from HEC, CMC and their mixtures. The broken line has been calculated according to equation (2). The comparison of the experimental results with the theoretical line shows that the crosslinking efficiency is quite different for HEC and CMC. With CMC the modulus achieved in a solution containing 7 wt% polymer amounts only to about 1–2% of the theoretical value, whereas with HEC the efficiency is of the order of 20–40% depending on polymer concentration. The moduli of the HEC/CMC mixtures are between the corresponding data of the pure substances.

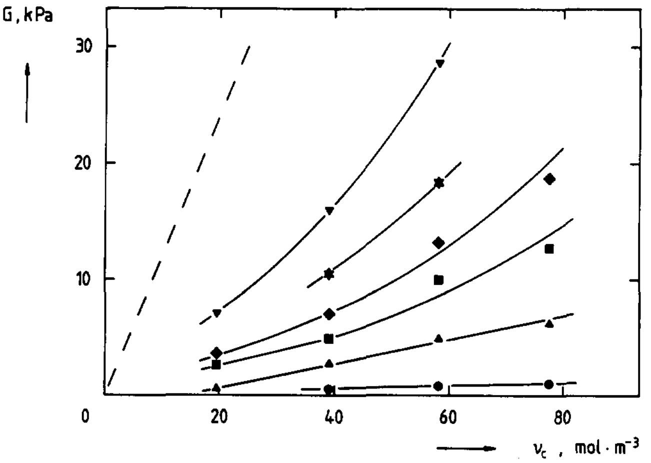

Figure 2 Shear modulus as a function of nominal network density of gels, crosslinked and measured at the concentrations indicated: (▼) HEC, 8 wt%; (★) HEC, 6 wt%; (◆) HEC/CMC, 4.5/1.5 wt%; (■) HEC/CMC, 3/3 wt%; (▲) HEC/CMC, 1.5/4.5 wt%; (●) CMC, 7 wt%. The broken line represents the theoretical modulus of an ideal phantom network

The crosslinker divinylsulphone reacts with the hydroxyl groups on the cellulose ethers. With CMC, the majority of the hydroxyl groups at the C6 position are substituted by carboxymethyl groups[15]. Only a few hydroxyl groups at C6 as well as most of the less reactive hydroxyl groups at C2 and C3 remain available for the crosslinking reaction. This may be one reason for the poor crosslinking efficiency achieved with CMC. The electric charges carried by the CMC chain could possibly be another reason. They impede intermolecular contacts because of electrostatic repulsion. Hence the divinylsulphone could mostly be used to link two hydroxyl groups of the same macromolecule instead of forming effective crosslinks.

HEC, on the other hand, is non-ionic and the electrostatic argument does not apply. Furthermore, during hydroxyalkylation a hydroxyl group on the substituent is introduced for every cellulosic hydroxyl group reacting. Hence the number of hydroxyl groups remains constant. The hydroxyl groups on the substituents may even be more reactive because of less steric hindrance. That is why HEC shows such a good crosslinking efficiency.

The idea to combine the good crosslinking behaviour of HEC with the better swelling properties of CMC (because of its ionic charges, cf. below) has initiated the use of mixtures of HEC and CMC for a preparation of hydrogels.

Swelling behaviour

The dependence of the total degree of swelling, q_0, obtained in 0.9% NaCl solution (0.15 mol l^{-1}, physiological ionic strength) on the nominal network density, ν_c, is shown in *Figure 3*. At constant ν_c the swelling is largest for pure CMC gels and decreases with increasing HEC content of the mixtures. Gels based solely on HEC show only minor swelling. This behaviour is in complete agreement with the elastic properties (cf. *Figure 2*). As expected, the degree of swelling decreases with increasing amount of crosslinker.

To examine the sensitivity of the swelling properties on the salt content of the fluid, *Figure 4* shows a plot of q_0 *versus* the sodium chloride concentration for three gels having the same nominal network density. It can be recognized that the non-ionic HEC gel is practically

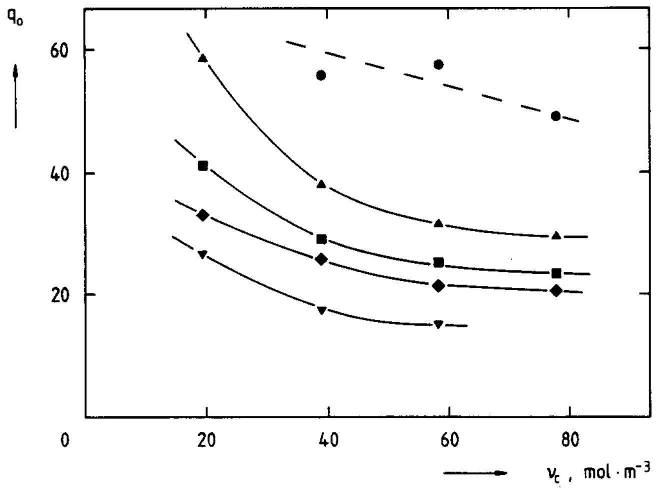

Figure 3 Total degree of swelling, q_0, in 0.9% NaCl solution as a function of nominal network density. The concentrations indicated are those where the gels were crosslinked: (▼) HEC, 8 wt%; (◆) HEC/CMC, 4.5/1.5 wt%; (■) HEC/CMC, 3/3 wt%; (▲) HEC/CMC, 1.5/4.5 wt%; (●) CMC, 7 wt%

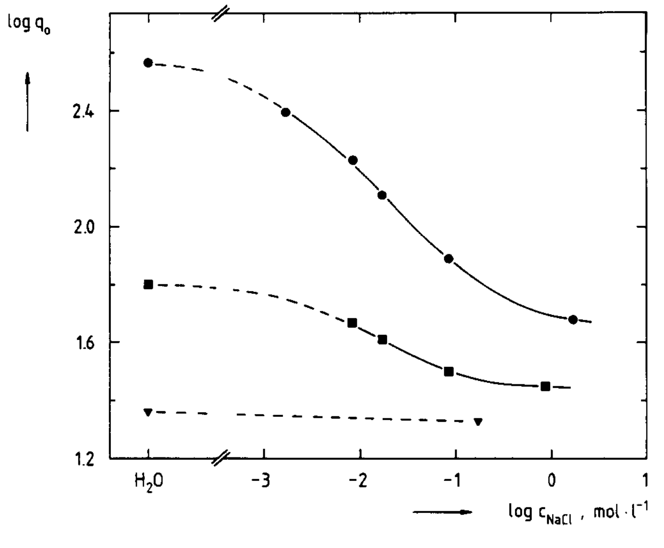

Figure 4 Dependence of the total degree of swelling as a function of NaCl concentration in the solution. The gels were crosslinked at 6 wt% polymer concentration; $\nu_c = 38.8$ mol m^{-3} in each case. Gels: (●) CMC; (■) CMC/HEC (50:50); (▼) HEC

insensitive to salt. The degree of swelling obtained in demineralized water is only insignificantly higher than in a 0.9% NaCl solution. On the other hand, the swelling behaviour of the CMC gel is strongly influenced by salt concentration. This gives rise to a more than fivefold decrease of the degree of swelling when going from water to a salt concentration in the range of 1 M. The properties of the HEC/CMC (50:50) mixed gel are intermediate.

Elastic properties as a function of the degree of swelling

At a first glance it seems to be evident that the modulus of a gel decreases with increasing degree of swelling. This follows also from the statistical theory of rubber elasticity, which predicts a decay in proportion to $q_0^{-1/3}$ (ref. 13). However, this result was obtained on the presumption of Gaussian chain statistics. When the degree of swelling is very large, deviations due to finite chain extensibility can be expected.

Figure 5 shows a plot of log G as a function of log q_0 for the HEC/CMC (50:50) mixed gels, obtained for four different nominal network densities. The broken line indicates the degree of swelling, q_c, where the gels were formed. Swelling in salt solutions of various ionic strengths leads to the data to the right of that line, whereas those to the left were reached by partial dehydration of the specimens. Only at rather high polymer concentration (low q_0) does the modulus decrease with increasing swelling. At some q_0 a minimum is reached, and then the modulus rises progressively with dilution. This rise starts at a lower degree of swelling when the network density is higher, in agreement with the notion that shorter network chains approach their maximum extensibility sooner than longer chains.

Figure 6 shows a corresponding graph. In this case the crosslinker concentration was kept constant and the composition of the mixture of cellulose ethers was varied. The general course of the curves is similar.

It needs to be mentioned that the reversibility with respect to modulus is not as good as with respect to degree of swelling. Thus, when a gel is brought from a 5% salt solution into a much less concentrated solution (or into pure water), where it attains a markedly higher

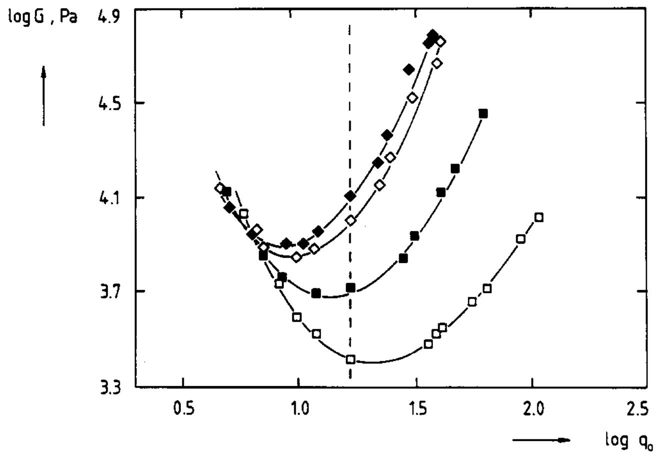

Figure 5 Shear modulus as a function of the total degree of swelling for HEC/CMC (50:50) gels crosslinked at 6 wt% polymer concentration: (◆) $\nu_c = 77.6$ mol m^{-3}; (◇) $\nu_c = 58.2$ mol m^{-3}; (■) $\nu_c = 38.8$ mol m^{-3}; (□) $\nu_c = 19.4$ mol m^{-3}

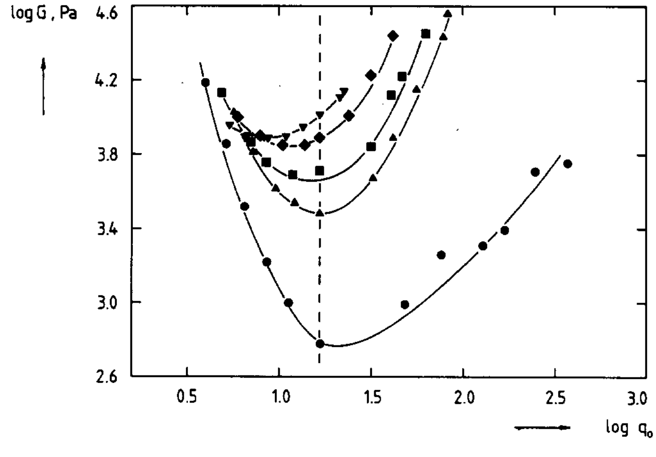

Figure 6 Shear modulus as a function of the total degree of swelling for various HEC/CMC mixtures, crosslinked at 6 wt% polymer concentration; $\nu_c = 38.8$ mol m^{-3}. Gels: (▼) HEC; (◆) HEC/CMC (75:25); (■) HEC/CMC (50:50); (▲) HEC/CMC (25:75); (●) CMC

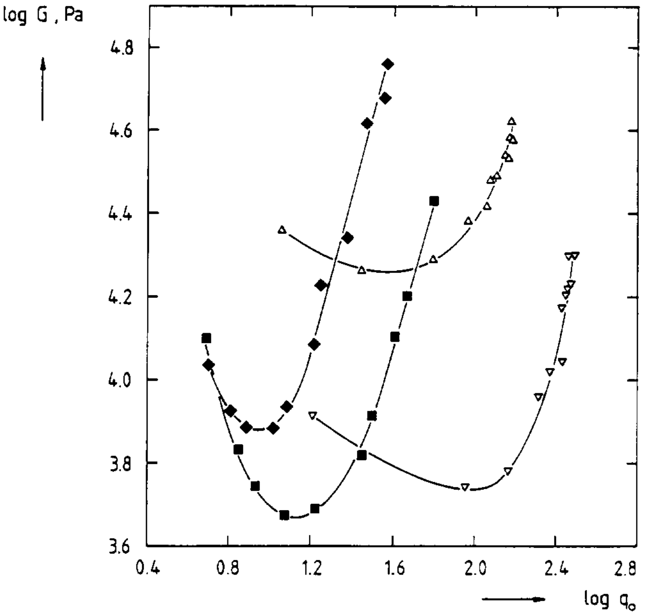

Figure 7 Shear modulus as a function of the total degree of swelling: (◆) HEC/CMC (50:50), formed at 6 wt% polymer, $\nu_c = 77.6$ mol m^{-3}; (■) HEC/CMC (50:50), formed at 6 wt% polymer, $\nu_c = 38.8$ mol m^{-3}; (△) acrylamide–sodium acrylate copolymer gel, formed at 15 wt% polymer concentration via crosslinking copolymerization with methylenebisacrylamide[16]; (▽) acrylamide–sodium acrylate copolymer gel, formed at 15 wt% polymer concentration via crosslinking copolymerization with 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane[16]

degree of swelling, and is afterwards brought back into the 5% salt solution, the degree of swelling agrees within 5% with the previously determined one, whereas the modulus is up to 30% lower. This corresponds to a shift of only 0.2 on the logarithmic scale in *Figures 5* and *6*, and it does not change the basic features substantially. It shows, however, that strong swelling gives rise to some irreversible processes within the network.

The remarkable fact about the increases of modulus with increasing swelling is that this rise begins at fairly low degrees of swelling, typically lower than q_c. The reason for this behaviour is seen in the high intrinsic chain stiffness (large persistence length) of the cellulose backbone[9]. In this connection it is illustrative to compare the behaviour shown by gels made from cellulose ethers with that of gels based on acrylic polyelectrolytes. In *Figure 7*, such a comparison is attempted. Two of the curves of *Figure 5* are reproduced, and two curves (log G *versus* log q_0) obtained with partially hydrolysed polyacrylamide gels selected to cover the same modulus range as the cellulosic gels are shown[6,16]. The latter also exhibit the upturn of the modulus at high degrees of swelling, but it occurs at a roughly tenfold q_0. This means that, with gels based on cellulose ethers, non-Gaussian behaviour occurs at much lower chain deformations.

CONCLUSIONS

Hydrogels based on hydrophilic cellulose ethers can be obtained by crosslinking HEC or CMC with divinylsulphone. The crosslinking reaction is much more efficient with HEC. On the other hand, the ionic CMC gels show larger swelling, particularly in solutions of low ionic strength. Mixtures of CMC and HEC can be used to form gels that retain to some extent the advantages of both materials.

In the swollen state, the mechanical behaviour of the gels is largely influenced by non-Gaussian effects. With the cellulosic gels, these become noticeable at considerably lower degrees of swelling than with gels made from acrylic polyelectrolytes. The enhancement of the modulus due to non-Gaussian behaviour of the chains is a highly desirable effect, when such gels are considered a potential material for superabsorbents.

ACKNOWLEDGEMENT

This study is supported by the Bundesministerium für Forschung und Technologie under Grant No. 0319156A.

REFERENCES

1 Phillips, P. *Nonwovens World* 1988, March, 53
2 Editorial, *Chemiefasern/Textilindustrie* 1988, **38/89**, 74
3 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, Ch. XIII
4 Manning, G. S. *J. Chem. Phys.* 1969, **51**, 924
5 Oosawa, F. 'Polyelectrolytes', Marcel Dekker, New York, 1971
6 Oppermann, W., Rose, S. and Rehage, G. *Br. Polym. J.* 1985, **17**, 175
7 Hasa, J., Ilavský, M. and Dušek, K. *J. Polym. Sci.-Phys.* 1975, **13**, 253
8 Koňák, C. and Bansil, R. *Polymer* 1989, **30**, 677
9 Nissan, A. H., Hunger, G. K. and Sternstein, S. S. 'Encyclopedia of Polymer Science and Technology', (Ed. H. F. Mark), Interscience, New York, 1965, Vol. 3, p. 190
10 Young, R. A. *Textile Sci. Technol.* 1985, **7**, 217
11 Holst, A. *Angew. Makromol. Chem.* 1979, **76/77**, 177
12 Oppermann, W. *Angew. Makromol. Chem.* 1984, **123/124**, 229
13 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Oxford University Press, Oxford, 1975
14 Flory, P. J. *J. Chem. Phys.* 1977, **66**, 5720
15 Balser, K. 'Polysaccharide', (Ed. W. Burchard), Springer, Berlin, 1985, p. 84
16 Rose, S. PhD Thesis, Technical University Clausthal, 1986