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Reinforced Superabsorbent Polyacrylamide Hydrogels

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Summary: The ability of linear stiff-chain poly(sodium p-phenylenesulfonate) to self-assemble in aqueous media with the formation of rodlike aggregates was used to immobilize it in a polyacrylamide network without covalent bonding. It was shown that polyelectrolyte rods impart simultaneously two useful properties to the gel: higher ability to absorb water and higher mechanical strength. The counterions of charged rods ensure the enhancement of the absorption capacity of the gel, while stiff elements strengthen the gel. This makes such systems potentially promising as superabsorbent materials.

Keywords: polyacrylamide gel; polyaromatics; self-assembly; superabsorbent gels; swelling

Introduction

Superabsorbent polymer gels that are capable of absorbing and holding large amounts of water have found various commercial applications, e.g. in the production of personal care products like diapers, in medicine, in agriculture, in civil engineering etc.[1]

For all these applications, the gel should possess not only high absorption ability, but also it should be rather strong in the swollen state in order to hold effectively the absorbed liquid. There is always a problem of how to reinforce the swollen gel, because most of the methods of reinforcing gels lead to significant loss of their absorption capacity.

Here we describe one of the possible ways of improving mechanical properties of swollen gels without loss of swelling ability. Our approach consists in strengthening the gel by filling it with stiff-chain linear polyelectrolyte. It is suggested that stiff chains of filler will strengthen the swollen gel, while charged groups of filler will ensure good swelling ability.

Absorption Ability and Mechanical Strength

As linear stiff-chain polyelectrolytes, which serve to strengthen the swollen gel, we used poly(sodium p-phenylene sulfonate) samples PPP2 (degree of polymerization $P_n = 23.5$) and

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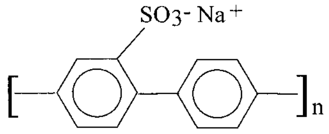
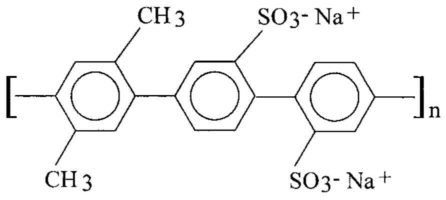
PPP3 (degree of polymerization $P_n = 105$). The details of their preparation and characterization are presented elsewhere.[2,3]



PPP2



PPP3

These polymers contain a hydrophobic stiff poly(p-phenylene) backbone and hydrophilic charged sulfogroups, which are responsible for the solubility of the polymers in water. Due to hydrophobic character of the backbone these polymers self-associate in aqueous media forming rodlike aggregates, in which single polymer chains are arranged parallel to each other.[4] The self-aggregation in water is a characteristic feature of these polymers. It was studied by different techniques: SAXS,[4] light-scattering[5] etc. Here this property is used to immobilize these polymers in the gel matrix.

To incorporate stiff-chain polyelectrolyte in a polyacrylamide (PAAm) gel, a free-radical copolymerization of acrylamide with the cross-linking agent N,N'-methylenebis(acrylamide) was performed in aqueous solution of the polyelectrolyte.[6] The details of the gel preparation are described elsewhere.[6] As a result of the formation of the three-dimensional PAAm network the linear polyelectrolyte becomes physically trapped by the gel.

We prepared a series of PAAm gels with PPP3 filler differing in the concentration of monomer (acrylamide) at the gel preparation, in the cross-linking density and in the content of filler molecules (Table 1). For the comparison we prepared in analogous conditions the reference PAAm gels without filler (Table 1).

The two main properties of these gels were studied: the ability to absorb water and the mechanical strength in the swollen state. From Figure 1 it is seen that the gels with PPP3 filler possess much higher elastic moduli than the corresponding reference gels without filler. At the same time, the introduction of polyelectrolyte chains into the uncharged gel improves the ability of the gel to absorb water (Table 1). The reason for that is rather obvious. When we introduce charged polymer chains into the uncharged gel, we introduce not only the chains themselves, but also their counterions. As soon as the charged chains are in the gel, their counterions cannot escape outside the gel because of the condition of macroscopic electroneutrality. But to gain in the translational entropy the counterions try to occupy as much volume as possible and as a result they exert an osmotic pressure leading to the gel swelling.

Table 1. Conditions of preparation and swelling characteristics of PAAm gels.

Sample	Concentration of acrylamide	Molar ratio N,N'-methylene (bisacrylamide) : acrylamide	Concentration of stiff-chain polyelectrolyte PPP3	The equilibrium degree of swelling in water m/m_0[a]
	g/l	mol/mol	g/l	g/g
PAAm1*	47	1:300	9.0	130
PAAm2*	47	1:200	9.0	99
PAAm3*	47	1:100	9.0	64
PAAm4*	90	1:200	9.0	31
PAAm5*	90	1:200	20.0	56
PAAm1	47	1:300	0	56
PAAm2	47	1:200	0	48
PAAm3	47	1:100	0	38
PAAm4	90	1:200	0	23

[a] the ratio of mass of swollen and dry gels

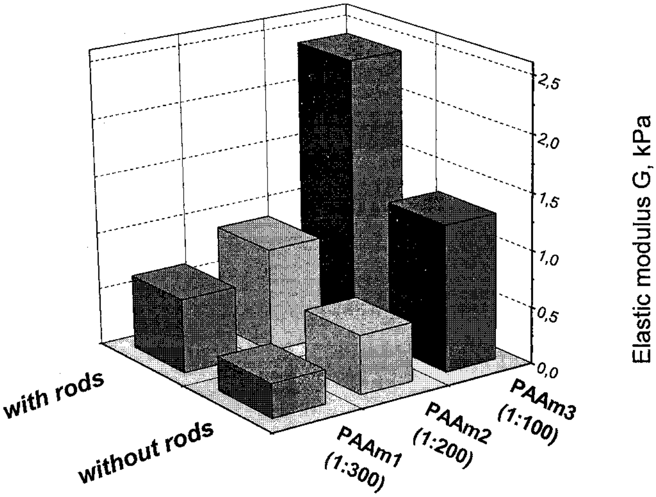


Fig. 1. Elastic moduli of PAAm gels with and without PPP3 rods at different cross-linking densities of the gels.

Therefore, stiff-chain polyelectrolyte imparts simultaneously two useful properties to the gel: higher ability to absorb water and higher mechanical strength. The counterions of polyelectrolyte are responsible for the enhancement of the absorption capacity of the gel, while the stiffness of polyelectrolyte gives rise to the increase of the modulus of elasticity. This makes such systems potentially promising as superabsorbent materials.

Immobilization

Having in mind the application of gels with physically entrapped filler, it is necessary to find out the conditions at which filler is held tightly in the gel.

The release of stiff-chain polyelectrolyte PPP3 from the gels was studied at different conditions. For this purpose we put a piece of gel just after synthesis in an excess of solvent and we determined the concentration of stiff-chain polyelectrolyte PPP3 in the solvent surrounding the gel sample until it reached a constant value. The results are presented in Table 2. It is seen that the most part of stiff linear macromolecules remains in the gel matrix. At the same time, the concentration of these macromolecules inside the gel is higher than outside by 1 to 2 orders of magnitude. Thus, filler molecules are effectively retained by the gel, although they are not covalently attached to the network chains.

Table 2. Release of stiff-chain polyelectrolyte PPP3 from PAAm gels into water.

Sample	Fraction of stiff-chain macromolecules PPP3 released into water from the gel	Ratio of concentrations of stiff-chain macromolecules PPP3 in the gel and in the solution [a)]
PAAm1*	0.34	34
PAAm2*	0.31	50
PAAm3*	0.28	90
PAAm4*	0.13	660
PAAm5*	0.24	150

[a)] the initial volume ratio between the solution and the gel was equal to 137.6

One could suggest that if we increase the degree of cross-linking of the gel, the filler should be more tightly held by the gel. In Table 2 the first three samples differ only in the degree of cross-linking. It is seen that indeed the fraction of filler molecules released by the gel decreases with increasing degree of cross-linking. But the effect is very small. Much more pronounced is the effect of concentration of acrylamide at the gel synthesis. If we compare the samples PAAm2* and PAAm4*, we see that a 2-fold increase of the concentration of acrylamide at the gel synthesis significantly reduces the fraction of the released filler molecules from 0.31 to 0.13 (Tables 1 and 2). So, the release of linear polyelectrolyte decreases with increasing degree of cross-linking of the network and with increasing concentration of monomer (acrylamide) at the gel preparation, but the effect of concentration of monomer is much more pronounced. These data may indicate some interactions between the gel chains and polyelectrolyte rods.

Figure 2 illustrates the influence of the addition of NaCl on the release of linear polyelectrolyte. It is seen that the low molecular weight salt almost completely suppresses the release of linear polyelectrolyte from the gel. Therefore, it is easy to find the conditions at which polyelectrolyte filler is tightly held by the gel.

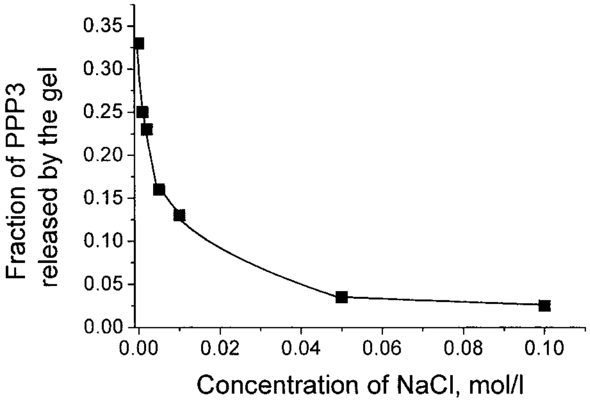


Fig. 2. Fraction of stiff-chain linear polyelectrolyte PPP3 released by PAAm gel (sample PAAm2*) as a function of the concentration of low molecular weight salt NaCl.

A question arises: why linear polyelectrolyte, which is not linked to the network, is effectively retained by the gel and why it affects the elasticity modulus of the gel? Obviously, this is due to the interaction between linear polyelectrolyte and network chains. As we cannot expect some strong specific interactions between them like H-bonds or electrostatic attraction, we suggest the following mechanism of interactions. Linear polyelectrolyte molecules self-aggregate inside the gel like they do in water solution. As the length of the linear polyelectrolyte is 10-fold higher than the mesh size of the gel, the polyelectrolyte molecules approaching each other jam some of the network chains. As a result linear polyelectrolyte becomes effectively immobilized inside the gel without covalent bonding.

When the gel with embedded linear polyelectrolyte is immersed not in pure water, but in a water/methanol mixture, where the aggregates are partially destroyed,[5] most of the linear macromolecules are released from the gel. This experiment unambiguously demonstrates that indeed the self-aggregation of linear polyelectrolyte can be a factor responsible for the effective immobilization of linear polyelectrolyte in the gel.

Self-Aggregation

Self-aggregation of stiff-chain polyelectrolyte in water and in water-swollen PAAm gels was studied by SANS technique. The measurements were performed for PPP2 polyelectrolyte. The details of the experiments are described elsewhere.[7]

In most of the SANS measurements heavy water was used as a solvent. The SANS spectra of aqueous solutions of PPP2 are presented in Figures 3 and 4. It is seen that at low concentrations of polymer no structure peak is observed (Figure 3). At these conditions the form-factor of the scattering objects was determined. It was shown that the scattering particles can be regarded as cylinders (rods) with the radius of gyration of the cross-section equal to 15 Å independently of the polymer concentration.

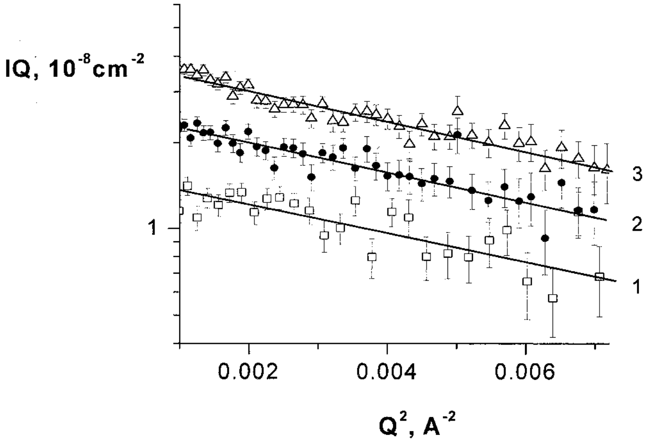


Fig. 3. SANS intensities I plotted as IQ versus the square of scattering vector Q^2 for solutions of PPP2 in D_2O at low polymer concentrations: 1- 0.4 wt.%, 2 - 0.6 wt.% and 3 -1.0 wt.%.

It is important to note that this radius is higher than the radius of a single molecule. Also, the estimation of the length of the rods shows that it far exceeds the average contour length of the individual polymer chain. Probably, in the aggregate single macromolecules are arranged parallel to each other and shifted with respect to each other so that the total length of aggregate is longer than the length of single chain.

At higher polymer concentrations a scattering peak appears (Figure 4). This peak can be regarded as a measure of the most probable distance d_b between the aggregates: $d_b = 2\pi/Q^*$, where Q* is the value of scattering vector corresponding to the scattering peak. The mean interaggregate distances d_b decrease with polymer concentration C_p according to a power law $C_p^{-0.5}$. This is an indication of the two-dimensional structure formed by rod-like aggregates in the plane normal to the axis of the aggregates.

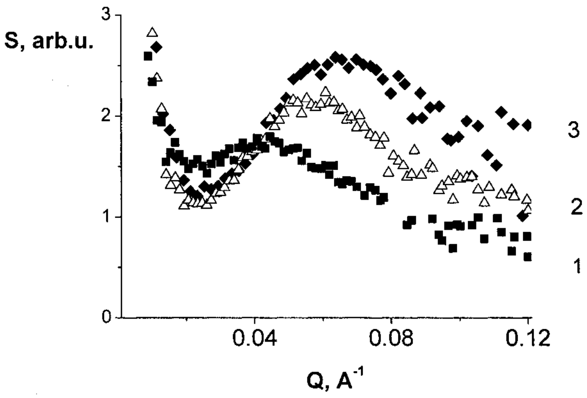


Fig. 4. Structure factor as a function of scattering vector for solutions of PPP2 in D_2O at different polymer concentrations: 1- 2 wt.%, 2 - 3 wt.% and 3 - 4 wt.%.

From the mean interaggregate distance and the concentration of single polymer chains it is possible to estimate the average aggregation number, i.e. an average number of single chains in the cross-section of the rod-like aggregate.[7] It equals to 9 independently of polymer concentration. Therefore, when we increase the concentration of polymer, the number of aggregates increases, but the size of each aggregate remains constant. This behavior of stiff-chain polyelectrolyte recalls the behavior of low molecular weight surfactants, in which the size of micelles remains constant in a rather wide range of surfactant concentrations.

Now let us consider the linear polyelectrolyte PPP2 embedded in the gel matrix. A significant difference in the scattering densities of the gel and of the linear macromolecules allowed us to apply a contrast variation technique in order to examine the scattering from the linear polymer at the conditions, when the solvent matches the scattering of the gel. It was shown that the SANS spectra of linear polymer PPP2 inside the gel are quite similar to those of the polymer PPP2 in heavy water solution. The data treatment performed in the same way as described above for the solutions shows that the aggregates are rodlike and each aggregate consists of 8 single polymer chains in the cross-section. So, the aggregation number of PPP2 inside the gel is almost the same as in the solution. Therefore, it was shown that the stiff-chain polyelectrolyte self-aggregates inside the gel and this self-aggregation is almost unaffected by the gel matrix.

The effect of low molecular weight salt (NaCl) on the scattering of the stiff-chain polyelectrolyte PPP2 was studied. It was shown that when salt is added, the effective radius of aggregates becomes 2 times higher and also the length of aggregates increases. So, salt promotes the aggregation of similarly charged polymer chains, probably due to the screening of electrostatic repulsion. Enhancement of self-assembly of stiff macromolecules in salt medium explains the fact that salt suppresses the release of these macromolecules from the gel.

Conclusion

Swollen hydrogels can be strengthened in a rather simple and efficient way – through incorporation of a small fraction of charged linear stiff chains as reinforcing agents. Although the stiff chains are not covalently attached to the network, they are effectively retained inside the gel and they contribute to the elastic modulus of the gel. It was suggested that this is due to the formation of self-aggregates of stiff polyelectrolytes, which include some network subchains.

Acknowledgements

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