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Structure of polyelectrolyte hydrogels studied by SANS

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The structure of hydrogels based on sodium polyacrylate and crosslinked by different low- and high-molecular-weight compounds is studied by small-angle neutron scattering (SANS). It is shown that the size of heterogeneities in the vicinity of crosslinking junctions does not depend on the molecular weight of the polyfunctional crosslinking agents used. The dependence of heterogeneity dimensions on the gel concentration (or degree of swelling) was measured. It showed a maximum which was interpreted by analogy to the concentration behaviour of specific viscosity of polyelectrolyte solutions. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Recently, the interest in studies of crosslinked hydrophilic polymers has increased significantly due to their wide range of applications in ecology, biotechnology, medicine, etc.[1,2]. These polymers are networks which swell in water up to several hundred times[1–3]. Studies of hydrogel swelling behaviour form the basis for understanding a number of important problems concerning the swelling mechanism of polyelectrolyte hydrogels[4,5] and of polyelectrolyte macromolecules in aqueous solutions. Thus it is very important to know substantial details of the hydrogel structure and to predict its changes during gel swelling.

Owing to the crosslinking process, the polymer chain distribution in the network tends to increase the local polymer concentration in the vicinity of junctions compared with the mean polymer concentration in the gel. The size and topology of the corresponding heterogeneities depend, in general, on the chemistry of the crosslinking process[6]. To our knowledge, to date there have been no studies comparing the structure of polyelectrolyte networks crosslinked by different compounds, including macromolecular and polyfunctional ones. Hydrogels crosslinked by macromolecular agents show good deformational and durability characteristics[3,7]. They can keep their shape when swollen in water up to 5000 times. The goal of this work is to compare the scattering properties of such hydrogels and to study the changes in the network junctions during gel swelling.

Different scattering techniques may be used for investigations of hydrogel structure[8]. Among them of special value is small-angle neutron scattering (SANS), which is a convenient tool for investigations of heterogeneities with dimensions from tens up to thousands of Å[8–10]. Also, SANS gives the possibility to make more general conclusions about fractal characteristics of the hydrogel structure.

We used SANS for studies of scattering parameters of hydrogels crosslinked by allylhydroxyethylcellulose (AHEC), allyldextran (AD) and *N*,*N*′-methylenebisacrylamide (MBA) at different degrees of gel swelling. The scattering curves were analysed using the approximation of additive contributions of scattering by the homogeneous network matrix (solution-like scattering) and the embedded heterogeneities of higher density which are connected with crosslinking junctions (solid-like scattering)[9].

MATERIALS AND METHODS

Polyelectrolyte hydrogels based on sodium polyacrylate and crosslinked by AHEC ($M = 1.4 \times 10^5$, degree of substitution of allyl groups $d = 0.19$, concentration in the reacting solution $c' = 3.8\%$ by mass) and allyldextran ($M = 5 \times 10^5$ (AD1) and 1.5×10^4 (AD2), $d = 0.5$, $c' = 1\%$) were synthesized using methods described elsewhere[3,7]. The equilibrium degree of swelling in water for all the samples is 1300 g/g. Gels of different degrees of swelling (or concentration) were prepared by direct mixing of the proper amount of the powdered dry gel and heavy water. We used D_2O as a reference. To compare the scattering by gels crosslinked with high-molecular-weight and low-molecular-weight agents, we used polyacrylate hydrogels with the 'standard' crosslinker; i.e. MBA. This gel was kindly provided by Atochem, France and has an equilibrium degree of swelling in water of 400 g/g.

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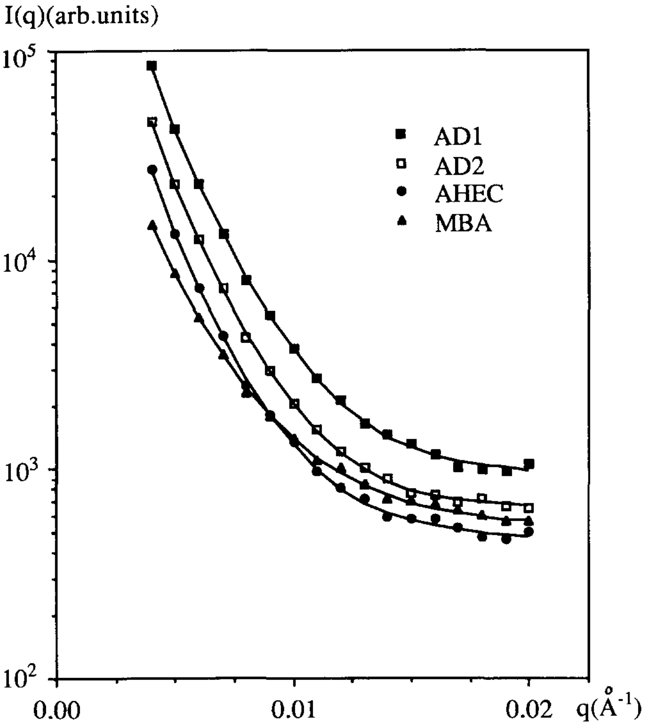

Figure 1 SANS curves for 5% hydrogels crosslinked by different compounds. The solid lines correspond to simulated dependences [according to equation (1)]

Table 1 Fit parameters for calculated curves in *Figure 1*

Crosslinking agent (gel concentration 5%)	I_G (0) (arb. units)	R_G (±50 Å)
AD1	1.04×10^7	900
AD2	5.94×10^6	910
AHEC	3.64×10^6	920
MBA	4.15×10^5	600

The SANS measurements were performed on the diffractometer 'Membrane-2' in St.-Petersburg Nuclear Physics Institute, Russia. The average wavelength of the incident beam was $\lambda = 3$ Å and the spectral half-width was $\Delta\lambda / <\lambda> = 0.35$. The spectral and collimation distortions of the diffractometer were taken into account for simulation curves while data processing. The contribution of incoherent scattering due to hydrogen was also corrected by assuming additivity of the incoherent scattering between gel and D_2O. As the intensity of the incident beam varied from experiment to experiment, to compare the obtained data correctly we reduced all the initial intensities to that in the first experiment (and, as a consequence, recalculated all data). All values of intensities are given in arbitrary units.

RESULTS AND DISCUSSION

To analyse the scattering pattern we used the following function proposed by Geissler and co-workers[9] for gels:

$$I(q) = I_G(0)\exp(-q^2R_G^2/3) + I_L(0)/(1+q^2\xi^2) \qquad (1)$$

where $I_L(0)$ and $I_G(0)$ are linear coefficients of the Lorentzian and Gaussian terms; ξ is the correlation length of polymer–polymer interactions which take place between the fluctuating chains of the gel network; R_G is the average radius of gyration of heterogeneities in the gel; and $q = (4\pi/\lambda)\sin(\theta/2)$ is a scattering vector, θ being a scattering angle.

The data processing showed that each term in equation (1) contributes to different parts of a scattering curve. Information about the excess scattering due to the presence of crosslinks may be extracted from the region of low q values ($q < 0.02$ Å^{-1}) and variation of the parameter ξ in the second term does not influence (within experimental error) the values of R_G. As only the radius of gyration is under consideration, the scattering curve will be analysed only for low values of q.

Scattering by gels crosslinked by different compounds

In *Figure 1* the dependences of intensity on scattering vector are given for the four above-described hydrogel samples at a gel concentration of 5.0 wt%. The curves calculated according to equation (1) are presented as solid lines. The fit parameters are given in *Table 1*.

Using equation (1) the sizes of heterogeneities R_G were calculated for each sample. It turned out that for gels with different macromolecular crosslinkers they are almost equal: $R_G = 900 \pm 50$ Å. For the gel crosslinked by MBA the value of R_G is lower, i.e. 600 ± 50 Å. For the gel crosslinked by AHEC the same values of R_G were obtained separately from light scattering experiments[11].

The obtained results, i.e. the difference between the values of R_G for low- and high-molecular-weight crosslinking agents, is predictable. Indeed, the functionality of MBA is 4, for AHEC it is 200, for AD1 3000 and for AD2 100. However, the large sizes of heterogeneities for all crosslinking agents used mean that the obtained values of R_G characterize not the dimension of the crosslinking junctions themselves, but the dense areas around them corresponding to polyacrylate chains. Thus, for hydrogels crosslinked by macromolecular polyfunctional compounds, the values of R_G do not depend on the molecular weight of the crosslinking agent used.

Information about the fractal dimensionality of the crosslinking junctions (which must be different owing to the different chemical structure of MBA, AHEC and allyldextran) can be obtained at lower scattering vectors ($q < 0.004$ Å^{-1}) and for gels swollen up to equilibrium state ($C = 0.07\%$). Unfortunately, the intensity of the initial beam in our set-up was not sufficient for this purpose, but we shall keep in mind this interesting problem for future studies.

Scattering by hydrogels crosslinked by allyldextrans of different molecular weight at different degrees of swelling

In *Figure 2* the dependence of scattering intensity on q is presented for the polyacrylate hydrogel crosslinked by the high-molecular-weight allyldextran (AD1, $M = 5 \times 10^5$) for different gel concentrations C (or degrees of swelling) (curves 1, 2, 3, 4 and 5 for $C = 0.1$, 0.2, 0.5, 1.5 and 5.0%, respectively). The fit parameters are presented in *Table 2*.

The mean size of heterogeneities R_G was calculated for each degree of swelling using the same procedure as described above. The dependence of R_G on C is given in *Figure 3*, curve 1. When the gel is swollen up to a rather low degree of swelling, less than 50–60 g/g (concentrations are greater than 1.5%), the change of the amount

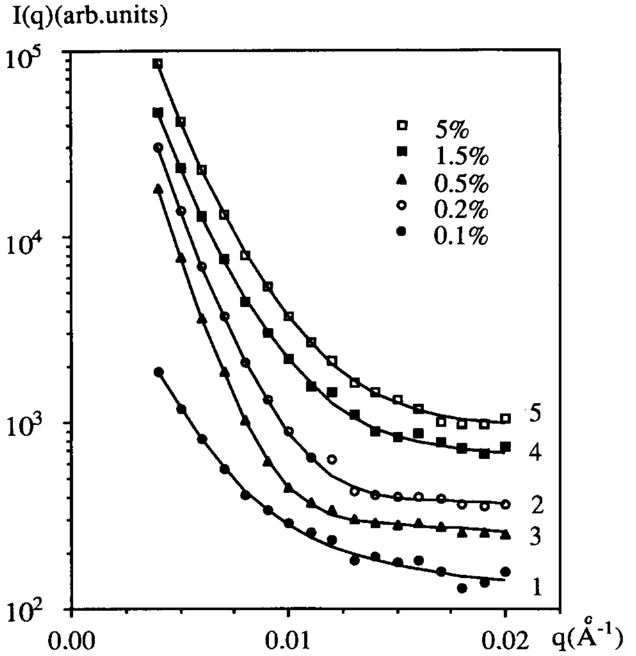

Figure 2 Scattering curves for the hydrogel crosslinked by allyldextran ($M = 5 \times 10^5$) for different gel concentrations (degrees of swelling)

Table 2 Fit parameters for calculated curves in *Figure 2*

Hydrogel concentration (%)	$I_G(0)$ (arb. units)	R_G (±50 Å)
5.0	1.04×10^7	900
1.5	6.15×10^6	910
0.5	1.48×10^7	1410
0.2	1.25×10^7	1200
0.1	3.30×10^4	500

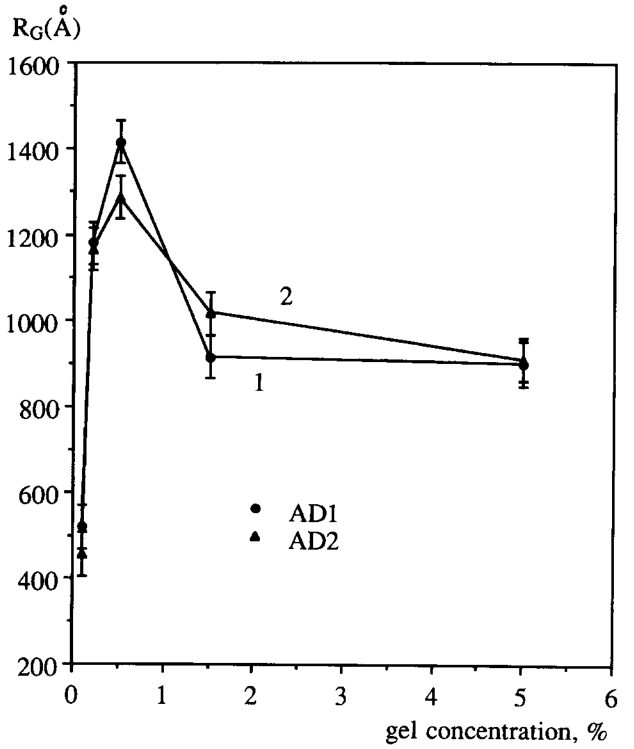

Figure 3 Concentration dependence of radius of gyration R_G for the hydrogels crosslinked by allyldextran of high (1) and low (2) molecular weight

of solvent does not have much influence on the size of heterogeneities (see the plateau on the curve R_G (C) in *Figure 3*). With further increase of the degree of swelling (dilution) the size of the more dense area around the crosslinking junctions increases and then decreases, going through the maximum at $C \cong 0.5\%$. An analogous dependence was obtained for the hydrogel crosslinked by the low-molecular-weight allyldextran AD2 ($M = 1.5 \times 10^5$) (see *Figure 3*, curve 2). The maximum position is at the same polymer concentration.

The appropriate interpretation of this phenomenon is as follows. When $C > 1.5\%$ the polyacrylate network behaves as a non-charged, say a non-hydrolysed polyacrylamide, gel. In this region of concentration the network swelling occurs as a result of the 'ordinary' swelling of chains between the junctions only. With further dilution ($0.2\% < C < 1.5\%$) electrostatic interactions start to play a more pronounced role due to the increase of polyacrylate dissociation. The osmotic pressure of the counterions increases, and the charged chains in the vicinity of junctions start to swell (Donnan mechanism of polyelectrolyte swelling[12]). Thus the size of heterogeneous areas around the crosslinking junctions increases. The polyelectrolyte chains still continue to swell and, owing to the electrostatic interactions, they tend to move aside from each other and thus from the junctions. Therefore further dilution ($C < 0.2\%$) leads to a decrease in the dimensions of the dense heterogeneous regions.

The above-described phenomenon seems to be similar to the rheological behaviour of linear polyelectrolyte chains in aqueous solution. Differing from the behaviour of non-charged linear polymers, the dependence of η_{sp}/C on C (where η_{sp} is the specific viscosity and is proportional to the effective volume occupied by a macromolecule) for a polyelectrolyte solution has a maximum at very low polymer concentration[13].

CONCLUSIONS

1. Comparison of the neutron scattering patterns for polyelectrolyte hydrogels crosslinked by different compounds shows that there is little difference in the size of heterogeneities in the vicinity of the junctions for the high-molecular-weight polyfunctional crosslinking agents used (no dependence on their chemical nature and molecular weight).
2. The dependence of heterogeneity dimensions on the degree of gel swelling shows that there is a maximum on the curve R_G (C). The concentration at which the size of this heterogeneity is maximum does not depend on the molecular weight of the crosslinking agent. The total behaviour is similar to that for linear polyelectrolytes in aqueous solution.

A very strong fractal transition, rare, if even observed among network fractals, was observed on simple swelling. Although one must be extremely careful when making generalizations, this result may represent a starting point for reconsideration of interrelationships between phase transitions, fractal transitions and other transitions including relaxational ones, or even deformation and fracture at stress. Being very tempting, this hypothesis certainly, needs more theoretical considerations and precise experimental studies.

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