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Swelling-induced structure changes of polyelectrolyte gels

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Abstract

The structural changes of hydrophilic polymer networks were studied by SANS. The size of heterogeneities in the network was measured for gels swollen in different amount of water. The type of cross-linking agent, degree of cross-linking and degree of ionisation were varied. The dependence of the size of heterogeneities on the degree of swelling shows a great difference for gels which exhibit strong polyelectrolyte properties (can swell hundreds of times) comparing with the ones which can swell less than 100 g/g. The interpretation of the observed phenomenon is based on the appearance of strong electrostatic interactions which are dominating in the gel-swelling mechanism at high degree of swelling. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polyelectrolyte gels—charged hydrophilic polymer networks swollen in water—are soft and gentle stimuli-responsive materials (so-called ‘intelligent’ polymers). Their structure and properties can be controlled by various physical or chemical inputs, such as changes in temperature, electric field, pH, solvents, etc. This allows to use hydrogels in a wide range of applications: medicine (drug delivery systems and medical devices, such as wound dressing, adhesion prevention formulations, synthetic articulate cartilage, etc.), biotechnology (controlled release or immobilisation of biomolecules), ecology (new sensitive materials for using in gaseous analytes for environmental control) [1, 2].

In order to understand and predict hydrogel swelling behaviour it is instructive to study its structure during swelling and to understand the mechanisms governing this process. There are several unsolved issues concerning the structure–properties relationship of polymer networks [3–9]. This concerns, in particular, strongly charged gels and their structure at high degrees of swelling (up to 500–1000 g/g), where the swelling mechanism is still under discussion (Donnan approach, Katchalsky’s interpretation) [4, 5]. As well as a difference in the behaviour of macromolecules (especially polyelectrolytes) in concentrated or diluted solutions [10], there is a difference in physicochemical properties of gels swollen up to low (maximum swelling up to 50 g/g) or high (strongly charged networks) degrees. The increase of the radius of gyration with the decrease of a linear polyelectrolyte concentration and a polyion reaching a very extended state was reported in Ref. [11]. Thus the information about hydrogel structure changes during swelling at low polymer concentrations will help in understanding elastic properties of strongly charged gels and also their interaction with water (which is not fully clear yet [3]).

The small-angle neutron scattering (SANS) is a convenient tool allowing to determine the structural characteristics of different polymer systems (including networks) in the scale of dimensions of heterogeneities from tens up to thousands of Ångstroms [12]. The changes in polymer spatial distribution induced by cross-linking lead to the increase of local polymer concentration in the vicinity of the network junctions which exceeds the mean polymer concentration in the gel. Thus the static (solid-like or frozen-in) heterogeneities appear among local concentration fluctuations of the network which have a liquid nature. The scattering measurements of such systems yield general information on the spatial distribution of concentration fluctuations. The exact solution for a scattering function of highly swelling gels has not been proposed yet and different authors discuss their approaches to analyse SANS and SAXS data [13].

In the present work we continue the SANS studies of the structure of highly swelling polyelectrolyte networks cross-linked by allyl ethers of polysaccharides. A maximum on the dependence of the size of static heterogeneities on

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Table 1
Characteristics of hydrogels

Cross-linking agent	Degree of cross-linking (wt%)	Maximal degree of swelling (g/g)	Degree of ionisation, α (mol%)
AHEC, $M = 10^5$	0.7	500	50
AHEC, $M = 10^5$	0.7	150	10
AHEC, $M = 10^5$	0.7	16	0
AD1, $M = 1.5 \times 10^4$	1.0	1400	100
AD2, $M = 5 \times 10^5$	1.0	1200	100
AD3, $M = 5 \times 10^5$	25	50	100
MBA	0.1	540	75
MBA, gel swollen in 1 M NaC	0.1	32	75

hydrogel degree of swelling at high dilution was reported [14]. Here we discuss the conditions when this maximum appears depending on gel concentration and its ability to absorb water: degree of ionisation, degree of cross-linking and chemical nature of the cross-linking agent.

2. Materials and methods

The samples were hydrogels based on polyacrylamide with different degrees of ionisation cross-linked by macromolecular compounds—allyldextran (AD) and allylhydroxyethylcellulose (AHEC). The detailed description of samples synthesis can be found in Refs. [15, 16]. In order to demonstrate that the results obtained do not depend on the molecular weight of a cross-linking agent and also on the synthesis procedure we used gels based on poly(0.75acrylate–0.25acrylic acid) cross-linked by N,N'-methylenebisacrylamide (MBA), kindly provided by Atochem, a French company. The characteristics of the samples are given in Table 1.

The gels of different swelling degrees were prepared by direct mixing of dry gel particles and heavy water. The degree of equilibrium swelling Q was calculated simply as $Q = W_s/W_d$, where W_d and W_s are the weights of the dry polymer and of the swollen gel, respectively.

The SANS measurements have been carried out at the small-angle neutron diffractometer 'Membrana-2' in St. Petersburg Nuclear Physics Institute, Russia [17]. The average wavelength of the incident beams was $\lambda = 3$ Å, the spectral half-width was $\Delta\lambda/\lambda = 0.35$. The experimental scattering curves were compared with simulated ones corrected for the spectra and collimation distortions of the diffractometer, detector efficiency, sample transmission and incoherent background scattering. The experimental intensities were converted to absolute differential scattering cross-sections per unit sample volume (in reciprocal centimetres) using water calibration data [18].

3. Results and discussion

In cross-linked gels the presence of random mechanical constraints generates spatial concentration fluctuations [19] in addition to thermodynamic temporal fluctuations which are present in polymer solutions and induce large scale concentration inhomogeneities. The scattering patters from gels were analysed from the point of view of additive contributions from a homogeneous, liquid-like (dynamic) fluctuating gel matrix, and embedded heterogeneities having a high cross-linking density (assemblies of monomer-rich domains).

Debye and Bueche have shown that if the scattering amplitude is squared prior to integration then the scattering equation for an isotropic substance may be written as the spatial Fourier transform of the correlation function $\gamma(r)$ [20]:

$$I(q) = 4\pi \int_0^\infty \gamma(r)\,\frac{\sin(qr)}{qr}\,r^2\,\mathrm{d}r \tag{1}$$

where $q = (4\pi \sin\theta)/\lambda$ is a scattering vector, 2θ being a scattering angle.

To analyse the scattering intensity in hydrogels we used the correlation function proposed by Mallam et al. [21]:

$$\gamma(r) = \langle\rho\rangle^2\,\frac{\xi}{r}\,\exp\left(-\frac{r}{\xi}\right) + \langle\Delta\rho^2\rangle\,\exp\left(-\frac{r^2}{2\Xi^2}\right) \tag{2}$$

where Ξ is the characteristic mean size of the static (frozen) heterogeneity in the gels; ξ is the correlation length of polymer–polymer interactions, which takes place between the fluctuating chains of the gel network, $\langle\Delta\rho^2\rangle$ represents the mean square amplitude of the neutron scattering density fluctuations, $\langle\rho\rangle$ is the ensemble averaged value of the local polymer scattering length density, $\langle\Delta\rho^2\rangle/\langle\rho\rangle^2$ is the fraction of polymer engaged in static fluctuations. The local value of the concentration (or neutron scattering length density) is assumed to vary slowly and randomly in space with a Gaussian probability of mean characteristic length $\Xi > \xi$.

The Fourier transform of Eq. (2) gives the following expression for the scattering function:

$$I(q) = I_G(0)\exp(-q^2\Xi^2/2) + I_L(0)/(1 + q^2\xi^2), \tag{3}$$

where $I_L(0) = \langle\rho\rangle^2\xi^3\sqrt{2/\pi}$ and $I_G(0) = \langle\Delta\rho^2\rangle\Xi^3$ are linear coefficients of the Lorentzian and Guassian terms, respectively. Thus, the model of the scattering system contains four independent variables, $I_G(0)$, $I_L(0)$, Ξ and ξ, which have been obtained from the best agreement between the

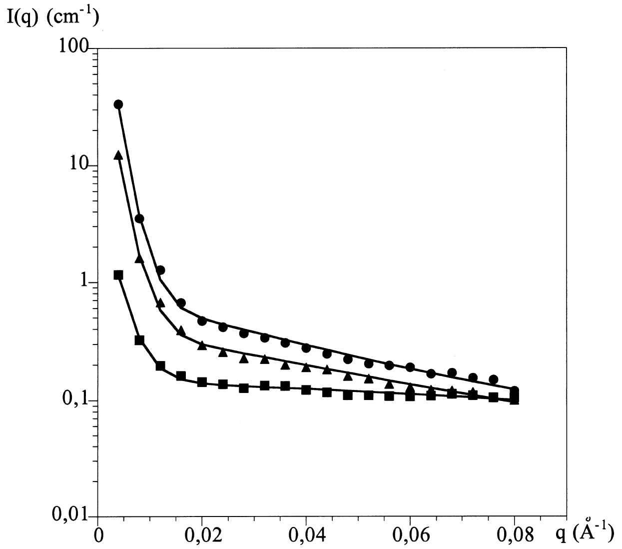

Fig. 1. The SANS curves for the hydrogel cross-linked by allylhydroxyethylcellulose, with 10% ionised groups, swollen up to 17 (■), 40 (▲) and 154 g/g (●). The solid lines were obtained by fitting Eq. (3) to experimental data by the method of the least squares.

experimental SANS curves and simulated ones in accordance with Eq. (3).

Fig. 1 shows an example of SANS intensity profiles for polyacrylamide gel with 10% ionised groups, cross-linked by AHEC, for different gel concentrations (or degrees of swelling). The analogous SANS curves were obtained for other gels cross-linked by AHEC with degrees of ionisation $\alpha = 0$ and 50%. The fitting parameters of the gel microstructure, obtained from expression (3) as described above, are given in Table 2. In Table 2 we also give the fraction of polymer engaged in static fluctuations, $\langle \Delta\rho^2 \rangle$, which are modelled by a Guassian distribution function of the Ξ width and amplitude $\langle \Delta\rho^2 \rangle$ (see Eq. (2)). These values have been obtained from SANS data by the following expression:

$$\frac{\langle \Delta\rho^2 \rangle^{1/2}}{\langle \rho \rangle} = \sqrt{\frac{2}{\pi}} \frac{I_G(0)\xi^3}{I_L(0)\Xi^3} \tag{4}$$

The dependencies of Ξ on gel degree of swelling for three samples crossed-linked by AHEC ($\alpha = 0$, 10 and 50%) are given in Fig. 2. The presence of charged units on the chain doubles the size of the dense areas in the vicinities of junctions as compared with the neutral gel. It is well known that even a small amount of charged groups in the network matrix induces many new physicochemical properties of the gel [4] (ability to absorb water, respond to electric field, swelling behaviour in low or high molecular weight aqueous solutions, etc.). SANS results showed that the area enriched with polymer chains around cross-linking junctions is acting as a microgel 'swelling' more when it is charged.

The Ξ vs Q curve shows a maximum for the case of gel with 50% ionised groups. This is quite different from the dependence of Ξ on the degree of swelling for the gel with low (10%) degree of ionisation. Also the dependence of the correlation length ξ (which characterises polymer–polymer interactions) on the degree of swelling is not smooth for a more ionised gel compared with that of $\alpha = 10\%$ (see Fig. 3). There is a maximum on the ξ vs Q curve at $Q \approx 200$, which is the same value of the maximum position on the dependence ξ vs Q. What we want to show here is that swelling-induced changes of structure parameters of gels strongly depend on its degree of swelling (or gel concentration) are going through a maximum at degrees of swelling $Q = 100$–300 g/g.

The same procedure of SANS data treatment was applied to fully ionised gels cross-linked by other compounds (allyldextran and MBA) and also for gels with different ability to absorb water (different degrees of cross-linking) (see Table 1). The data treatment showed that each term in Eq. (3) contributed to different parts of a scattering curve. The

Table 2
Fit parameters obtained from Eq. (3) for hydrogels cross-linked by AHEC

Gel degree of swelling (g/g)	$I_G(0)$ (cm^{-1})	Ξ (Å)	$I_L(0)$ (cm^{-1})	ξ (Å)	$\langle \Delta\rho^\nu \rangle / \langle \rho \rangle^\nu$
$\alpha = 0$					
16	31.2 ± 2.6	373 ± 11	0.36 ± 0.04	7.7 ± 0.3	0.025
$\alpha = 10\%$					
17	2738 ± 93	674 ± 6	0.65 ± 0.06	26.5 ± 0.7	0.45
40	584 ± 31	578 ± 9	0.34 ± 0.04	20.1 ± 0.7	0.24
114	8.0 ± 1.3	309 ± 20	0.17 ± 0.03	12.9 ± 0.9	0.052
154	13.0 ± 2.0	370 ± 23	0.13 ± 0.02	6.7 ± 0.7	0.022
$\alpha = 50\%$					
18	2280 ± 103	683 ± 9	0.28 ± 0.04	24.8 ± 1.5	0.56
100	561 ± 81	696 ± 26	0.14 ± 0.02	11.8 ± 1.1	0.12
200	1290 ± 150	779 ± 23	0.14 ± 0.02	13.4 ± 1.3	0.19
345	1084 ± 150	852 ± 28	0.10 ± 0.02	10.0 ± 1.0	0.11
500	50 ± 19	533 ± 61	0.05 ± 0.03	5.0 ± 3.0	0.03

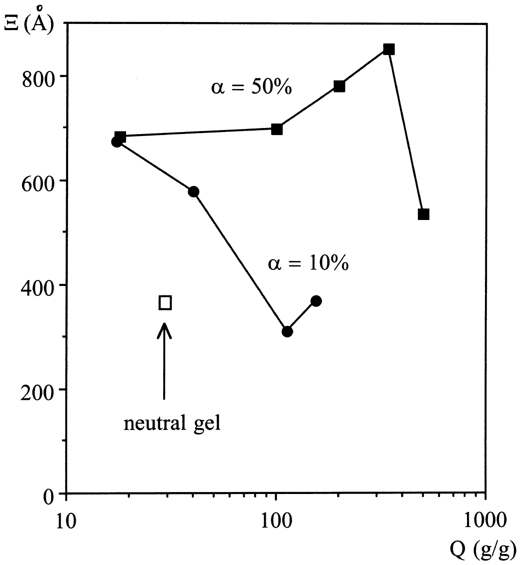

Fig. 2. The dependence of the mean size of the spatial heterogeneities on the degree of swelling of hydrogels cross-linked by AHEC, 10 and 50% of ionised groups. We also give the value of Ξ for a neutral polyacrylamide gel cross-linked by AHEC and swollen at maximum.

information about the excess scattering due to the present of cross-links can be extracted from the region of low q values ($q < 0.02$ Å^{-1}) and variation of ξ from 5 to 25 Å in the second term does not influence (within the experimental error limits) on the values of Ξ (see also Table 2). Thus we assumed that for obtained scattering patterns the second term may be considered as a 'background' and we followed only the changes of a solid-like heterogeneities size. The mean size of heterogeneities was calculated for each degree of swelling. The fitting parameters obtained by data processing of initial scattering curves are given in Table 3.

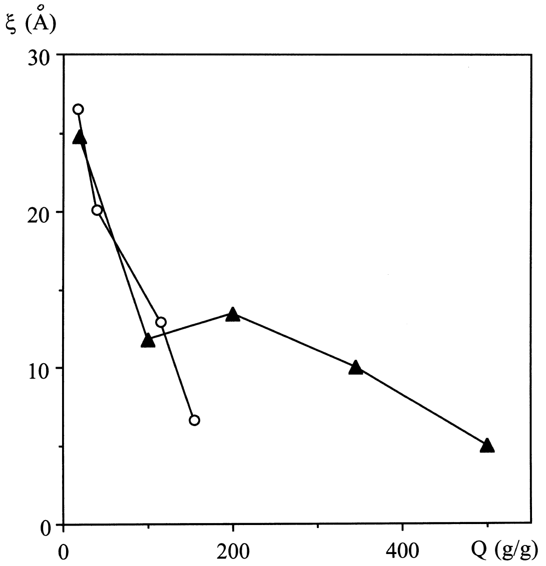

Fig. 3. Correlation length ξ versus gel degree of swelling for the same samples as in Fig. 2.

Table 3
Fit parameters for the gels cross-linked by allydextranes and MBA

Gel degree of swelling (g/g)	$I_G(0)$ (cm^{-1})	Ξ (Å)
AD1		
20	555 ± 41	743 ± 14
67	794 ± 72	833 ± 18
200	865 ± 180	1008 ± 49
500	1103 ± 113	954 ± 21
1000	1.8 ± 0.8	357 ± 57
AD2		
20	972 ± 38	736 ± 80
67	575 ± 48	745 ± 16
200	1383 ± 307	1151 ± 56
500	1168 ± 137	984 ± 26
1000	3.0 ± 1.0	408 ± 101
AD3		
20	2168 ± 65	678 ± 9
100	568 ± 50	684 ± 9
200	981 ± 50	700 ± 9
250	1589 ± 78	782 ± 11
333	31 ± 7	471 ± 36
AD4		
10	17 972 ± 180	722 ± 8
20	15 045 ± 152	723 ± 8
33	19 905 ± 200	727 ± 8
50	14 765 ± 150	737 ± 8
MBA		
20	2710 ± 28	496 ± 5
67	556 ± 14	489 ± 7
200	405 ± 18	536 ± 7
333	197 ± 20	549 ± 10
500	132 ± 18	548 ± 16
540	22 ± 2	340 ± 12
MBA, in 1 M NaCl		
20	1290 ± 19	437 ± 4
25	860 ± 18	440 ± 5
29	813 ± 18	439 ± 5
33	336 ± 9	404 ± 7

The dependence of Ξ on hydrogel degree of swelling shows a maximum (see Fig. 4) for most of the samples. It does not exist only for gels with low absorption ability (maximal degree of swelling 50 g/g) and for gel swollen in 1 M NaCl solution. The peak position corresponds to the gel degree of swelling $\approx$ 200 g/g. Such high degrees of swelling can be reached only if a network is strongly charged and can swell more than 200 times. The maximum is more pronounced for gels having the highest capability to absorb water (cross-linked by AD1 or AD2). The peak vanishes with the increase of the degree of cross-linking and it does not exist for the gel having the equilibrium degree of swelling 50 g/g (see curve for AD4). Also there is no maximum on the dependence of Ξ on Q for the gel swollen in 1 M NaCl solution. Here the gel has a low degree of swelling because polyelectrolyte swelling is suppressed.

We suppose that the observed phenomenon takes place due to the strong ionisation of polyacrylate chains at very low polymer concentrations which can be reached when a gel can swell more than 200–300 times (see, for instance, Ref. [22]). The vicinities of cross-linking junctions are

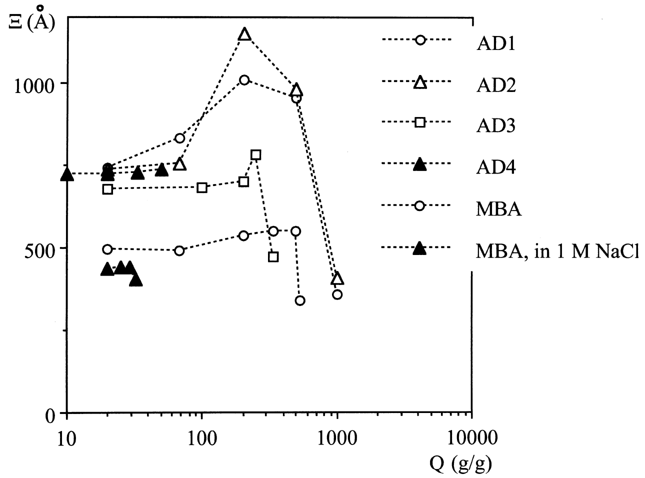

Fig. 4. The dependence of the mean size of the spatial heterogeneities on the degree of swelling of hydrogels cross-linked by high (AD1–AD4) and low (MBA) molecular weight compounds. The dashed lines are given to guide the eye.

enriched with entangled sodium polyacrylate macromolecules and the increase of the heterogeneities sizes is due to the polyelectrolyte swelling mechanism. This becomes apparent when a gel is strongly charged and has a low degree of cross-linking. The result does not depend on the chemical nature or the molecular weight of the cross-linking agent.

It should be noted that in all the cases the decrease of the contrast between static heterogeneities and the gel matrix takes place. The information about the contrast (or the relative density) may be extracted from the value of I_G0) [23]:

$$I_G(0) \propto NV^2\langle\Delta\rho^2\rangle \qquad (5)$$

$I_G(0)$ being determined by extrapolation of the coherent intensity to zero angle, N is the number of scattering centres, V is the volume of the size of heterogeneity, $\Delta\rho$ being the same value as determined in Eq. (2), but which is also interpreted here as a contrast (the difference between the densities of the scattering amplitudes of the heterogeneity and the matrix). It is possible to roughly estimate the change of the contrast taking, for example, sample AD1 (see Table 3). For this gel the swelling from $Q = 20$ to 200 g/g (maximal Ξ) increases the value of $I_G(0)$ by 1.6 times. At the same time the value of V^2 ($\propto \Xi^6$) increases by 6.3 times. As the gel is chemically cross-linked the number of scattering centres does not change during the gel swelling. Thus the contrast $\Delta\rho$ decreases by about 2 times.

Both results considered together—the dependence of the size of heterogeneities and the contrast on the degree of swelling—may help in understanding how the hydrogel structure is changing during swelling depending on the ability of a gel to absorb water. For the gels with relatively low maximal degrees of swelling ($<$ 100 g/g) the size of static heterogeneities does not change much with dilution and the contrast decreases. For the gels with high ability to absorb water ($>$ 200 g/g) the size of heterogeneities increases during swelling accompanied by the contrast decrease. It means that in the latter case the gel ‘homogenisation’ occurs, this being more pronounced at intermediate degrees of swelling ($\approx$ 200 g/g).

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