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Structural changes in hydrogels immersed in a linear polymer solution, studied by SANS

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Abstract

The structural changes in polyelectrolyte gels immersed in a linear polymer solution were studied by the small-angle neutron scattering technique. Two cases were considered: (i) when the gel absorbed mainly water and did not interact with the linear polymer; and (ii) when a linear polymer formed an interpolymer complex with the gel and thus penetrated the network. It was shown that in the first case the gel contracted almost as a unit due to the osmotic pressure difference. In the second case the gel contracted through microphase separation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogel; Interpolymer complex; Small-angle neutron scattering

1. Introduction

Hydrophilic polymer networks are known as intelligent materials readily responding to many changes in the surrounding medium or to external inputs. Their unique physico-chemical properties (capability to retain very large amounts of water, to absorb and release low or high molecular weight compounds, etc) allow them to be used in different bio-medical applications for making contact lenses, wound dressing, in drug-release systems, etc. One up-to-date research topic connected with the above mentioned application areas is the investigation of hydrogel swelling behaviour in linear polymer solutions and the absorption/release of macromolecules by a gel. Several authors have reported: (i) the changes of hydrogel degree of swelling when the gel is immersed in a polymer solution; and (ii) macromolecules penetration inside the gel, and, as a consequence, the gel undergoing conformational transitions [1–7]. In the paper [5] it was reported that if these are no special interactions between the gel and the linear polymer macromolecules, the hydrogel absorbs mainly solvent (water) and thus increases outside polymer concentration. If the gel forms an interpolymer complex with the linear polymer, the linear polymer is absorbed by the gel from the surrounding solution [5].

The goal of this work is to compare how the hydrogel structure changes in these two different cases. The studies were performed using the small-angle neutron scattering (SANS) technique, which allows to follow the changes of the size and density of network inhomogeneities [8–10].

2. Experimental part

2.1. Materials

The hydrogel sample used in this study was a poly(0.75 sodium acrylate–0.25 acrylic acid) gel cross-linked by N,N'-methylenbisacrylamide (kindly provided by Atochem). The mole fraction of the cross-linking agent with respect to the monomer was 0.06%. This material will be called Na-gel in the following. The initial state is a powder of dry gel particles. In order to change the gel degree of ionisation, but to keep the same gel topology, a hydrogel based on cross-linked polyacrylic acid (PAAc-gel) was obtained by a simple chemical modification of the Na-gel. The Na-gel was placed in a hydrochloric acid solution where sodium ions were replaced by hydrogen, then precipitated in acetone and dried to a constant weight in vacuum in the presence of P_2O_5. As for the initial Na-gel,

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the initial state of the PAAc gel was a powder of dry spherical particles. The Na-hydrogel has the maximal degree of swelling Q_{max} in water at equilibrium of 400 g/g and PAAc-hydrogel—of 40 g/g.

Aqueous solutions of hydroxypropylcellulose (HPC) (Klucel type E, molecular weight 6×10^4 as given by manufacturer), kindly provided by Aqualon (a Hercules Company), were prepared by mixing HPC and heavy water. In order to compare the results obtained for different samples, reduced coordinates C_{HPC}/C_{gel} (C_{HPC} being the HPC concentration, C_{gel} being the hydrogel concentration) were used. All the concentrations were calculated in mol/l for the total volume of the system hydrogel + solution.

2.2. Methods

The dependence of the degree of swelling of the two hydrogel samples on the initial HPC concentration was measured as $Q = m(C_{HPC}/C_{gel})/m_0$, where $m(C_{HPC}/C_{gel})$ is the weight of the hydrogel in the equilibrium state after interaction with a HPC solution of certain concentration, m_0 is the weight of the dry gel.

The SANS experiments were performed for both hydrogels swollen in D_2O and in HPC solutions of different concentrations. In order to compare structural parameters of the gels swollen in HPC and in water, hydrogels were swollen in D_2O at the same degrees as in HPC solutions. Different degrees of swelling in D_2O (smaller than maximal swelling in water) were obtained by adding a fixed amount of D_2O.

The instrument used for the SANS experiments was the small-angle neutron diffractometer "Membrana-2", St Petersburg Nuclear Physics Institute, Russia. The average wavelength of the incident beam 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 spectral and collimation distortions of the diffractometer, detector efficiency, sample transmission and incoherent background scattering. The scattering intensities were converted to the absolute differential scattering cross-sections per unit sample volume using H_2O calibration data [11].

3. Results and discussion

3.1. Theoretical background for the analysis of SANS curves

The scattering equation for an isotropic substance may be written as the spatial Fourier transform of the correlation function $\gamma(r)$ [12]:

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

where $q = 4\pi \sin\theta/\lambda$ is the scattering vector, 2θ is the scattering angle.

The variety of scatterers contributing to the experimental scattering pattern especially in such a complicated case as hydrogels immersed in polymer solutions makes the determination of the structural characteristics rather difficult. Scattering measurements provide general information on the spatial distribution of the concentration fluctuations in a system, but the obtained results depend on additional information or assumptions regarding the supermolecular structure, and are defined by the model used for calculating the scattering profile.

Different approaches can be used to approximate the scattering intensity. The scattering patterns from chemically cross-linked gels were analysed from the point of view of additive contributions from a homogeneous, liquid-like (dynamic) fluctuating gel matrix, and embedded heterogeneities (static) having a high cross-linking density [13,14]. The excess scattering in gels as compared with the equivalent solutions of uncrosslinked polymers is due to the static concentration fluctuations, which are associated with the cross-linked regions in the vicinity of the network junctions. As it will be shown in the following, we did not obtain any peaks on the scattering curves neither for hydrogels immersed in D_2O nor in hydroxypropylcellulose solutions. The peaks were reported in Refs. [15,16] for weakly charged gels immersed in a poor solvent. The structure factor used in Refs. [15,16] corresponds to the case where the gel would undergo upon cooling a microphase separation transition. In the present paper we used a more general correlation function proposed by Mallam et al. [8] which has been proved to fit well the scattering information both for hydrogels and for other heterogeneous systems [8–10,17–27]:

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

where Ξ is the characteristic mean size of the static (frozen) heterogeneity in a gel; ξ the correlation length of polymer–polymer interactions, which takes place between the fluctuating chains of the gel network, $\langle c \rangle$ the ensemble-averaged value of a local polymer concentration, and $\langle \Delta c^2 \rangle$ is the mean square amplitude of the concentration fluctuations in the gel. The Fourier transform of Eq. (2) gives 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 $I_G(0) \cong \Xi^3\langle \Delta c^2 \rangle$ and $I_L(0) \cong \langle c^2 \rangle \xi^3 (2/\pi)^{1/2}$ are linear coefficients of the Gaussian and Lorentzian terms describing static and dynamic components of scattering by the network, respectively. Thus, the model of the scattering system contains four independent variables, $I_G(0)$, $I_L(0)$, Ξ and ξ, which were calculated from the best agreement between the experimental SANS curves and simulated ones (Eq. (3)).

Additional information on the dense areas around cross-linking junctions can be obtained from the dependence of the contrast $\Delta\rho$ (a relative density between the inhomogeneity and the matrix) on gel degree of swelling or on linear polymer concentration:

$$\Delta\rho^2 = I_G(0)/(NV^2) \tag{4}$$

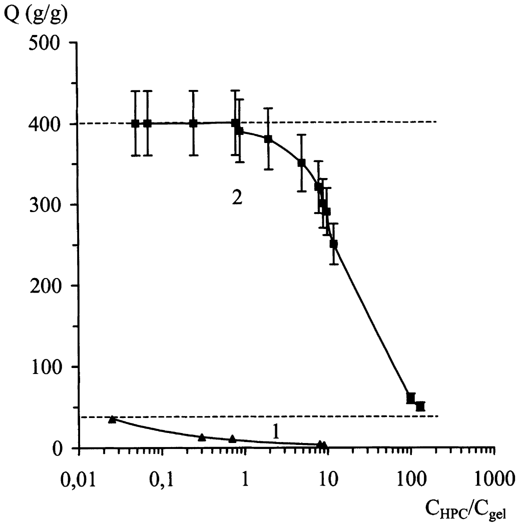

Fig. 1. Dependence of PAAc-gel (1) and Na-gel (2) degrees of swelling on the relative linear polymer concentration ($C_{\mathrm{HPC}}/C_{\mathrm{gel}}$). The equilibrium degrees of swelling in water are shown by dashed lines.

where N is the number of scattering centres in the volume unit (roughly proportional to $1/Q$), V is the volume of a heterogeneity ($\sim\Xi^3$).

3.2. Experimental results and discussion

The dependence of gel degree of swelling on the reduced HPC concentration $C_{\mathrm{HPC}}/C_{\mathrm{gel}}$ is shown in Fig. 1 for both PAAc- and Na-gels. It reflects the ability of preferential absorption by the hydrogel of either water (by Na-gel) or the linear polymer (by PAAc-gel) [5]. For the Na-gel, the results show that when the HPC concentration was less than or equal to the polymer concentration, its degree of swelling was almost the same as in pure water. The Na-gel swelling decreases only when C_{HPC} was more than 10 times higher than C_{gel}. At high concentrations, it had a degree of swelling similar to the non-charged polymer network. Contrary to this behaviour, the PAAc-gel swells quite weakly in the HPC solutions even at low linear polymer concentrations. The decrease of its degree of swelling compared with the one in water began when C_{HPC} was ten times lower than C_{gel}.

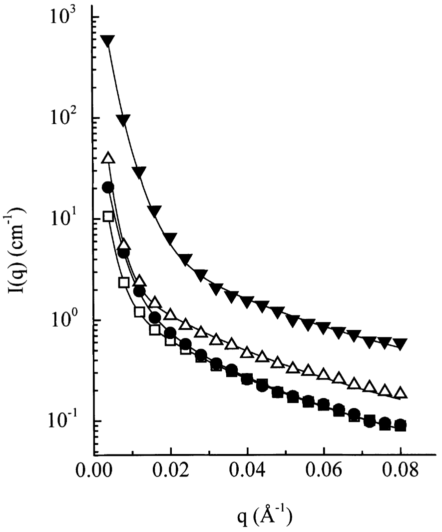

Fig. 2. SANS curves for the PAAc-gel swollen in D_2O at degrees of swelling $Q = 40$ g/g (□) and $Q = 10$ g/g (△) and in HPC solutions of various concentrations $C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 0.02$, $Q = 40$ g/g (●) and $C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 5$, $Q = 10$ g/g (▼). The solid lines correspond to the best fit of Eq. (3) to the experimental data. The errors are of the size of the points.

In Figs. 2 and 3 the dependences of scattering intensity $I(q)$ on q are presented for PAAc- and Na-gels swollen in pure D_2O and aqueous solutions of HPC, respectively. Two different relative HPC concentrations for each gel were chosen: (i) when the degree of gel swelling in the polymer solution was close to the swelling in water ($C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 0.02$ for PAAc-gel and 5 for Na-gel); and (ii) when degree of swelling differed from the one in water ($C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 5$ for PAAc-gel and 30 for Na-gel). The solid lines in Figs. 2 and 3 correspond to the best fit of Eq. (3) to the experimental data. The parameters characterising gel structure calculated from Eq. (3) are given in Table 1 for both PAAc- and Na-gels.

From the SANS data it is clear that the increase of the initial HPC concentration leads to the increase of scattering for both gel samples. This means that the linear polymer was absorbed by the gel in both cases. However, the network structure was changing in different ways depending on whether the interpolymer complexes were formed or not between the gel and the linear polymer. This is shown in Fig. 4 where intensity ratios are presented for both PAAc- and Na-gels swollen in HPC solutions and in pure water. The intensity ratio indicates the influence of HPC macromolecules on the gel structure. For both gels swollen in solutions of low relative HPC concentrations ($C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 0.02$ for PAAc-gel and $C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 5$ for Na-gel), there was almost no identifiable influence of HPC on the gel structure within the experimental errors over the q-range studied. In such HPC solutions the degrees of swelling of both gels was the same as in pure water. A significant difference in the scattering by PAAc- and Na-gels occured for networks swollen at more high relative HPC concentrations ($C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 5$ for PAAc-gel and $C_{\mathrm{HPC}}/C_{\mathrm{gel}} = 30$ for Na-gel), where the degrees of swelling differed from those in pure water. For PAAc-gel there was an increase in $I_{\mathrm{HPC}}/I_{D_2O}$ ratio at low q-values and for Na-gel $I_{\mathrm{HPC}}/I_{D_2O}$ increased at $q > 0.02$ Å^{-1}.

For a better understanding of how the heterogeneities in the gel structure were changing as a function of HPC concentration, a comparison between the relative values of the scattering intensity at zero q of the static component $I_{\mathrm{HPC}}/I_{D_2O}$ (which characterises the scattering mass—size, density and number of scattering entities); the relative volume of heterogeneities $V_{\mathrm{HPC}}/V_{D_2O}$; and the contrast between the static heterogeneity and the network matrix $\Delta\rho$ (see Eq. (4)) was performed (see Table 2). In evaluating the contrast for both gels we assumed that each being

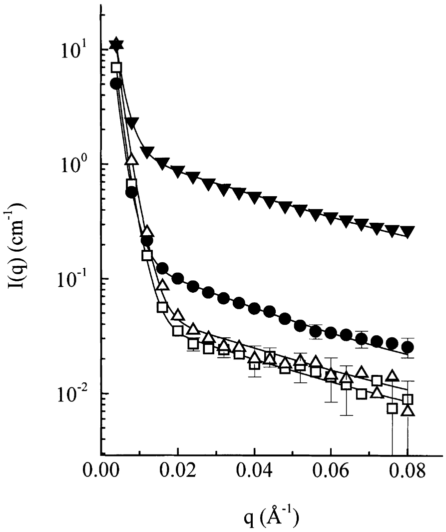

Fig. 3. SANS curves for the Na-gel swollen in D_20 at $Q = 400$ g/g (□) and $Q = 280$ g/g (△) and in HPC solutions of $C_{HPC}/C_{gel} = 5$, $Q = 400$ g/g (●) and $C_{HPC}/C_{gel} = 30$, $Q = 280$ g/g (▼). The solid lines correspond to the best fit of Eq. (3) to the experimental data.

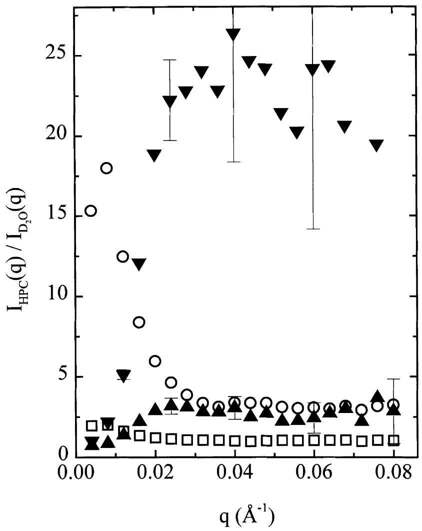

Fig. 4. Intensity ratios for PAAc-gel ($C_{HPC}/C_{gel} = 0.02$, $Q = 40$ g/g (□) and $C_{HPC}/C_{gel} = 5$, $Q = 10$ g/g (○)) and Na-gel ($C_{HPC}/C_{gel} = 5$, $Q = 400$ g/g (▲) and $C_{HPC}/C_{gel} = 30$, $Q = 280$ g/g (▼)).

swollen at the same degree in pure water and in HPC solutions has the same concentration of scattering centres *N*. For comparison, all the results for each PAAc- or Na-gel swollen in pure water at its equilibrium swelling were taken as a point of reference.

In the case of Na-gel the increase of HPC concentration lead to a decrease of: (i) gel degree of swelling; (ii) the relative intensity at zero *q*; and (iii) the volume of heterogeneities. The contrast increased slightly. These results considered together lead to the conclusion that Na-gel contracts in the HPC solutions almost as a unit. The contraction was caused by the increase of outside linear polymer osmotic pressure.

The situation with PAAc-gel swelling in the HPC solution was more complicated. Here the gel collapsed mainly due to the interpolymer complex formation between HPC and PAAc macromolecules. As a consequence, HPC was strongly adsorbed by the gel from the surrounding solution [5]. With the increase of HPC concentration gel degree of swelling decreased as did the volume of heterogeneities (see Table 2). However, the contrast and the relative intensity at zero *q* increased. The discrepancy between the changes in the volume of heterogeneities and the contrast increased with the increase of HPC concentration (at $C_{HPC}/C_{gel} = 5$, $V_{HPC}/V_{D_2O} = 0.4$ and $\Delta\rho = 5.9$). This can be interpreted as a microphase separation induced by the formation of interpolymer complexes between the linear polymer and the network.

SANS studies showed that if a polyelectrolyte gel was immersed in a polymer solution where there were no special interactions between the gel and the linear polymer, the gel contracted as a unit and absorbed mainly solvent (water) from the outside solution. If the gel formed interpolymer complexes with the linear polymer (via hydrogen bonding), the gel absorbed the polymer from the solution and collapsed through the microphase separation between the cross-linking junctions and the gel matrix.

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Table 1
Structural characteristics of PAAc- and Na-gels obtained from Eq. (3)

Sample	Degree of swelling *Q* (g/g)	C_{HPC}/C_{gel}	$I_G(0)$ (cm^{-1})	Ξ (Å)	$I_L(0)$ (cm^{-1})	ξ(Å)
PAAc-gel	40	0	237 ± 7	478 ± 6	1.65 ± 0.04	58 ± 5
	40	0.02	276 ± 10	401 ± 6	2.1 ± 0.1	70 ± 5
	10	0	1570 ± 100	593 ± 16	2.5 ± 0.1	51 ± 5
	10	5	9900 ± 200	426 ± 5	8.3 ± 0.4	51 ± 5
Na-gel	400	0	340 ± 40	621 ± 20	0.05	≈ 30
	400	5	235 ± 30	615 ± 20	0.14 ± 0.02	30 ± 4
	280	0	500 ± 50	606 ± 20	0.05	≈ 25
	280	30	220 ± 25	476 ± 15	1.12 ± 0.06	25 ± 1

Table 2
Relative values of the scattering intensity at zero q of the static component (Eq. (3)) $I_{HPC}(0)/I_{D_2O}(0)$, relative volume of heterogeneities V_{HPC}/V_{D_2O} and contrast $\Delta\rho$ between the static heterogeneity and the network matrix (Eq. (4))

Sample	Degree of swelling Q (g/g)	C_{HPC}/C_{gel}	$I_{HPC}(0)/I_{D_2O}(0)$	V_{HPC}/V_{D_2O}	$\Delta\rho$
PAAc-gel	40	0	1	1	1
	40	0.02	1.3	0.6	2
	10	0	1	1	0.9
	10	5	6.3	0.4	5.9
Na-gel	400	0	1	1	1
	400	5	0.7	1	0.9
	280	0	1	1	1.1
	280	30	0.5	0.5	1.5

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