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NANOSTRUCTURED COMPOSITES BASED ON POLYMER GELS

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Polymer gels have found multiple applications in our everyday life. Some of them are connected with high absorption ability of the gels with respect to water and water-based fluids (e.g., personal care products like diapers, potting compounds for civil engineering) [1–3]. Another set of applications of polymer gels is due to their responsive properties, which manifest themselves in the ability of the gels to drastically and reversibly change their volume in response to a very small variation of external factors such as composition of the solvent, temperature, electric or magnetic field, etc. [2,4,5]. This feature determines the use of polymer gels as functional materials, e.g., sensors, actuators, carriers for controlled drug release, membranes with regulated permeability. [5,6].

During past years there has been an increased interest in the preparation of nanocomposite materials by embedding nanosized particles into polymer gels [7-14]. In such nanocomposite materials the properties inherent to polymer gels are combined with the properties of filler component properly distributed throughout the gel volume. Depending on the structure of filling nanoparticles, different architectures of nanocomposite gels can be realized. This chapter will concern mainly three types of structures of nanocomposite gels depicted in Fig. 12.1.

In the first type of structure, long one-dimensional rods are embedded into the matrix of a flexible polymer network [9–11]. This system is promising for the use in different applications exploiting the superabsorbent properties of the gels, the rods of filler serving as a reinforcing agent for highly swollen gels. Such a synthetic nanocomposite system is reminiscent of the nanocomposite realized by nature in the vitreous body of the human eye, which is composed of highly flexible hyaluronic acid interwoven by semirigid collagen threads that serve to provide mechanical stabilization of the body [15].



Fig. 12.1 Schematic representation of different nanostructured composite gels under consideration: (a) 1-D polyelectrolyte rods in the gel matrix, (b) 2-D clay platelets in the gel matrix, (c) 3-D voids in the gel matrix.

In the second type of structure, flat two-dimensional) clay platelets are embedded into the gel matrix in order to impart to the gel ion-exchange properties combined with high absorption ability of the clay with respect to organic compounds [8,12–14].

In the third type of structure, three-dimensional nanovoids are introduced into the gel matrix. These cavities serve to concentrate small ions of salt having the same charge as the gel chains (co-ions) [16–18]. This property makes such gels very promising for new nanotechnologies as a medium with a specially designed set of microreactors.

12.1 Gels with embedded polyelectrolyte rods

The first system under consideration is the nanocomposite hydrogels with embedded rods of a linear polyelectrolyte. Hydrogels that can absorb and hold large amount of water have found various commercial applications as superabsorbents; e.g., in the production of personal care products, in medicine, in agriculture, and in civil engineering [1,2,19]. For all these applications, the gel should not only possess high absorption ability but also be rather strong in the swollen state in order to hold the absorbed liquid effectively. There is always a problem as to how to reinforce the swollen gels, because most of the methods of gel strengthening lead to significant loss of their absorption capacity [1]. Filling of hydrogels with stiff-chain linear polyelectrolytes presents one of the possible ways to improve mechanical properties of swollen gels without loss of swelling ability [9]. In this nanocomposite system, stiff chains of filler strengthen the swollen gel, while charged groups of filler ensure good swelling of the gel.

Such new type of nanocomposite system was prepared [9] on the basis of a polyacrylamide (PAAm) network and a linear stiff-chain polyelectrolyte – poly(sodium *p*-phenylene sulfonate): samples PPP2 (degree of polymerization $P_n = 23.5$) and PPP3 ($P_n = 105$) (Fig. 12.2a).





Fig. 12.2 (a) Chemical structures of poly(sodium p-phenylenesulfonate) samples used in the preparation of nanocomposite gel. (b) Model representation of cylindrical aggregates formed by poly(sodium p-phenylenesulfonate) samples PPP3 in aqueous solutions. Source of Fig.12.2b [20]: Reprinted with permission from Rulkens, R., G. Wegner, and T. Thurn-Albrecht. 1999. Cylindrical micelles of wormlike polyelectrolytes. *Langmuir* 15(12):4022-4025. Copyright 1999 American Chemical Society.

The linear polyelectrolytes contain a hydrophobic stiff poly (*p*-phenylene) backbone and hydrophilic charged sulfogroups, which are responsible for the solubility of the polymers in water. Because of the 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 (Fig. 12.2b) [20]. The self-aggregation in water is a characteristic feature of these polymers. It was studied by different techniques: small-angle X-ray scattering (SAXS) [20], light scattering [21], etc. This property makes possible the immobilization of the polymers in the gel matrix without covalent bonding to the gel chains [9].

To incorporate a stiff-chain polyelectrolyte in the PAAm gel, a freeradical copolymerization of acrylamide with a cross-linking agent, N, N'methylenebis(acrylamide), was performed in aqueous solution of the polyelectrolyte [9]. As a result of the formation of a three-dimensional PAAm network, the linear polyelectrolyte becomes physically trapped by the gel. A series of PAAm gels with the 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 was prepared (Table 12.1). For comparison in the analogous conditions, the reference PAAm gels without the filler were synthesized as well (Table 12.1).

	Concentration of acrylamide	Molar ratio <i>N</i> , <i>N'</i> -methylene (bisacrylamide): acrylamide	Concentration of stiff-chain polyelectrolyte PPP3	Equilibrium degree of swelling in water, <i>m/m</i> ₀ ^{<i>a</i>}
Sample	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

 Table 12.1
 Conditions of preparation and swelling characteristics of PAAm gels.

^a The ratio of mass of swollen and dry gels.

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To evaluate the significance of the prepared nanocomposite gels for use as superabsorbents, two main properties of these gels were studied: the ability to absorb water and the mechanical strength in the swollen state [9]. From Fig. 12.3 it is seen that the gels with the PPP3 filler possess much higher elastic moduli than the corresponding reference gels without the filler. Introduction of only 0.9 wt % of filling rods can double the elasticity modulus of the gel. At the same time, the introduction of polyelectrolyte chains into the uncharged gel improves the ability of the gel to absorb water (Table 12.1). The reason for this is rather obvious. When one introduces charged polymer chains in the uncharged gel, one introduces 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; as a result, they create an exerting osmotic pressure, leading to gel swelling.

Therefore, a stiff-chain polyelectrolyte simultaneously imparts two useful properties to the gel: higher ability to absorb water and higher mechanical strength. The counterions of the polyelectrolyte are responsible



Fig. 12.3 Elastic moduli of PAAm gels with and without PPP3 rods at different cross-linking densities of the gels (expressed in the number of monomer units per 1 cross-link). The concentration of PPP3 in all samples is equal to 9.0 g/l. Source [10]: Copyright 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Philippova, O. E., Yu. D. Zaroslov, A. R. Khokhlov, and G. Wegner. 2003. Reinforced superabsorbent polyacrylamide hydrogels. *Macromolecular Symposia* 200:45-53. Used with permission.

for the enhancement of the absorption capacity of the gel, while the stiffness of the polyelectrolyte gives rise to the increase in the modulus of elasticity. This makes such systems potentially promising as superabsorbent materials.

Keeping in mind the application of gels with a physically entrapped filler, it is necessary to find out the conditions at which the filler is held tightly in the gel. The release of stiff-chain polyelectrolyte PPP3 from the gels was studied at different conditions [9]. For this purpose a peace of gel just after synthesis was put in the excess of solvent, and then the concentration of stiff-chain polyelectrolyte PPP3 in the solvent surrounding the gel sample was determined several times until it reached a constant value. The results are presented in Table 12.2. It is seen that most of stiff linear macromolecules remains in the gel matrix. The concentration of these macromolecules inside the gel is higher than in the external solution by

Sample	Fraction of stiff-chain macromolecules PPP3 released in water from the gel	Ratio of concentrations of stiff-chain macromolecules PPP3 in the gel and in the solution ^{<i>a</i>}
PAAm1*	0.34	34
PAAm2*	0.31	50
PAAm3*	0.28	90
PAAm4*	0.13	660
PAAm5*	0.24	150

 Table 12.2
 Release of stiff-chain polyelectrolyte PPP3 from PAAm gels to water.

^{*a*} The initial volume ratio between the solution and the gel was 137.6

Source: Ref. [10]. Copyright 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

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.

It was shown that if the degree of cross-linking of the gel is increased, the filler is more tightly held by the gel (see the first three samples in Table 12.2), but the effect is very small. Much more pronounced is the effect of the concentration of acrylamide at the gel synthesis. Comparison of the samples PAAm2* and PAAm4* shows that a two-fold increase in the concentration of acrylamide at the gel synthesis significantly reduces the fraction of the released filler molecules from 0.31 to 0.13 (Tables 12.1 and 12.2). Therefore, the release of the linear polyelectrolyte decreases with increasing degree of cross-linking of the network and with increasing concentration of monomer (acrylamide) at the gel preparation, the effect of concentration of monomer being much more pronounced. These data may indicate some interactions between the gel chains and polyelectrolyte rods.

The release of the linear polyelectrolyte is strongly affected by the addition of low-molecular-weight salt. It was shown that 0.05 M NaCl almost completely suppresses the release of the linear polyelectrolyte from the gels PAA2*, PAA4*, and PAA5* [9]. Therefore, it is easy to find the conditions, at which polyelectrolyte filler is tightly held by the gel.

A question arises: why is linear polyelectrolyte, which is not covalently linked to the network, effectively retained by the gel, and why it does it affect the elasticity modulus of the gel? Obviously, this is due to the interaction between the linear polyelectrolyte and network chains. As there is no reason to expect some strong specific interactions between them, like H bonds or electrostatic attraction, the following mechanism of interactions was suggested. Linear polyelectrolyte molecules self-aggregate inside the gel as they do in water solution. As the length of the linear polyelectrolyte (~150 nm) is more than 10-fold larger than the mesh size of the gel

(\sim 12 nm), the polyelectrolyte molecules approaching each other jam some of the network chains.

To prove the key role of self-aggregation of stiff-chain polyelectrolyte in the immobilization of rods inside the gel, the release of the polyelectrolyte from the gel matrix was studied not in pure water but in water-methanol mixture, where the aggregates are partially destroyed [21]. It was shown that in water-methanol mixture, most of the linear macromolecules are released from the gel. This experiment unambiguously demonstrates that indeed the self-aggregation of the linear polyelectrolyte is a factor responsible for the effective immobilization of the linear polyelectrolyte in the gel.

A comparative study of the self-aggregation of a stiff-chain polyelectrolyte in water solution and inside the water-swollen PAAm gels was performed by the small-angle neutron scattering (SANS) technique with heavy water as a solvent [11]. The measurements were made for PPP2 polyelectrolyte (Fig. 12.2a).

Let us first consider aqueous solutions of PPP2 (without gel). It was shown that at low concentrations of polymer, there is no structure peak in the SANS spectra [11]. 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 [11]. 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. On the basis of these data, it was suggested that in the aggregate single macromolecules are arranged parallel to each other and shifted with respect to each other so that the total length of the aggregate is longer than the length of a single chain.

At higher polymer concentrations a scattering peak, which characterizes the mean distances between the aggregates (d_b), appears (Fig. 12.4). The experimental data obtained show [11] that the values of d_b decrease with polymer concentration C_p according to the power law $C_p^{-0.5}$, indicating the shortening of interaggregate distances in the plane normal to the axis of the aggregates.

From the mean interaggregate distance and the concentration of single polymer chains, the average aggregation number (i.e. an average number of single chains in the cross section of the rodlike aggregate) was estimated [11]. It equals to 9 independently of polymer concentration. Therefore, with increasing concentration of polymer the number of aggregates increases, but the size of each aggregate remains constant. This behavior of stiff-chain polyelectrolytes reminds one of the behavior of low-molecular-weight surfactants, in which the size of micelles remains constant in a rather wide range of surfactant concentrations.



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Fig. 12.4 Structure factor as a function of scattering vector for solutions of PPP2 in D₂O at different polymer concentrations: 1–2 wt.%, 2–3 wt.% and 3–4 wt.%. Source [11]: Reprinted with permission from Zaroslov, Yu. D., V. I. Gordeliy, A. I. Kuklin, A. H. Islamov, O. E. Philippova, A. R. Khokhlov, and G. Wegner. 2002. Self-assembly of polyelectrolyte rods in polymer gel and in solution: small-angle neutron scattering study. *Macromolecules* 35(11):4466–4471. Copyright 2002 American Chemical Society.

Now let us consider linear polyelectrolyte PPP2 embedded in the gel matrix. A significant difference in the scattering densities of the gel and of the linear macromolecules allowed one 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 [11]. 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 eight single polymer chains in the cross section. Therefore, the aggregation number of PPP2 inside the gel is almost the same as in the solution. Therefore, the stiff-chain polyelectrolyte self-aggregates inside the gel and the self-aggregation is almost unaffected by the gel matrix.

The influence of low-molecular-weight salt (NaCl) on the scattering of the stiff-chain polyelectrolyte PPP2 was studied [11]. It was shown that when salt is added, the effective radius of aggregates becomes two times higher and simultaneously the length of aggregates increases. Therefore, salt promotes the aggregation of similarly charged polymer chains,

which is 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.

Thus, the data obtained show that swollen hydrogels can be strengthened by 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 contribute to the elasticity modulus of the gel. It was suggested that this is due to the formation of self-aggregates of the stiff polyelectrolyte, which include some network subchains.

12.2 Gels with embedded clay platelets

Another nanocomposite system under consideration is the gels loaded with dispersed clay platelets. Owing to their natural abundance, clays are very promising for use as fillers for hydrogels. The gel-clay nanocomposite materials combine the elasticity and permeability of gels with the high ability of clays to absorb different substances [7,8]. The clay platelets are of the order of 1 nm thick and have extremely high aspect ratios (e.g. 50–1000); thus a few weight percent of clay that are properly distributed throughout the polymer gel create significantly higher active surface area than do conventional composites. Among clays, montmorillonite (MMT) and bentonite (BENT), which contains a big fraction of MMT, possessing a large active surface area (700–800 m²/g) are the most important absorbents for organic compounds [22].

Layered aluminosilicate clays such as MMT are structurally well defined. MMT is three-sheet clay, whose platelet is constructed from an octahedral aluminum sheet sandwiched between two tetrahedral silica sheets. A single platelet of MMT is shown schematically on Fig. 12.5a. Its size is of ca. $100 \times 100 \times 1$ nm³. The surface of the platelet has a negative charge, which is counterbalanced by counterions such as Na⁺ that are residing near the surface. The anionic particles of clay can absorb organic substances because of the ion exchange with the counterions of the clay and also because of additional adsorption and intercalation of the organic substance between the platelets of the clays [22].

In a dry MMT the platelets are arranged into multilayer crystals [14], schematically shown in Fig. 12.5b. The swelling of MMT in water results in the increase in interplatelet spacing and finally in a disorder of the platelets. Because of attraction forces, especially between the edges and



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Fig. 12.5 Schematic representation of the structure of BENT suspension in water and in the gel phase: a single platelet (a), the dried clay powder with multilayered crystals (b), the card-house structure (c), the dispersion of BENT embedded in PAAm gel after ultrasonication (d), the formation of surfactant aggregates on the surface of BENT platelets (e) and the structure of lamellas with intercalated CPC (f). Each line in parts b-f represents a single platelet, which is composed of three sheets (a). Source [13]: Reprinted with permission from Starodoubtsev, S. G., A. A. Ryabova, A. T. Dembo, K. A. Dembo, I. I. Aliev, A. M. Wasserman, and A. R. Khokhlov. 2002. Composite gels of poly(acrylamide) with incorporated bentonite. Interaction with cationic surfactants, ESR and SAXS study. *Macromolecules* 35(16):6362-6369. Copyright 2002 American Chemical Society.

the surface of the platelets, clays form highly viscous liquids with a cardhouse structure schematically illustrated in Fig. 12.5c [22]. At high dilution, the clay platelets form stable colloid dispersions with a disordered orientation of the platelets. Such a disordered state of the clay dispersion was used in the synthesis of gel-clay nanocomposites.

The nanocomposite gels were prepared by three-dimensional polymerization of monomers in the presence of a suspension of clay particles [8,12-14], the suspension being preliminarily treated by ultrasound to eliminate the interplatelet interactions. As a result of polymerization the clay platelets become trapped by the polymer network formed. The dimensions of the clay platelets in the composite were large in comparison with the mesh size of the network; therefore, they were unable to diffuse out of the gel.

The swelling behavior of the nanocomposite gels was studied in aqueous salt solutions [12]. The results are presented in Fig. 12.6. Let us first consider uncharged PAAm gel (curves 1 and 2). It is seen that at low content of salt the degree of swelling of the gel with embedded clay is two-fold higher than for the analogous gel without clay. At increasing salt content the gel with clay shrinks and reaches the degree of swelling of the gel without clay (Fig. 12.6, curve 2). Such behavior of the uncharged nanocomposite gel is typical for polyelectrolyte (i.e. charged) gels. Polyelectrolyte gels swell significantly in salt-free water because of osmotic pressure exerted by mobile counterions and because of the electrostatic



Fig. 12.6 Dependencies of the degree of swelling of the gels on the concentration of sodium chloride for uncharged PAAm gel (1) and for gel/BENT nanocomposites based on uncharged PAAm gel (2) and anionic PAAm gel containing 10 mol.% of sodium 2-acrylamide-2-methyl-1-propane-sulfonate units (3). Source [12]: Reprinted with permission from Starodoubtsev, S. G., N. A. Churochkina, and A. R. Khokhlov. 2000. Hydrogel composites of neutral and slightly charged poly(acrylamide) gels with incorporated bentonite. Interaction with salt and ionic surfactants. *Langmuir* 16(4):1529–1534. Copyright 2000 American Chemical Society.

repulsion of similarly charged groups on the network. In excess of salt, both these effects are suppressed and the degree of swelling of the polyelectrolyte gel decreases and approaches that of the neutral gel. Thus, the sensitivity to salt (Fig. 12.6) indicates that the uncharged gel with embedded clay acquires the properties of the polyelectrolyte gel because of the presence of charges on the surface of clay particles.

But it should be noted that the degree of swelling of such composite gel is much smaller than the degree of swelling of the gel, with charged groups located on the network chains (Fig. 12.6, curve 3). A similar effect of "limited" swelling was also observed for the uncharged gels with embedded polyelectrolyte rods [9,23]. In both the cases, the reason for the limited swelling is connected with the inhomogeneous distribution of charges inside the nanocomposite gel. Recently, such situation was described theoretically [23]. It was shown that the nonuniform distribution of the electric potential inside inhomogeneous gels leads to effective traps for the counterions. The trapped counterions become osmotically passive and do not contribute to the osmotic pressure, which is the main reason of the gel swelling. In polymer gel-clay system the inhomogeneity of the charge and potential distribution comes from the anionic plates of the clay inside the gel. Most of the clay counterions remain mainly in the local volume around the clay particles or between the plates and do not contribute strongly to the total osmotic pressure inside the gel.

Thus, the gel-clay nanocomposite based on uncharged gel acquires the properties of polyelectrolyte gel because of clay charges, but the charges of clay are less effective in inducing gel swelling in comparison with the charges of the network chains.

It was demonstrated that the swelling of the gels with clays strongly depends on their prehistory [14]. A complete drying of the nanocomposite PAAm gel followed by its reswelling results in decrease in the degree of swelling. This behavior was explained by the formation of the additional bonds between the edges and the surfaces of the clay platelets in the dry state (Fig. 12.5c), which partly remain after the gel swelling. It was observed that the gels with higher acrylamide content are less sensitive to drying, because "dense" networks prevent additional interactions between the clay platelets. Thus, the effect of memory can be eliminated by the increase of the polymer concentration in the gel. Another way to restore the initial degree of swelling of the gel with clay is ultrasonication. It was shown that the ultrasound destroys the new contacts between the clay crystals formed in the dry state and the gel "remembers" its original highly swollen state.

Thus, the gel-clay nanocomposites are soft materials with "memory," the memory being due to the interactions between clay particles inside the dried gel, which are not completely disrupted at the gel swelling.

An important feature of gel-clay nanocomposites consists in the fact that the particles of clays embedded in the PAAm gel do not coagulate under the action of flocculating agents [12]. For instance, the addition of Al_2 (SO₄)₃ leads to fast flocculation of clay suspensions in water, while the suspension embedded in the gel remains in a highly dispersed state. Thus, the network prevents coagulation of dispersed clay particles, which is very promising for the applications of gel-clay nanocomposites exploiting the high absorption ability of clay.

Gel-clay nanocomposites can be easily modified by the addition of a surfactant [12-14]. The formation of clay-surfactant complexes between the charged clays and oppositely charged surfactants inside the gel matrix leads to the creation of new nanocomposite materials with excellent absorption characteristics that exhibit ordered structures.

The complexes of clay-containing gels with surfactant cetyl pyridinium chloride (CPC) were studied [13] on an example of PAAm gel-BENT clay system. In this system the gel is uncharged, the clay is anionic, and the surfactant is cationic. It was shown that the interaction of the anionic clay-containing gels with oppositely charged surfactant CPC is a multistep process depending on the surfactant concentration.

Already at a very low surfactant concentration, much smaller than its critical micelle concentration (cmc) 9×10^{-4} mol/L, surfactant molecules start to form ordered aggregates on the surface of clay particles. These aggregates were detected by two independent methods: SAXS and electron spin resonance (ESR) [13]. SAXS spectra demonstrate a broad, weak maximum at the scattering vector q = 1.6 nm⁻¹ corresponding to d = 3.9 nm. The maximum appears at the surfactant-to-clay charge ratio Q of as low as ~0.3. The obtained value of periodicity (d = 3.9 nm) in the clay-CPC complex inside the gel is significantly higher than the characteristic d value for the dried clay-containing gel without CPC (d = 1.34 nm). This indicates that the surfactant ions penetrate between the clay platelets. The ESR data show that at these conditions the rotational mobility of the amphiphilic nitroxide spin probe solubilized inside the aggregates is low in comparison with its mobility in the micelles of the surfactant in solution.

The following driving forces for the interaction of a cationic surfactant with the anionic clay platelets inside the gel are suggested [13]: (1) the release of the counterions of the clay, (2) the aggregation of the hydrophobic "tails" of the surfactant, and (3) the electrostatic interaction between the charges of the surfactant and of the clay surface. The additional stabilization of such contacts comes from the low local "dielectric constant" in the area of the contacts between the surfactant aggregate and the clay platelet. The release of the counterions results in a large gain in translational entropy. Hence, even a few electrostatic contacts between the surfactant aggregate and the platelet should be sufficient to make the

aggregate stable enough from the thermodynamic point of view. At a low surfactant concentration, such aggregates occupy only some small areas on the platelets of the clay. At the same time, because of high hydrophobicity of the cetyl groups of CPC, the surfactant's tails should be closely packed inside the aggregates and form double-layer structures. It was assumed that the ordered aggregates of CPC on the surface of BENT particles in the gel phase can be represented as double-layer fragments schematically shown in Fig.12.5e. From this schematic representation it follows that the appearance of the double layers of the cationic surfactant should result in a strong Coulomb attraction between the anionic platelets. Indeed, the experimental results show that the formation of aggregates is accompanied by the gel shrinking.

The increase of CPC concentration leads to further contraction of the gels. The amount of CPC adsorbed on the clay platelets increases and the attraction between the platelets becomes stronger. At Q values close to 1 in the SAXS spectra, the second maximum appears. The positions of both the maxima observed in the SAXS spectra at these conditions $(q_1 = 1.53 \text{ nm}^{-1} \text{ and } q_2 = 3.06 \text{ nm}^{-1})$ correspond to spacings $d_1 = 4.1$ nm and $d_2 = 2.05$ nm (with the d_1/d_2 ratio 2:1). The two reflections are the first and the second order of the same 4-nm periodicity and evidence of the formation of the lamellar structure of the BENT-CPC complex in the gel. The resulting structure is schematically shown in Fig. 12.5f. It consists of the lamellas built of the clay platelets with double layers of the surfactant intercalated between them. The value of the mean long-range order dimension perpendicular to the platelet surface in the BENT-CPC complex in the gel was determined from the full width at half of the diffraction maximum as ~ 25 nm [13]. This indicates that the ordered domains are built of five to six alternating surfactant bilayers and clay platelets.

The strong shrinking of the gel nanocomposite occurs during these first steps of the adsorption. At high concentration of the surfactant (0.01-0.1 M) the gel reswells [13]. It was shown [13] that this is due to the covering of the outer surfaces of the clay aggregates by CPC double layers, which results in the overcharging of the aggregates of BENT-CPC complexes. The change of the sign of the charge of the mobile ions in the gel phase was demonstrated by the experiments on the electroosmotic transport of water in the gels. It was shown that in the nanocomposite gel free of CPC (PAAm gel-BENT), the release of water under the action of DC current is near the cathode, while after modification of the nanocomposite gel by the cationic surfactant (0.01 M CPC) the inversion of the charge of the mobile ions occurs and water is released near the anode. These experiments clearly demonstrate that in the solutions of the cationic surfactants, the surface charge of BENT is reversed. Therefore, at surfactant

concentrations higher than 0.01 M the overcharging induces the Coulomb repulsion between the particles, leading to their partial separation and, hence, to the reentrant swelling of the nanocomposite gel [14].

Let us consider in more detail the influence of different factors on the structures of gel-clay-surfactant nanocomposites (at fixed surfactant concentration of 0.01 M). How does the network affect the structure of the BENT-CPC complex? To answer this question, the SAXS profile of the BENT-CPC complex inside the gel was compared with that of the BENT-CPC complex without the gel [14]. It was shown that the moderately cross-linked polymer network does not hinder the smectic organization of the clay platelets.

Another factor affecting the structure of BENT-surfactant aggregates is the concentration of clay. It should be high enough (>2.4 wt %) for the formation of smectic structures: in a dilute system, the platelets of BENT are located too far from each other, which prevents their aggregation.

One more factor affecting the smectic structure of BENT-surfactant aggregates is the length of hydrophobic tail of the surfactant [14]. One of the main driving forces for the aggregation of the clay platelets in the gels is the hydrophobic interaction between the surfactant bilayers arranged in the galleries between the flat sheets of BENT. The free energy of hydrophobic interactions depends strongly on the size of the hydrocarbon groups, i.e., on the number of methylene units in the hydrophobic tail of the surfactant. Figure 12.7 shows the scattering curves obtained from the gel with 2.4 wt % BENT immersed in the solutions of alkyltrimethylammonium bromide with dodecyl (R12), tetradecyl (R14), and hexadecyl (R16) alkyl tails and in CPC having hexadecyl alkyl tail linked to pyridinium ring [14]. The scattering curves obtained from the gels treated with longer tail surfactants (R16 or CPC) show intense first- and second-order maxima. The gel treated with R14 shows a rather weak first-order maximum, while the second-order maximum is not observed. R12 with its rather short tail hardly induces smectic ordering of the clay particles, and only a very broad and weak maximum in the scattering curve is observed [14]. This feature is absent in the scattering curves obtained from the same gel without R12. Thus, some organization of the clay platelets and their weak orientation occur even in this case.

By using the observations of Starodoubtsev *et al.*, it was shown that gel-clay composites modified with cationic surfactants can absorb effectively hydrophobic substances, e.g. toluene. Surface modification of the clay platelets by cationic surfactants makes them hydrophobic, and because of this fact the hydrophilic PAA network acquires the ability to absorb hydrocarbons.

Thus, as a result of the interaction of the nanocomposite PAAm-BENT gels with cationic surfactants, initially disordered BENT clay platelets in



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Fig. 12.7 Effect of the length of the hydrophobic tail of the surfactant on the selfarrangement of the clay platelets in the gel/clay nanocomposites. SAXS profiles obtained from the composite gel with 2.4 wt % BENT and treated with 0.01 M solutions of different surfactants: CPC (1), R16 (2), R14 (3), and R12 (4). The content of PAAm was 6.0 %, and the ratio of BAA to AAm was 1/500 mol/mol. Source [14]: Reprinted with permission from Starodoubtsev, S. G., Ryabova, A. A., Khokhlov, A. R., Allegra, G., Famulari, A., Meille, S. V. 2003. Smectic arrangement of bentonite platelets incorporated in gels of poly(acrylamide) induced by interaction with cationic surfactants. *Langmuir* 19(26):10739–10746. Copyright 2003 American Chemical Society.

the gel can rearrange into highly ordered smectic structures composed of alternating layers of BENT platelets and bilayers of the surfactants. The observed transition occurs despite the relatively large size of clay platelets compared with the mesh size of the PAAm network. It was demonstrated that the existence and extent of the transition depend on the length of the hydrophobic tail of the surfactant, on the concentration of clay, and on the structure of the PAAm network.

12.3 Gels with embedded voids

Some years ago a neutral PAAm hydrogel containing an array of monodisperse water voids (a so-called Swiss-cheese gel (Fig. 12.1c)) was prepared and used as an entropic trapping medium for the separation of linear macromolecules such as biopolymers and DNA [24]. The described work concerned an uncharged Swiss-cheese gel.

A charged Swiss-cheese gel was recently considered theoretically [16,17]. It was shown that the most interesting feature of such gels is their ability to concentrate ions within the voids. It concerns both small mono- or multivalent ions and polymeric ions. This feature is based on the Donnan (or entropic) effect of redistribution of ions within the polyelectrolyte gel. Let us first consider the redistribution of monovalent ions [16]. To be definite, let us take a positively charged gel with negatively charged counterions. When such gel is immersed in a solution of a low-molecularweight 1:1 salt, for entropic reasons there is a tendency for homogeneous distribution of small ions (both counterions and ions of salt) throughout the whole system. However, to preserve the condition of electroneutrality of positively charged gel chains, some negative ions should be kept in the interior of the gel sample in excess to that which would be required for the homogeneous distribution of these ions. Therefore, the concentration of other small ions within the gel, in particular the concentration of co-ions (i.e. ions having the same sign of charges as that of the gel chains), should be lower than that in the bulk solution. Therefore, as a result of Donnan effect the concentration of co-ions within the gel is much lower than in the external solution. Moreover, in many cases the polyelectrolyte gel can be practically free from such ions of the low-molecular-weight salt. However, when the gel matrix contains the water voids, the co-ions (together with countercharged ions) will penetrate inside these voids. This means that in the cationic Swiss-cheese gel the positively charged ions of the salt will be predominantly concentrated within the water voids and almost unavailable in the polymer matrix [16].

The simple theory of swelling and of sorption properties of polyelectrolyte Swiss-cheese gels in solutions of low-molecular-weight salt was constructed [16] on the basis of the mean field theory of swelling and collapse of a homogeneous polyelectrolyte gel. The theory takes into account the Donnan effect of redistribution of ions within the polymer matrix and embedded water voids. The swelling ratio of polyelectrolyte Swiss-cheese gel and the concentration of salt ions within it was analyzed as a function of different system parameters, i.e., the quality of solvent, the size and the concentration of the water voids in the gel, the valence of ions of added salt and their concentration, etc. [16,17]. The results of calculations were compared with those obtained from the corresponding homogeneous gel.

The calculated distribution of monovalent co-ions in a Swiss-cheese gel between the polymer matrix and the water voids is shown in Fig. 12.8a as a function of solvent quality [16]. It is seen that the concentration of co-ions within water voids, n_s^{void} (dashed curves), is always higher than that in polymer matrix, n_s^{matrix} (solid curves). In other words, because of the Donnan effect in the Swiss-cheese gel the co-ions of the salt are



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Fig. 12.8 (a) Dependencies of the ratio of concentration of co-ions in polymer matrix to salt concentration in the external solution n_s^{matrix}/n_s (solid curves) and of the ratio of concentration of co-ions inside water voids in the gel to salt concentration in the external solution n_s^{void}/n_s (dashed curves) on the solvent quality (Flory-Huggins interaction parameter χ) at different salt concentration of co-ions inside water voids in the gel to salt concentration in the external solution n_s^{void}/n_s (dashed curves) on the solvent quality (Flory-Huggins interaction parameter χ) at different salt concentrations $n_s : 10^{-3}$ (a), 10^{-4} (b), 10^{-5} (c). (b) Dependencies of the ratio of concentration of co-ions inside water voids in the gel to salt concentration in the external solution n_s^{void} / n_s on the ratio of the size of water void R_{void} to the size of elementary lattice cell in the Flory-Huggins model d (which also defines the size of monomer unit and size of low molecular weight ions) for collapsed gel at $\chi = 2$ and different salt concentrations $n_s: 10^{-4}$ (a), 10^{-5} (b). Source [16]: Copyright 2002 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Vasilevskaya, V. V., and A. R. Khokhlov. 2002. Swelling and collapse of Swiss-cheese polyelectrolyte gels in salt solutions. *Macromolecular Theory and Simulations* 11(6):623-629. Used with permission.

distributed in an extremely inhomogeneous way: they are concentrated mainly within the voids [16].

The salt concentration in the voids (n_s^{void}) can be as high as that in the external solution (n_s) or slightly lower (Fig. 12.8a). The ratio n_s^{void}/n_s depends on the size of water voids, R_{void} (Fig. 12.8b). For small water voids this ratio is close to zero because of the relatively high concentration of floating counterions in the voids [16]. With increasing size of voids, the concentration of counterions within them drops to zero, the condition of electroneutrality of coexisting phases (polymer matrix and water voids) tends to be fulfilled, and n_s^{void} becomes approximately equal to $n_s : n_s^{void}/n_s = 1$ (Fig. 12.8b). It was estimated that for two sets of parameters represented in Fig. 12.8b, R_{void} , starting from which the salt concentration within water voids is approximately equal to that in the external solution, is about 500 nm or 5 μ m, correspondingly. In the the general case, characteristic radii can vary from a few nanometers to a few micrometers [16].

Now let us consider the effect of valence z (i.e. of charge) of co-ions on their distribution between water voids and the polymer matrix. The extent of this distribution is characterized by partition coefficient $k_{\rm D}$, i.e. the ratio of concentration of co-ions in water voids to that in polymer matrix: $k_{\rm D} = n_{\rm s}^{\rm void}/n_{\rm s}^{\rm mat}$. Figure 12.9a shows the partition coefficient $k_{\rm D}$ for ions of different valences z as a function of salt concentration in the external solution n_s . It is seen that the partition coefficient k_D is always higher than unity and that it increases with increasing valence (i.e. charge) of co-ions. At low salt concentrations n_s , the partition coefficient k_D is about 10 for monovalent ions (z = 1), reaches 10³ for bivalent ions (z = 2), and is greater than 10^6 for tetravalent ions (z = 4). The increase of the partition coefficient with increasing valence of co-ions is due to the enhancement of the Donnan effect. Indeed, the replacement of multivalent ions is accompanied by the replacement of the corresponding number of the counterions. Their simultaneous removal from the external solution to the polymer matrix should lead to a much higher loss in translational entropy in comparison with the case of monovalent saltions.

The effect of concentrating co-ions within voids in the gel is also valid for polymeric co-ions [17] if their size is smaller than the size of the voids. Fig. 12.9b shows the dependencies of the partition coefficient k_D on the degree of polymerization M and on the degree of ionization f_p of polyions. It is seen that the partition coefficient k_D increases with increasing length and degree of ionization of macroions. Note that at relatively high degrees of polymerization M and/or high degrees of ionization f_p , the macroions do not penetrate into the polymer matrix at all and the partition coefficient tends to infinity. This is caused by strong electrostatic repulsion of similarly charged macroions and the polymer matrix. Generally speaking, because of this repulsion, macroions cannot penetrate inside the polymer



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Fig. 12.9 (a) Partition coefficient k_D of ions between water voids and polymer matrix as a function of salt concentration in the external solution n_s for different valences of salt ions z: 1 (a), 2 (b), 3 (c), 4 (d). $R_{void} / d = 45$, $\chi = 0$. (b) Partition coefficient k_D of polymeric co-ions between the water voids and the gel matrix as a function of the degree of polymerization M of polyelectrolyte for $R_{void}/d = 10000$ and different values of the degree of ionization of polyelectrolyte f_p : 0.1 (*a*), 0.2 (*b*). Source [17]: Copyright 2004 American Institute of Physics. Vasilevskaya, V. V., A. A. Aerov, and A. R. Khokhlov. 2004. "Swiss-cheese" polyelectrolyte gels as media with extremely inhomogeneous distribution of charged species. *Journal of Chemical Physics* 120(19):9321-9329. Used with permission.

matrix and reach water voids in a finite time. Therefore, some additional procedures have to be applied to make macroions penetrate the polymer matrix and get trapped in water voids. For example, one could affect them with a strong electrostatic field. Another possibility is to use macro-molecules whose charge depends on pH (e.g. weak polyacid). In this case the penetration of macromolecules inside the gel can be accomplished in an acidic medium when macromolecules are neutral, while strong trapping in water voids can be achieved at elevated values of pH when the macromolecules acquire charges.

Thus, it was shown theoretically that polyelectrolyte Swiss-cheese gel can be used to concentrate charged species (both small ions and polymer ions) within water voids. This property makes such gels very promising for new nanotechnologies as a medium with a set of microreactors with well-defined and easily modified form and size.

One of the first experimental evidences of the concentrating of lowmolecular-weight ions with the same charge as network chains was obtained recently [25] on an example of anionic poly(sodium acrylate) gels with a specially designed porous structure and an anionic low-molecularweight dye – pyrocatechol violet. It was shown that the Swiss-cheese gel is enriched by co-ions of the dye in comparison with the homogeneous gel by 20%. Thus, indeed, Swiss-cheese polyelectrolyte gels are able to absorb similarly charged ions more efficiently than the corresponding homogeneous gels.

Another interesting feature of Swiss-cheese polyelectrolyte gels was recently observed by Starodoubtsev [18]. He managed to prepare Swisscheese polyelectrolyte gels containing embedded voids with charged walls. These gels were synthesized by three-dimensional copolymerization of cationic ((3-acrylamidopropyl) trimethylammonium chloride, APTAC) and uncharged (acrylamide) monomers in the presence of "oil in water" emulsion stabilized by an anionic surfactant. As the cationic monomer in the polymerization mixture was predominantly concentrated around emulsion droplets covered by the anionic surfactant, in the resulting network the surfaces of voids (formed in the place of droplets) became enriched in ionic monomer units in comparison with the polymer matrix. It was shown that such gels are much more efficient absorbers of oppositely charged surfactants in comparison with the gels with random distribution of the charged monomer units [18]. A striking difference in the absorption ability of the gels was attributed to the fact that the gels having regions enriched with cationic groups form a much stronger complex with the anionic surfactant because of high density of ionic groups [18].

Therefore, preparation of nanostructured inhomogeneous gels can significantly improve the ability of the gels to absorb ionic species from the solution, which is very promising for various applications of gels.

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