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Charge-Induced Microphase Separation in Polyelectrolyte Hydrogels with Associating Hydrophobic Side Chains: Small-Angle Neutron Scattering Study

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The structure of amphiphilic hydrogels of copolymers of acrylic acid and *n*-alkylacrylate swollen by D_2O was studied by small-angle neutron scattering (SANS). For most of the uncharged gels, a scattering peak is observed. It is attributed to the correlation between hydrophobic domains formed by self-assembled *n*-alkyl side chains. From the SANS data, the aggregation number of the hydrophobic domains was derived. It increases with increasing length of hydrophobic groups and also as a result of absorption of hydrophobic additives that are solubilized inside hydrophobic domains. The most important observation of this work consists of the fact that the introduction of charged groups into the gel leads to microphase separation with the formation of hydrophobic regions including several densely packed hydrophobic domains that alternate with hydrophilic regions swollen by water where most of the charged repeat units and counterions are located. The size of the hydrophobic regions decreases with increasing charge content. The microphase separation seems to be due to the effective interplay of two counteracting tendencies: hydrophobic association and electrostatic repulsion. When salt screening is added, the microphase separation disappears.

Introduction

Hydrophobically modified (HM) polyelectrolyte gels attract considerable attention because of their ability for molecular self-organization.[1−8] They contain hydrophilic groups responsible for the swelling of the gel in water and hydrophobic groups responsible for the association with the formation of hydrophobic domains. The counteracting tendencies provided by two antagonist types of groups in one hydrogel can lead to the formation of ordered nanostructures consisting of hydrophobic domains regularly dispersed in a matrix of water-swollen hydrophilic groups. These nanostructures can be controlled by changing the hydrophobic−hydrophilic balance of the gel, for example, by varying the content and the size of hydrophobic groups, by varying the degree of charging of the gel, or by adding hydrophobic substances, which are preferentially solubilized in the hydrophobic domains. Self-assembly in HM hydrogels is of interest not only for fundamental investigations, but also for practical applications. For instance, due to self-organization the HM gels show an interesting shape memory behavior.[5] Due to the ability of hydrophobic domains to absorb nonpolar substances, the HM gels are very promising for removing hydrophobic impurities from water. Also, they can be regarded as carriers for controlled drug delivery, since hydrophobic domains can serve as reservoirs for drugs that are poorly soluble in water.[8]

Obviously, there is a need for understanding the structural organization of HM gels at a molecular level. The aggregation of hydrophobic side chains in HM polyelectrolyte gels was studied by the fluorescence probe method and NMR spectroscopy.[6] These methods allowed one to estimate the critical aggregation concentration and the fraction of hydrophobic groups included in the domains. The structure of hydrophobic domains in HM water-swollen gels was studied by Osada et al. using wide-angle and small-angle X-ray diffraction.[2−5,7] These structural studies were performed for hydrogels with long *n*-alkyl side groups (*n*-octadecyl and *n*-hexadecyl groups), which are able to crystallize upon self-assembly into hydrophobic domains. These crystalline domains are very stable and can be disrupted only upon heating above the melting temperature. It is expected that the use of shorter hydrophobic side groups with lower attraction energy should provide HM gels that are more susceptible to the variation of the external conditions. As the self-assembly in HM polyelectrolyte gels is governed by the competition between hydrophobic attraction and electrostatic repulsion, one of the most efficient factors affecting the self-

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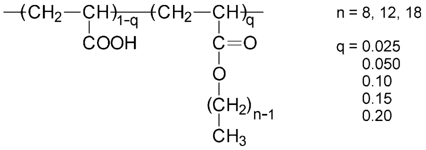

Figure 1. Chemical structures of HM PAA gels studied in this paper.

assembly is the degree of charging of the gel. To our knowledge, there has been no systematic investigation of the effect of the degree of charging (at the fixed content of hydrophobic groups) on the structure of HM polyelectrolyte gels.

The present paper is dedicated to the small-angle neutron scattering (SANS) study of the structure of water-swollen polyelectrolyte gels based on copolymers of acrylic acid (hydrophilic units) and *n*-alkylacrylates (hydrophobic units) with different lengths of *n*-alkyl chains (*n*-octyl, *n*-dodecyl, and *n*-octadecyl) (Figure 1). Emphasis is given to the effect of charging on the structure of the gels.

This paper is organized as follows. In the first part of the paper, we describe the study of uncharged gels (at pH 3). The hydrophobic attraction in these gels was varied by changing the content of hydrophobic *n*-alkyl side groups and the length of their *n*-alkyl chains. In the second part of the paper, we describe the effect of charging of the gel chains (counteracting the hydrophobic attraction) on the gel structure. For this purpose, we fixed the content and the length of hydrophobic groups inside the gel, but we varied the content of charged repeat units from 0 to 20 mol %.

Experimental Section

1. Materials. HM hydrogels were prepared by free-radical copolymerization of acrylic acid (AA) and *n*-alkylacrylate in *N*,*N*′-dimethylformamide using *N*,*N*′-methylenebis(acrylamide) as a cross-linker (1 cross-link per 66 repeat units). Details of preparation and characterization of the polymer gels are described elsewhere.[6] Here it is important to emphasize that by ^{13}C NMR spectroscopy it was shown[6] that *n*-alkylacrylate units are randomly distributed along the polymer chains. The gels are denoted in terms of type and molar content of hydrophobic comonomer units. For example, C8-20% indicates a gel containing 20 mol % of *n*-octylacrylate (C8) and 80 mol % of AA repeat units.

D_2O (99.9 atomic % D, Fluka) and ethanol (Fluka) were used as received. Water was purified with a Milli-Q system (Millipore).

2. Sample Preparation. To obtain the gel powder, the gels swollen by ethanol were crushed by passing through the syringe ($d = 2.5$ mm) and then freeze-dried. The samples for SANS measurements were prepared by weighing the gel powder and by adding a calculated amount of solvent (D_2O) to attain a required degree of swelling β ($\beta = (m_{sw} - m_0)/m_0$, where m_{sw} is the mass of the swollen gel and m_0 is the mass of the dry gel). The obtained gel was allowed to swell at room temperature for at least 2 weeks before the measurements. Comparison of spectra from the gels stored for different periods of time shows that 2 weeks is enough time to get equilibrated samples.

To prepare charged gels, a calculated amount of sodium hydroxide solution was added to uncharged gel samples. The content of charged repeat units in the gel α is equal to the sum of the degree of neutralization α_1 and the degree of self-dissociation of AA units α_2: $\alpha = \alpha_1 + \alpha_2$. In our conditions, assuming a dissociation constant $K_a = 1.8 \times 10^5$ for an AA unit in pure water,[6,9] the degree of dissociation of AA units is very low ($\alpha_2 < 3\%$) at zero degree of neutralization ($\alpha_1 = 0$).

3. Methods: SANS Measurements. SANS measurements were done at the YuMO instrument of the high-flux pulsed reactor IBR-2 at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia.[10,11] Sample holders were specially designed homemade dismountable disklike quartz cells with a diameter of 2 cm and a path length of 2 mm. The samples were kept at 20.00 ± 0.03 °C.

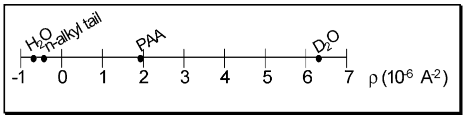

Figure 2. Scattering length densities of the components of HM PAA hydrogels.

All data were treated according to standard procedures of small-angle isotropic scattering. The spectra were corrected for the sample transmission, the sample thickness, and electronic noise. The pure solvent (D_2O) was used as background for the samples. The SANS intensity distribution was then presented as a function of the scattering vector $Q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the neutron wavelength and θ is the scattering angle. The Q range in this study was from 0.006 to 0.5 $Å^{-1}$.

SANS arises from the spatial variations of the scattering length density in the sample. The values of the scattering length densities of the components of HM poly(acrylic acid) (PAA) hydrogels are indicated in Figure 2.

From these data, it is evident that when D_2O is used as a solvent the hydrophobic side chains of the gel have higher contrast and therefore they cause stronger scattering in comparison with the PAA backbone. The polymer backbone can be matched by a 40/60 D_2O/H_2O mixture, but in this medium the scattering by hydrophobic tails is rather weak. Therefore, in this paper D_2O was used as a solvent and it was assumed that in HM PAA gel swollen by D_2O the hydrophobic *n*-alkyl side chains are mainly responsible for the scattering, if the content of these chains is rather significant.

Results and Discussion

1. Uncharged Gels. First we consider uncharged HM PAA gels swollen by D_2O in an acidic medium (at pD 3) in order to suppress the self-dissociation of carboxylic groups. From NMR data, it is known[6] that in these gels most of the hydrophobic side chains are aggregated into hydrophobic domains in order to avoid contact with water.

Figures 3 and 4 show the dependencies of neutron scattering intensity I on the scattering vector Q for uncharged HM PAA gels at degree of swelling $\beta = 0.5$. It is seen that for most of the gels a scattering peak is observed. No peak is detected only for the less hydrophobic gel under study (C8-2.5%) as well as for PAA gel without *n*-alkyl side groups. With increasing content and length of hydrophobic side chains, the peak becomes more pronounced. We suggest that the peak is due to a correlation between hydrophobic domains formed by self-assembled *n*-alkyl side chains.

It is important to note that the peak position is independent of the way of sample preparation: by addition of solvent to the dry gel or by partial evaporation of solvent from highly swollen gel. Therefore, we can conclude that the hydrophobic domains are equilibrium structures.

1.1. Form of Domains. In a general case, the scattering intensity from a system of particles is described by the equation $I(Q) = |F(Q)|^2 S(Q)$, where $F(Q)$ is the form factor of the particle and $S(Q)$ is the structure factor. In our case, the form factor contains the information about the shape and size of hydrophobic domains, while the structure factor depends on the mutual arrangement of hydrophobic domains.

In side-chain amphiphilic linear and cross-linked polymers, a great variety of structures can be observed.[2,7,12−21] Let us consider the shape and size of hydrophobic domains in our system. The easiest way to estimate the form factor of hydrophobic domains is to realize the conditions at which

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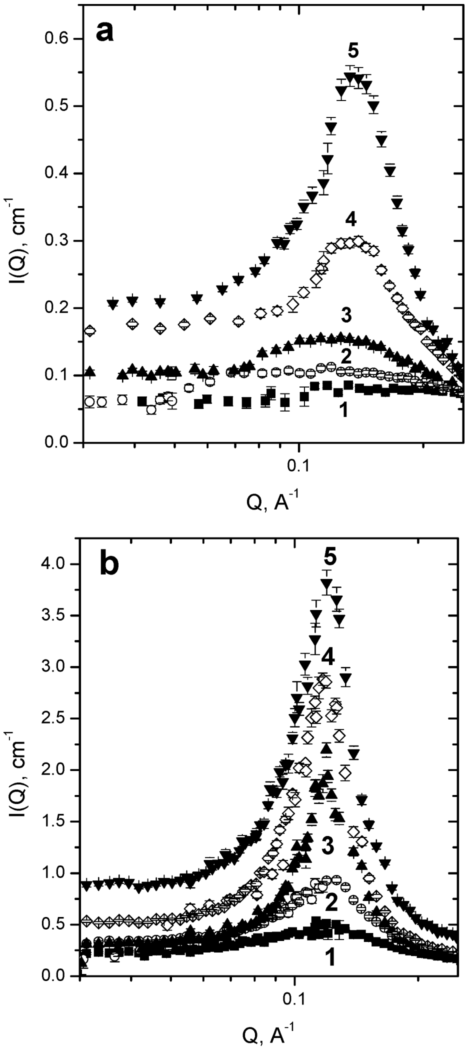

Figure 3. SANS profiles for uncharged HM PAA gels (swollen by D_2O at pD = 3) with fixed polymer concentration (60 wt %) and different contents of *n*-octylacrylate (a) repeat units ((1) 0 mol %; (2) 2.5 mol %; (3) 5 mol %; (4) 10 mol %; (5) 20 mol %) and *n*-dodecylacrylate (b) repeat units ((1) 2.5 mol %; (2) 5 mol %; (3) 10 mol %; (4) 15 mol %; (5) 20 mol %).

there is no correlation in the positions of the domains or *Q* corresponds to larger scales than the interdomain distances. In these cases, the scattering can be regarded as the scattering of independent particles, that is, $I(Q) = |F(Q)|^2$.

Weak interdomain interactions can be observed at a small volume fraction of associating hydrophobic groups and at a high degree of swelling of the gel. For uncharged gels, such a situation takes place only for the samples with low content of short hydrophobic groups, for instance, for C8-2.5% and C8-5% gels that are able to swell significantly in water.

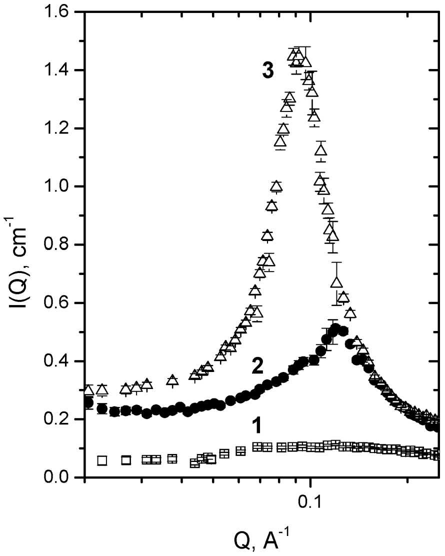

Figure 4. SANS profiles for uncharged HM PAA gels (swollen by D_2O at pD = 3) with *n*-alkyl chains of different lengths: *n*-octyl (1), *n*-dodecyl (2), and *n*-octadecyl (3). In all samples, the polymer concentration is 60 wt %, and the content of hydrophobic units is 2.5 mol %.

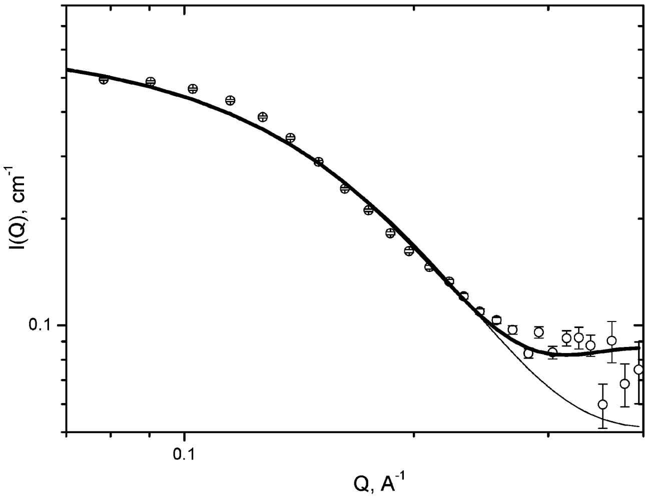

Figure 5. The scattering curve of the uncharged C8-5% gel (swollen by D_2O) (circles) and the fits of experimental data by the form factors of an ellipsoid with the semiaxes of 10 ± 2 Å and 19 ± 2 Å (normal line) and a sphere with the radius of 14 ± 2 Å (bold line). The polymer concentration is 10 wt %.

The scattering curve of C8-5% gel at a rather high degree of swelling ($\beta = 9$) is presented in Figure 5. It is seen that the curve does not contain a structure peak, which indicates that the interdomain correlations are eliminated or small. The scattering curve can be well described by the form factor of a sphere of radius 14 ± 2 Å or by the form factor of an ellipsoid with the semiaxes of 10 ± 2 Å and 19 ± 2 Å (for comparison, the length of a fully extended *n*-octyl side chain is equal to ca. 10 Å[22]). Thus, in the gels with low content of hydrophobic groups the hydrophobic domains are of spherical or ellipsoidal shape. The spherical (or ellipsoidal) form of the domains at such a high concentration of hydrophobic groups (0.09 mol/L for C8-5% gel at a degree of swelling equal to 9) can be due to the large effective volume of the twin-tailed hydrophilic headgroup.

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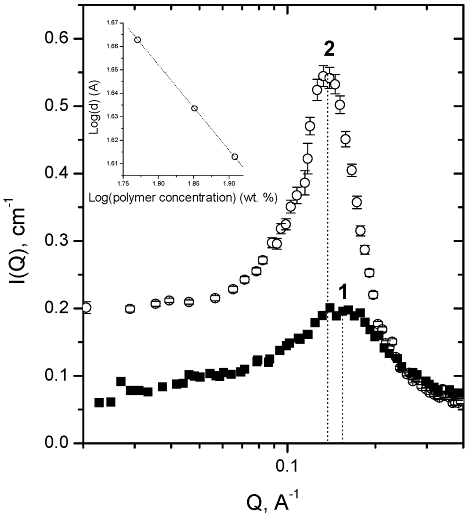

Figure 6. SANS profiles for uncharged C8-20% gels with different polymer concentrations: (1) 80 wt %; (2) 60 wt %. In the inset: the dependence of characteristic distances d on the polymer concentration. The slope of the straight line is equal to -0.35.

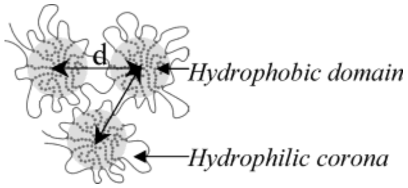

Figure 7. Schematic representation of the HM gel structure.

In our further consideration, we will assume that hydrophobic domains are of spherical (or ellipsoidal) form in all the samples of uncharged gels under study, independent of the content and length of hydrophobic groups.

1.2. Aggregation Number of Domains. In most of the samples of uncharged gels, the structure peak is always present, indicating the correlation between hydrophobic domains (Figures 3 and 4). With increasing degree of swelling, the position of the structure peak shifts toward small angles, which indicates that hydrophobic domains become farther apart (Figure 6). The distance between hydrophobic domains gradually increases with decreasing polymer concentration according to the power law $C_p^{-0.35}$. The exponent close to $-1/3$ can be attributed to an isotropic dilution process of scattering objects of a given size.[16]

From the positions of the peaks, the mean distances d between the domains were determined ($d = 2\pi/Q^*$) (Figure 7). They are compiled in Table 1. From Table 1, it is seen that the interdomain distances increase with increasing chain length of n-alkyl groups but do not depend on the content of hydrophobic groups.

From SANS data, the values of the average aggregation number (N_{agg}) were determined as the ratio of the concentration of hydrophobic tails C_{tail} to the concentration of hydrophobic domains C_{domain}: $N_{agg} = C_{tail}/C_{domain}$. The concentration of hydrophobic domains can be estimated from the interdomain distances d and the character of distribution of the domains in the bulk according to the equation $C_{domain} = n_{domain}/(N_A a^3)$, where N_A is the Avogadro number, a^3 is the volume of the unit cell, and n_{domain} is the number of hydrophobic domains in one unit cell. Since we do not know exactly the character of distribution of the domains, the estimation of N_{agg} was made for different types of arrangement of hydrophobic domains: simple cubic (SC, with $a = d$ and $n_{domain} = 1$), body-centered cubic (BCC, with $a = (2/\sqrt{3})d$ and $n_{domain} = 2$), face-centered cubic (FCC, with $a = (\sqrt{2})d$ and $n_{domain} = 4$), and densely packed hexagonal (DPH, with $a = (\sqrt{2})d$ and $k = 4$) lattices.[16,23,24] The most densely packed lattices (BCC, FCC, or hexagonal) seem to be more probable, because the experimental and theoretical studies of similar systems with spherical hydrophobic domains have found FCC and BCC structures in most cases.[25] The results obtained are summarized in Table 1.

Table 1. Estimation of Aggregation Numbers of Hydrophobic Domains in Uncharged HM PAA Gels in D_2O^a

gel	scattering maximum Q^*, Å^{-1}	spacing d, Å	aggregation number SC^b	BCC^b	FCC/DPH^b
C8-10%	0.137	46	47	36	33
C8-15%	0.137	46	65	50	46
C8-20%	0.137	46	82	63	58
C8-20% + benzene	0.130	49	96	74	68
C12-2.5%	0.119	53	19	15	14
C12-5%	0.119	53	37	28	26
C12-10%	0.119	53	66	51	47
C12-15%	0.119	53	91	70	64
C12-20%	0.119	53	112	86	79
C18-2.5%	0.093	67.5	39	30	28

^{a} The polymer concentration is 60 wt % in all cases. ^{b} SC, simple cubic lattice; BCC, body centered cubic lattice; FCC, face centered cubic lattice; DPH, densely packed hexagonal lattice.

1.2.1. Effect of the Content of Hydrophobic Side Chains. From Table 1, it is seen that both for C8 and C12 gels the aggregation number increases with the increase of content of hydrophobic groups. This means that for the gels with a low fraction of associating units the formation of big domains that ensure complete screening of hydrophobic groups from water becomes difficult. Indeed, theoretical considerations[13,14] show that in uncharged amphiphilic side-chain polymers the size of the domains is determined by a balance between the following opposing driving forces. On one hand, the tendency to decrease the contact of the surface of the hydrophobic core with water favors the growth of the domains in size. On the other hand, the steric repulsion and the loss of conformational entropy of polymer chains in the shell region limit the growth of domains to a finite size. The smaller the fraction of associating units in the gel, the bigger the size of hydrophilic chains attached to one associating group and the more overcrowded the shell region of the domain. Therefore, the steric repulsion between headgroups and the loss of conformational entropy of polymer chains in the shell region are responsible for the smaller aggregation number hydrophobic domains in the gels with a low content of associating hydrophobic units. Also, when the associating units in the gel are located farther apart, this lowers the cooperativity of their interaction.

1.2.2. Effect of the Length of Hydrophobic Side Chains. From Table 1, it is seen that the aggregation number of hydrophobic domains increases with increasing length of associating groups, which is expected. The analogous behavior is observed for low molecular weight surfactants.[26] In the case of amphiphilic side-chain polymers, the growth of hydrophobic domains with increasing length of associating groups can be explained

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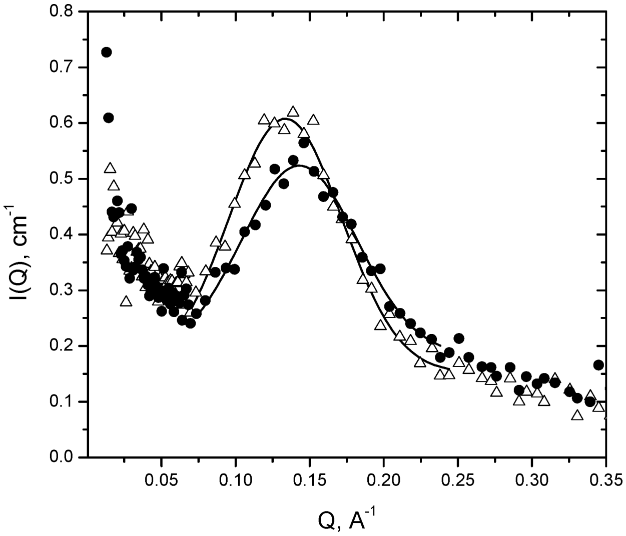


Figure 8. SANS profiles for uncharged HM PAA gels C8-20% (swollen by D$_2$O at pD = 3) before (dark circles) and after (triangles) the absorption of benzene (the sample with absorbed benzene contains 1 mol of benzene per 1.15 mol of hydrophobic side chains). The polymer concentration is 77 wt % in both cases. The solid lines were obtained by approximation of the experimental data by a Gaussian function.

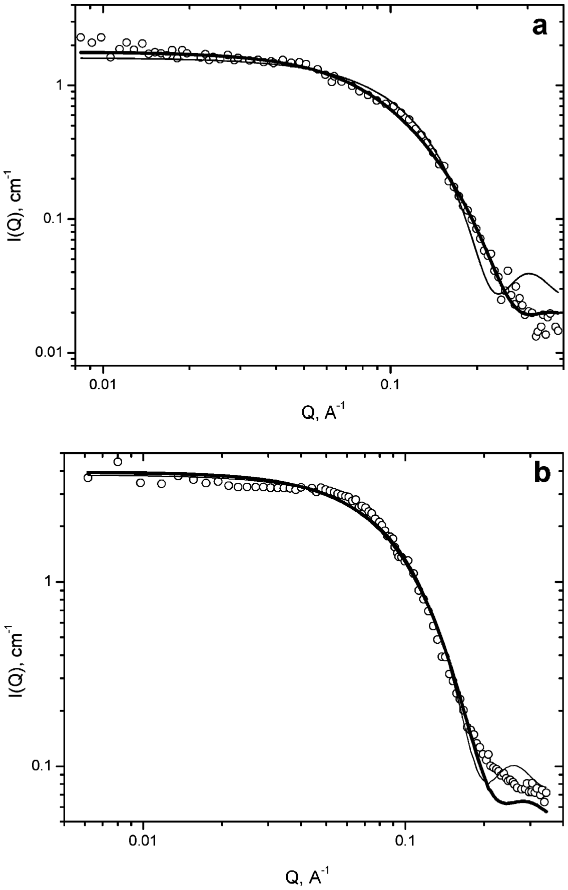


Figure 9. The scattering curves of C8-20% (a) and C12-20% (b) gel samples with 6 mol % of charged groups (swollen by D$_2$O) (circles) and the fits of experimental data by the form factors of an ellipsoid with the semiaxes of 14 ± 2 Å and 34 ± 2 Å (bold line) and a sphere with the radius of 19 ± 2 Å (normal line) in the case of C8-20% gel (a) and by the form factors of an ellipsoid with the semiaxes of 18 ± 2 Å and 32 ± 2 Å (bold line) and a sphere with the radius of 22 ± 2 Å (normal line) in the case of C12-20% gel (b). The polymer concentration is 5 wt % in both cases.

by two factors.[13] First, the attractive force of longer *n*-alkyl groups is stronger. Second, the longer associating side chains form larger cores and hence larger shell volume, which is less crowded and therefore can accommodate more units of hydrophilic backbone.

Figure 4 shows that with increasing chain length of the *n*-alkyl side group the intensity of scattering peak increases. Moreover, for the gels with longer *n*-alkyl chains the correlations in the arrangement of hydrophobic domains start to appear at lower content of *n*-alkyl groups (Figure 4). These facts result from stronger association of *n*-alkyl groups with longer chains.

1.3. Effect of a Hydrophobic Additive. For C8-20% and C18-2.5% gels, it was shown that the absorption of hydrophobic low molecular weight substances such as benzene leads to the shift of the scattering peak to lower Q values (Figure 8). This is obviously due to the growth of the domains (Table 1) as a result of solubilization of the hydrophobic additive in the hydrophobic core of the domains.

Thus, uncharged HM gels are composed of densely packed hydrophobic domains surrounded by a hydrophilic shell of acrylic acid units (Figure 7). These domains are homogeneously dispersed in the bulk of the gel.

2. Charged Gels. Charged gels were obtained by addition of a calculated amount of sodium hydroxide solution to HM PAA gels in acidic form.

2.1. Form of Domains. For charged gels that are able to swell significantly in water, it is easy to prepare the samples with small polymer concentration, at which the interdomain correlations are eliminated. For such highly swollen gels, the scattering curves do not contain any structure peak, and this enables us to determine the form factor. It was shown that these curves can be well fitted by the form factor of a sphere or an ellipsoid. For example, for C8-20% gel with 6 mol % of charged groups the scattering curves are well described by the form factor of either a sphere with the radius of 19 ± 2 Å or an ellipsoid with the semiaxes of 14 ± 2 Å and 34 ± 2 Å (Figure 9a). For C12-20% gel with 6 mol % of charged groups, the scattering curves are well described by the form factor of a sphere with the radius of 22 ± 2 Å or an ellipsoid with the semiaxes of 18 ± 2 Å and 32 ± 2 Å (Figure 9b). When comparing the data for charged C8-20% and C12-20% gels, we see that the radius of the hydrophobic domain increases with increasing length of the hydrophobic tail, which is expected.

2.2. Aggregation Number of Domains. For charged gels at a rather low degree of swelling (which is achieved by the addition of solvent in deficiency in comparison with the equilibrium swelling), the structure peak is observed (Figure 10). From Figure 10, it is seen that with increasing content of hydrophobic groups the peak becomes more pronounced, but its position remains unchanged as for the case of uncharged gels. For charged C8 gels, the values of the average aggregation number (N_{agg}) of hydrophobic domains were estimated, as was described above. The obtained data are compiled in Table 2. It is seen that similarly to the case of uncharged gels, the values of the aggregation number increase with increasing content of *n*-alkyl side chains.

Let us compare the scattering curves for uncharged and charged C8-20% gels at the same polymer concentration (i.e., at the same degree of swelling) (Figure 11). It is seen that the structure peak for the charged gel is shifted to higher Q values. Since for both cases all hydrophobic groups are aggregated, this shift indicates that the charged gel contains a higher concentration of smaller hydrophobic domains. Comparison of the values of N_{agg} in charged and

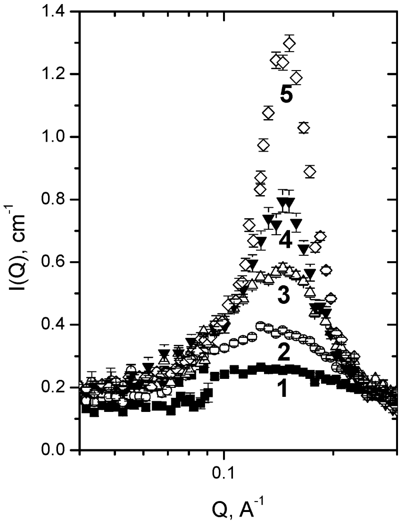


Figure 10. SANS profiles for HM PAA C8 gels containing 20 mol % of charged units with a fixed polymer concentration (60 wt %) and different contents of the hydrophobic units: (1) 2.5 mol %; (2) 5 mol %; (3) 10 mol %; (4) 15 mol %; (5) 20 mol %.

Table 2. Estimation of Aggregation Numbers of Hydrophobic Domains in Charged HM PAA Gels with 20% of Charged Groups Swollen by D_2O[a]

gel	scattering maximum Q^*, Å^{-1}	spacing d, Å	aggregation number SC[b]	BCC[b]	FCC/DPH[b]
C8-10%	0.148	42	37	28	26
C8-15%	0.148	42	52	40	36
C8-20%	0.148	42	65	50	46

[a] The polymer concentration is 60 wt % in all cases. [b] SC, simple cubic lattice; BCC, body centered cubic lattice; FCC, face centered cubic lattice; DPH, densely packed hexagonal lattice.

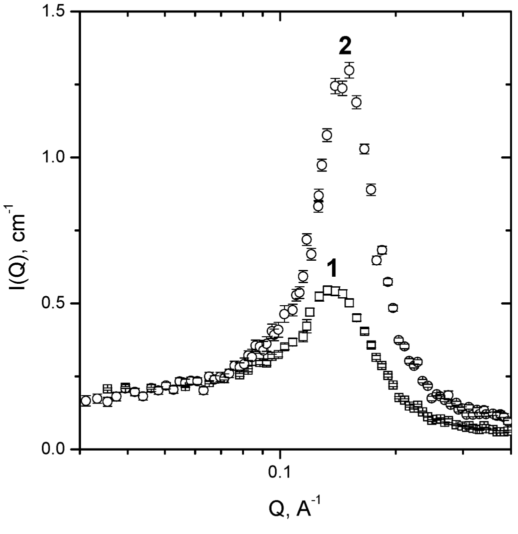


Figure 11. SANS profiles for uncharged C8-20% gels (1) and charged C8-20% gels containing 20 mol % of charged groups (2). The polymer concentration is 60 wt % for both cases.

uncharged C8-20% gels (Tables 1 and 2) also shows that charging leads to the decrease of the aggregation number, which may result from the electrostatic repulsion of the charged headgroups.

From Figure 11, it is also seen that with increasing charge density the intensity and the half-width of the structure peak increase, indicating better ordering in the mutual arrangement of the domains. This may be due to free counterions that counteract the formation of spatial inhomogeneities, which may entrap some of these counterions. A similar effect is observed for C12 gels.

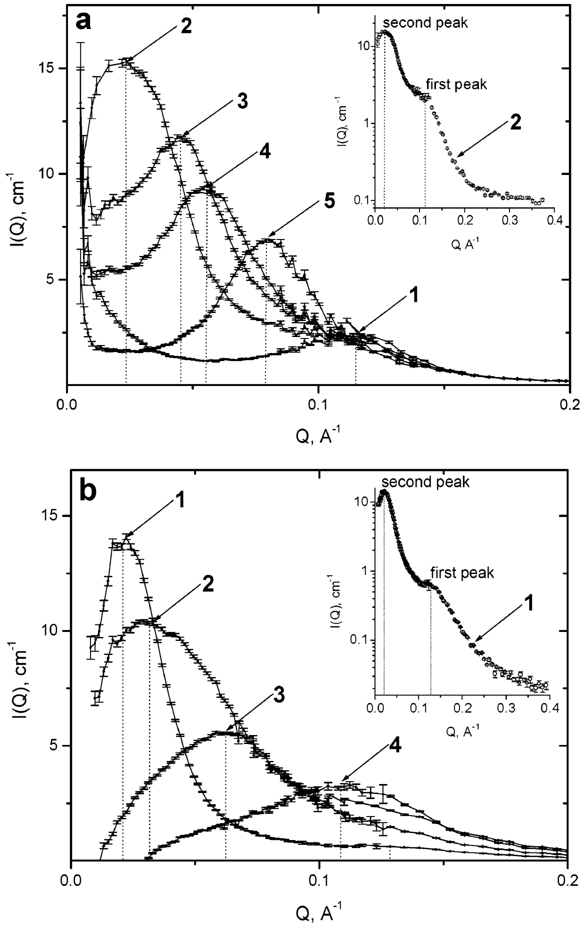


Figure 12. SANS profiles for charged C12-20% (a) and C8-20% (b) HM PAA gels with a fixed polymer concentration (30 wt %) and different contents of charged carboxylic groups: (1) 1 mol %; (2) 2 mol %; (3) 4 mol %; (4) 6 mol %; (5) 20 mol %. In the insets, some of the curves are presented in logarithmic scale.

3. Microphase Separation. 3.1. C12 Gels. Let us consider the effect of charging on the scattering of C12-20% gels swollen by D_2O. From Figure 12a, it is seen that at a low content of charged groups (1 mol %) the scattering curve contains one correlation peak at 0.115 Å^{-1}, which corresponds to a characteristic distance of 55 Å, the same as for the uncharged C12-20% gel (Table 1). Increasing the charge content from 1 to 2 mol % leads to dramatic changes of the scattering curve: in addition to the first peak at 0.115 Å^{-1}, a second strong scattering peak at low angles appears; its position corresponds to a characteristic distance of 280 Å (Figure 12a (inset)). Simultaneously, the first scattering peak slightly shifts to wider angles. Therefore, along with densely packed hydrophobic domains responsible for the first peak, new scattering objects located far from each other appear in the system.

The presence of two scattering peaks at a low charge content means that in the gels either the new scattering objects coexist with densely packed hydrophobic domains or the new scattering objects are composed of densely packed hydrophobic domains. To discriminate between these two possibilities, we studied the effect of polymer concentration on the position of the scattering peak (at a fixed charge content). The results are presented in Figure 13. It is seen that when the polymer concentration in the gel decreases the position of the first peak remains uncharged (at 55 Å), while the second peak shifts to smaller *Q* values (i.e., higher spacing). In other words, dilution of the gel does not affect the interdomain distances. This

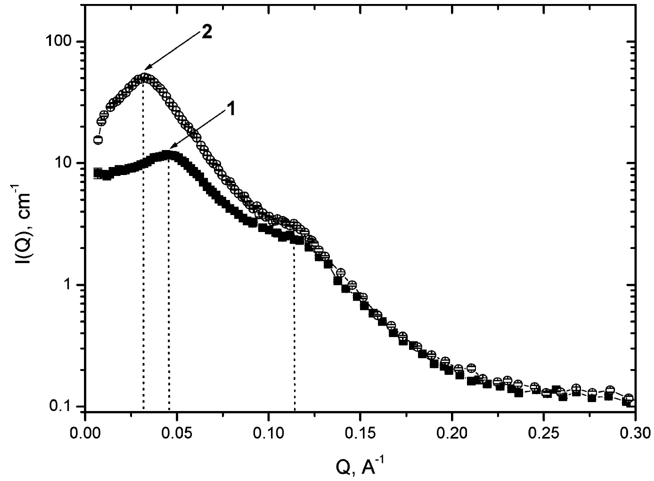


Figure 13. SANS profiles for charged C12-20% HM PAA gels containing 4 mol % of charged units with different polymer concentrations: (1) 30 wt %; (2) 20 wt %.

indicates the nonuniform arrangement of hydrophobic domains with the formation of clusters composed of several densely packed hydrophobic domains. Gel swelling (i.e., decrease of polymer concentration) leads to the increase of the distances between clusters, while the mean interdomain distance inside the cluster remains unchanged. Therefore, the appearance of the second peak seems to be due to the formation of clusters consisting of densely packed hydrophobic domains.

The peak responsible for intercluster distances becomes less intensive and shifts to higher *Q* values with increasing charging (Figure 12a). These observations can be explained by breaking of big clusters into smaller ones at charging. As a result of such breaking, the total number of clusters in the system increases, leading to the decrease of the average intercluster distances (the intercluster second peak shifts to higher *Q* values). Simultaneously, the intensity of the peak becomes lower because of the smaller size of the scattering objects.

Two peaks are observed in gels with a low content of charged units (2−6 mol %). In rather highly charged gels with 20 mol % of charged groups, only one peak is present. The position of this peak gradually shifts to low *Q* values with decreasing polymer concentration (Figure 14), indicating that the distribution of scattering objects in this gel is uniform. Therefore, clusters disappear when the gel is highly charged.

The data obtained allow us to propose the following structural organization of the gel (Scheme 1). Uncharged gel consists of densely packed hydrophobic domains (Scheme 1a). When 2 mol % of charged groups are introduced in the gel, some of the hydrophobic domains are disrupted as a result of electrostatic repulsion. Disruption of some amount of the hydrophobic domains leads to the formation of hydrophilic channels, which contain polymer chains swollen by water and counterions. These channels break the gel into clusters consisting of several hydrophobic domains. The charged polymer units are located mainly on the surface of these clusters, while the interior of the clusters remains uncharged. Such nonhomogeneous distribution of charged units gives the possibility to conserve a significant amount of hydrophobic domains of the optimum size (Scheme 1b). With further increase of the content of charged groups, the size of clusters decreases because of electrostatic repulsion (Scheme 1c). Finally, at 20 mol % of charged groups the clusters disappear, and the gel swells isotropically (Scheme 1d).

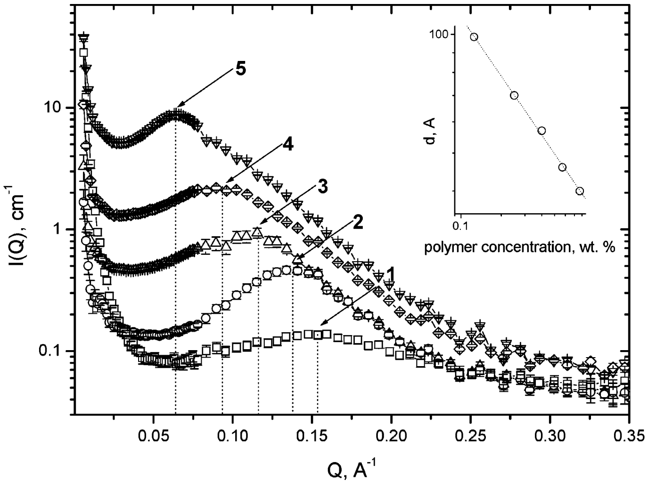
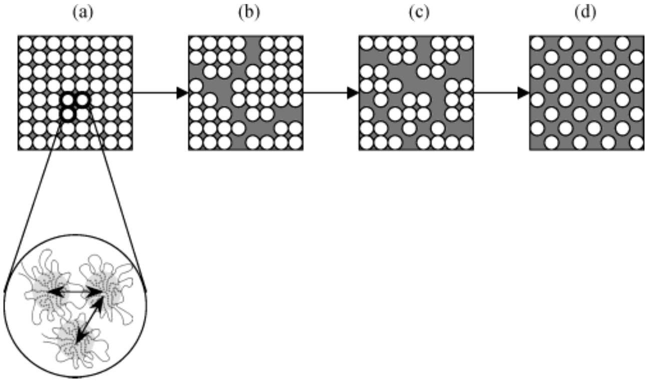


Figure 14. SANS profiles for C8-20% gels containing 20 mol % of charged groups with different polymer concentrations: (1) 77 wt %; (2) 57 wt %; (3) 40 wt %; (4) 25 wt %; (5) 12.5 wt %. In the inset: the dependence of characteristic distances *d* on the polymer concentration. The slope of the straight line is equal to −0.5.

Scheme 1. Schematic Representation of the Charge-Induced Microphase Separation Process[a]



[a] (a) Structure of uncharged and slightly charged (1 mol %) HM gels. (b,c) Structures of moderately charged gels (2 and 4 mol %, respectively). (d) Structure of highly charged gels (20 mol %).

So, what we observe is some kind of microphase separation, which arises as a result of competition of hydrophobic association and electrostatic repulsion, when the electrostatic repulsion is rather weak. When the electrostatic repulsion becomes stronger, the microphase separation disappears.

The conditions of stability of the microphase structure are shown in the phase diagram presented as content of charged units α versus concentration of polymer β (Figure 15). It is seen that the area of existence of microphase separation is confined within low α and β values. So, the strengthening of electrostatic repulsion (at increasing content of charged units α) destroys the microphase separation.

3.2. C8 Gels. A similar phenomenon (i.e., microphase separation) is observed for HM gels with shorter hydrophobic side chains, C8-20% gels (Figure 12b). From Figure 12b, it is seen that a strong intercluster peak at low *Q* values appears at the introduction of charged units in the C8-20% gel. With the increase of charge content, the intercluster peak shifts to higher *Q* values and its intensity gradually decreases as was observed for C12-20% gels. So, for both gels (C8-20% and C12-20%) the characteristic correlation length of the microphase structure can be

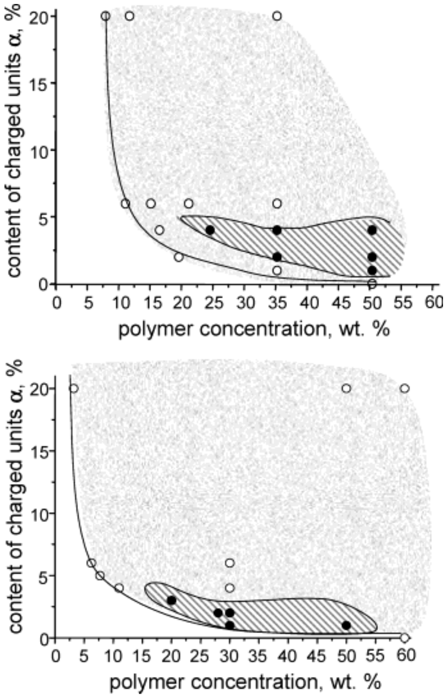


Figure 15. Phase diagram for HM PAA C12-20% (top) and C8-20% (bottom) hydrogels with different contents of charged units swollen by D_2O. In the phase diagram, the microphase separation region is shaded by inclined lines, the region of the swollen gel with homogeneously distributed hydrophobic domains is marked by gray color, and the regions corresponding to the phase separation are left white. The line dividing the area of the phase diagram between white and gray regions corresponds to equilibrium degrees of swelling of the C12-20% gels. The filled symbols denote systems with two structure peaks (case of microphase separation), and the open symbols denote the systems with a single structure peak (absence of microphase separation).

regulated in a wide range by changing the content of charged units. At the same time, the intercluster peak in C12 gels is narrower, which indicates that in more hydrophobic gels the microphase structure is more ordered.

From the comparison of the scattering curves of C8 and C12 gels (Figure 12a,b), it is seen that in C8-20% gels the microphase separation was observed already at 1% of charged groups, that is, at a lower content of charged units α than in the case of C12-20% gels. This may be due to the fact that C8-20% gels are less hydrophobic than C12-20% gels and therefore in these gels a smaller increase of the content of charged groups could lead to appreciable reorganization of hydrophobic domains.

Comparison of phase diagrams for C8-20% and C12-20% gels shows that the area of microphase separation is smaller in the gels with lower hydrophobicity (Figure 15a,b). In other words, in less hydrophobic gels it is enough to introduce a smaller amount of charged units in order to destroy the hydrophobic clusters. Also, from Figure 15 it is seen that in contrast to the C12-20% gel, the lower border of the microphase separation region for the C8-20% gel coincides with the line corresponding to equilibrium degrees of swelling of the gel. Thus, in the case of C8-20% gels microphase separation exists not only under conditions of deficiency of solvent, but also at the equilibrium swelling.

3.3. Effect of Salt. Microphase separation with the formation of microdomain structures can be observed for many polymer systems:$^{27-37}$ melts and solutions of block copolymers, mixtures of weakly charged polyelectrolytes with neutral polymers, solutions of weakly charged polyelectrolytes in a poor solvent, and so forth. In all these systems, microphase separation appears as a result of the interplay of the trend toward segregation acting on a microscopic scale and a stabilizing factor on a somewhat larger scale, which counteracts segregation. In the present case, the hydrophobic association is responsible for segregation, while charged units oppose segregation.

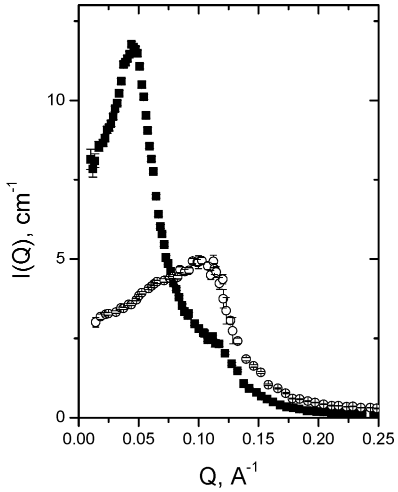


Figure 16. SANS profiles for charged C12-20% gels with fixed polymer concentration (30 wt %) and content of charged groups (4 mol %) in the absence of salt (circles) and in the presence of 0.077 mol/L NaCl (squares).

To prove the crucial role of electrostatic repulsion and translational entropy of counterions in the microphase separation observed in the present system, the effect of salt was studied. For this purpose, the C12-20% gel containing 4 mol % of charged groups was used. It was shown that the addition of salt leads to total disappearance of the second peak corresponding to intercluster distances (Figure 16). At the same time, the first interdomain peak is shifted toward low *Q* values corresponding to 63 Å instead of 55 Å in the salt-free case. These data evidence that salt leads to suppression of microphase separation and to homogenization of the arrangement of hydrophobic domains. This can be due to screening of the electrostatic repulsion by salt molecules.

Thus, we can conclude that the observed microphase separation is induced by charging. When the effect of charging is suppressed, the microphase separation disappears.

Conclusions

Amphiphilic polyelectrolyte hydrogels of HM PAA being immersed in aqueous media undergo self-organization

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with the formation of hydrophobic domains. In SANS spectra of most of the gels, the structure peak arising from the correlation in the arrangement of the hydrophobic domains is observed. It was shown that for uncharged gels the homogeneous distribution of the hydrophobic domains takes place, while for slightly charged gels the microphase separation with the formation of regularly arranged hydrophobic regions consisting of several densely packed hydrophobic domains is observed. In this case, hydrophobic regions are separated by hydrophilic regions swollen by water where most of the charged repeat units and counterions are located. The microphase separation is due to effective competition of two counteracting factors: hydrophobic association and electrostatic repulsion. In contrast to microphase separation in other gels observed up to now,[36,37] in the present system the size of microdomains can be regulated in a wide range by varying the content of charged units, the content and length of hydrophobic *n*-alkyl tails, and so forth.

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