

Effect of the Mobility of Charged Units on the Microphase Separation in Amphiphilic Polyelectrolyte Hydrogels

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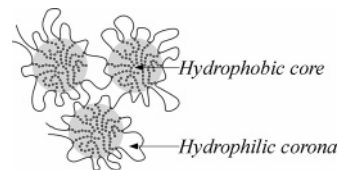
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The effect of the migration of charged units on the structure of hydrophobically modified polyelectrolyte gels swollen by D₂O was studied by small-angle neutron scattering on an example of gels of terpolymers of acrylic acid, *n*-dodecylacrylate, and 2-acrylamido-2-methyl-1-propanesulfonic acid (quenched charged units) and gels of copolymers of partially neutralized acrylic acid and *n*-dodecylacrylate (annealed charged units). The content of charged units did not exceed 20 mol %, so that the electrostatic repulsion was too weak to disrupt the hydrophobic domains formed by self-assembled *n*-dodecyl chains, which was evidenced by NMR data. It was shown that upon increasing the charge content both types of gels undergo microphase separation with the formation of hydrophobic clusters consisting of several densely packed hydrophobic domains and hydrophilic regions swollen by water, where most of the charged repeat units and counterions are located. The dimensions of the nanostructure of the gels with quenched and annealed charged groups were compared. It was shown that the size of clusters in the gels with annealed charged units is much bigger than that in the gels with the same fraction of quenched charged units. This effect was attributed to a much weaker electrostatic repulsion in the corona of the hydrophobic clusters in the gels with annealed charged groups, because the charged units repelling each other are able to move farther apart.

Introduction

A microphase separation with the formation of microdomain structures was observed for many polymer systems: melts and solutions of block copolymers,^{1–14} mixtures of weakly charged polyelectrolytes with neutral polymers,¹⁵ solutions of weakly charged polyelectrolytes in a poor solvent,^{16–18} polymer gels,^{19–21} and so forth. In

Scheme 1. Schematic Representation of the Micelle-like Domains Formed Inside HM Gels



all of these systems, the microphase separation appears as a result of the interplay of the strongly attractive interactions between one kind of the monomer units and the repulsion between the others.

When the polymer contains charged units, the electrostatic interactions play a crucial role in the microphase separation. For example, in ref 21, it was shown that the introduction of charged groups into an amphiphilic polyelectrolyte gel of hydrophobically modified poly(acrylic acid) (HM PAA) not only induces the microphase separation but also governs the size of structures that emerge as a result of microphase separation. When the HM PAA gel is immersed in an aqueous medium, the hydrophobic tails inside the gel aggregate with each other in order to avoid contact with water, thus forming the micelle-like domains (Scheme 1). In the case of uncharged gels, these domains are homogeneously distributed in the bulk of the gel and on the small-angle neutron scattering (SANS) curve one can see only one correlation peak corresponding to the average interdomain distance, d_{id} (Scheme 2a).

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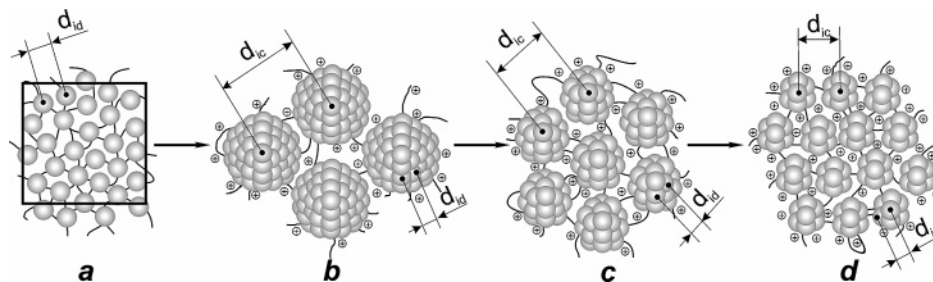
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Scheme 2. Schematic Representation of Microphase Separation in HM Gels at Increasing Content of Charged Units Starting from Uncharged Gel



When the charged units are introduced into the gel, the second structure peak appears in a small-angle area. It was assigned to microphase separation with a formation of hydrophobic regions (“clusters”) consisting of several densely packed micelle-like domains and hydrophilic regions (“channels”) swollen by water that separate clusters from each other. The new peak corresponds to the average distance between neighboring clusters, d_{ic} (Scheme 2b). In the system, the charged units and counterions are located on the surface of the clusters or in the nanochannels between the clusters (Scheme 2b). Such a nonhomogeneous distribution of hydrophobic domains and charged units in the gel volume is triggered by the segregation of nonpolar hydrophobic moieties that expel water and charged hydrophilic moieties that prefer to reside in water. When the content of charged units increases, the big clusters break up into many smaller ones (Scheme 2b–d). In this way, the system promotes an expansion of the total surface area of the clusters, where the charged units are located, thus reducing the electrostatic repulsion. For example, increasing the charge content from 2 to 20 mol % leads to a decrease of the average radius of clusters from 134 to 40 Å for HM PAA gel bearing 20 mol % *n*-dodecylacrylate hydrophobic units (at a degree of swelling equal to 2).²²

The data obtained are consistent with the results of theoretical consideration made for weakly charged polyelectrolyte gels with associating groups.²³ Indeed, the theoretical treatment²³ evidences that (i) the microphase separation is possible only if the polymer chains are charged and (ii) the period of microphase-separated structure decreases with increasing content of charged units.

One can expect that not only the content of charged units but also their mobility can affect the microphase separation. A significant influence of the migration of charged groups bound to polymer chains on the phase behavior of polymer solutions was demonstrated in ref 24. It was shown both theoretically and experimentally that quenched charged units (“q-charges”) prevent effectively the macrophase separation under poor solvent conditions, because the precipitation of polymer (together with counterions) causes a huge loss of the translational entropy of counterions. By contrast, annealed charged units (“a-charges”) can migrate from the precipitate to the macromolecules still residing in solution, thus minimizing the loss of the translational entropy of counterions. As a result, the macrophase separation in solution of polyelectrolyte with a-charges is more favorable than that

in solution of polyelectrolyte with the same fraction of q-charges.

The migration of charged units has a significant impact not only on macrophase separation but also on microphase separation. According to the theoretical consideration²⁵ performed in the line of the theory of microphase separation in weakly charged polyelectrolytes in a poor solvent,^{26,27} the mobile charges introduce an additional contribution to the Debye–Hückel screening length, because they are able to screen the electrostatic interactions without having to carry the polymer chain with them. As a result, the period of microphase structure in the annealed case becomes slightly larger.

The experimental study of temperature-induced microphase separation in aqueous solutions of polyelectrolytes with q- and a-charges was performed by SANS.²⁸ For this experiment, two samples of random copolymers of *N*-isopropylacrylamide (NIPAM) and *N,N*-[(dimethylamino)propyl] methacrylate (MADAP) differing in the mobility of charged MADAP units were used. The copolymer sample with q-charges contained 5 mol % MADAP units, with all of them being ionized. The copolymer sample with a-charges contained 10 mol % MADAP units, with only half of them being ionized. Thus, in both samples, the total number of charged MADAP units was the same, but in the latter sample, the charges were able to migrate from one MADAP unit to another. It was shown that, under poor solvent conditions for NIPAM units, both copolymers undergo a microphase separation, but in the case of the copolymer with q-charges, the size of the microphase-separated structures was much smaller. Although this tendency is consistent with theoretical predictions,²⁵ the difference between a- and q-charged systems appeared to be more significant than it follows from the theory.

To the best of our knowledge, ref 28 is the only experimental work that considers the role of the mobility of charged units in the microphase separation. At the same time, the possibility of migration of charges is among the most important factors that determine the nanostructure of ion-containing polymeric systems.

Therefore, we initiated an investigation of the influence of the mobility of charged units on the microphase separation on an example of HM PAA gel, whose nanostructure is quite sensitive to the presence of charges. When the degree of ionization of HM PAA gel is lower than the fraction of monomer units potentially able to be ionized, COO[−] and COOH groups coexist in the chain (Chart 1a). In this case, the migration of counterions is allowed because there is no difference between neighboring

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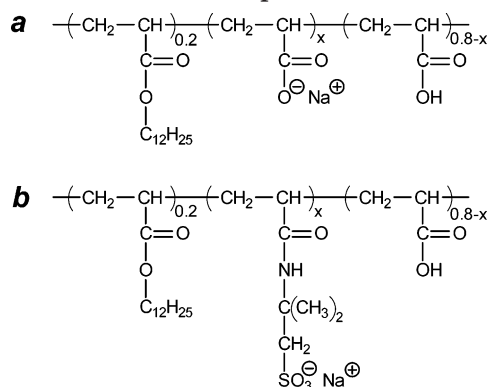
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Chart 1. Chemical Structure of HM Polyelectrolyte Gel with (a) Annealed and (b) Quenched Charged Groups^a

^a The fraction of charged units, x , was varied from 0 to 0.2.

acrylic units and therefore the ions can freely move from one carboxylic group to another. These conditions are the case of a-charged groups. To obtain a gel with q-charged groups, we introduced in HM PAA chains a small fraction of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) units (Chart 1b). In this case, charged groups will be located on AMPS units, because AMPS is a strong acid with a high dissociation constant, while acrylic acid only slightly dissociates. The same will be true for partially neutralized gel, if the degree of neutralization does not exceed the content of AMPS units. The nanostructure of the microphase-separated HM PAA gels with a- and q-charges was investigated by SANS. The results obtained clearly show that the dimensions of the nanostructures depend dramatically on the ability of charged groups to move from one repeat unit to another.

Experimental Section

1. Materials. HM hydrogels with a-charged units (Chart 1a) were prepared by free-radical copolymerization of acrylic acid and *n*-dodecylacrylate in *N,N'*-dimethylformamide using *N,N'*-methylenebis(acrylamide) as a cross-linker (1 cross-link per 66 repeat units). Details of the preparation and characterization of these gels are described elsewhere.²⁹ The composition of the gels was confirmed by ¹H NMR. By ¹³C NMR spectroscopy, it was shown that *n*-dodecylacrylate units are randomly distributed along the polymer chains.

HM hydrogels with q-charged units (Chart 1b) were prepared by free-radical copolymerization of acrylic acid, *n*-dodecylacrylate, and AMPS sodium salt under the same conditions. The composition of the terpolymer gels was confirmed by quantitative elemental analysis of S, N, and C. The distribution of monomer units along the backbone was found to be random by ¹³C NMR spectroscopy.

The gels are denoted in terms of the type and molar content of hydrophobic monomer units. For example, C12-20 indicates a gel containing 20 mol % *n*-dodecylacrylate (C12) units.

D₂O (99.9 atom % 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 them 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 (D₂O) to get a desired resulting 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 gels obtained were allowed to swell at room temperature for at least 1 week before the measurements. For the preparation of charged gel samples, the calculated amount of sodium

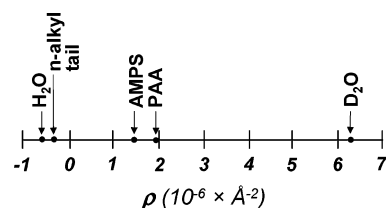


Figure 1. Scattering length densities of the components of HM PAA hydrogels.

hydroxide was added to reach a desired resulting degree of charging.

3. SANS Measurements. SANS experiments were performed with the YuMO instrument using the two-detector system³⁰ of the high-flux pulsed reactor IBR-2 at Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. 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.

All data were treated according to standard procedures of small-angle isotropic scattering.³¹ The spectra were corrected for the sample transmission, sample thickness, and electronic noise. Subtraction of the incoherent background was done by using a blank solvent (D₂O) spectrum and estimating the incoherent contribution of the polymer. The SANS intensity distribution was then presented as a function of the magnitude 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 \AA^{-1} .

SANS arises from the spatial variations of the density of scattering length in the sample. The values of the scattering length densities of the components of HM PAA hydrogels are indicated in Figure 1. From these data, it is evident that when D₂O is used as a solvent the hydrophobic side chains of the gel have higher contrast and therefore cause stronger scattering in comparison with the PAA backbone and AMPS units. The polymer backbone can be matched by a 40/60 D₂O/H₂O mixture, but in this medium, the scattering by hydrophobic tails is rather weak. Therefore, in this paper, D₂O was used as a solvent and it was assumed that in HM PAA gel swollen by D₂O the hydrophobic *n*-alkyl side chains are mainly responsible for the scattering.

4. NMR Measurements. ¹³C NMR spectra were recorded with proton decoupling on a Bruker WM-250 spectrometer operating at 62.9 MHz. The acquisition and delay times were 1 and 10 s, respectively. The total number of scans was equal to 79 000. A trace of methanol was added to the solutions as an internal reference ($\delta(\text{CH}_3\text{OH}) = 49.9$ ppm).

Results and Discussion

Figure 2 shows the scattering curves for C12-20 gels with different contents of q-charges at the same polymer concentration (33 wt %). Let us first consider the uncharged gel (curve 1). The SANS curve from the uncharged gel contains one peak at the scattering vector $Q = 0.12 \text{ \AA}^{-1}$ (Figure 2, curve 1). The analogous scattering curves were already observed for HM PAA gels with different lengths (*n*-octyl, *n*-dodecyl, and *n*-octadecyl) and contents (10, 15, and 20 mol %) of *n*-alkyl groups.¹⁹ It was shown that the peak is due to a correlation between micelle-like domains (interdomain peak) formed by self-assembled *n*-alkyl side chains. The peak position indicates that the average distance between adjacent hydrophobic domains in C12-20 gel is equal to 55 Å.

The addition of only 1 mol % q-charged units leads to the appearance of a second scattering peak at low angles ($Q = 0.02 \text{ \AA}^{-1}$), while the first peak position remains almost

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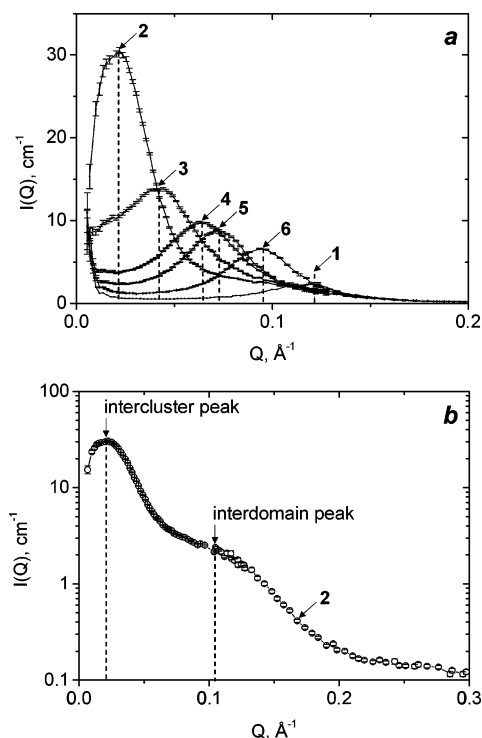


Figure 2. SANS profiles for HM PAA C12-20 gels with different contents of quenched charged groups: (1) 0 mol %; (2) 1 mol %; (3) 2 mol %; (4) 4 mol %; (5) 6 mol %, (6) 20 mol % in (a) linear and (b) logarithmic scales. The polymer concentration is equal to 33 wt % in all cases.

unchanged (Figure 2, curve 2). From Figure 2, it is seen that the second peak position depends essentially on the content of charged AMPS units in the gel. With increasing content of charged units, the position of this peak gradually shifts toward high Q values with the simultaneous decrease of its intensity. At the same time, the first peak position is almost independent of the content of charged units and corresponds to the characteristic distance 55 Å. The first scattering peak is clearly seen only on the curves from the gels containing a rather low amount of charged units, 1–2 mol % (Figure 2b). At the high content of charged units, this peak becomes hidden by approaching the more intense second peak.

The analogous behavior of the SANS spectra at the increase of the content of charged groups was observed previously for HM PAA gels with a-charges.²¹ The existence of the two scattering peaks was attributed to charge-induced microphase separation with the formation of hydrophobic dense clusters that are separated from each other by hydrophilic channels swollen by water (Scheme 2).²¹ It was shown that the first structure peak corresponds to interdomain distances inside the clusters, while the second structure peak corresponds to intercluster distances. The shift of the intercluster peak to higher Q values with the increase of the degree of charging was explained by the breaking of big clusters into many smaller ones (Scheme 2), when the electrostatic repulsion of similarly charged units in the corona of the clusters becomes too strong. As a result of such breaking, the overall number of clusters in the system increases, leading to the shortening of the average intercluster distances (the intercluster peak shifts to higher Q values). Simultaneously, the intensity of the peak becomes lower because of the smaller size of the scattering objects. As was mentioned above, these data fully coincide with the theoretical predictions made in ref 23 for weakly charged polyelectrolyte gels with associating groups.

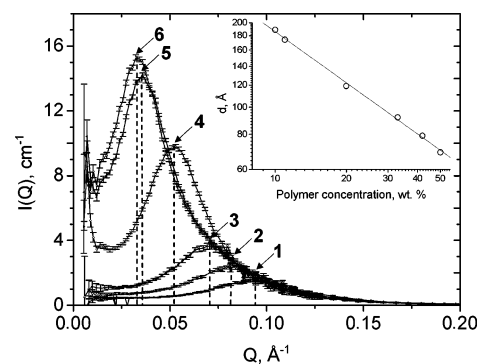


Figure 3. SANS profiles for HM PAA C12-20 gels with 6 mol % quenched charged units at different polymer concentrations: (1) 50 wt %; (2) 42 wt %; (3) 33 wt %; (4) 20 wt %; (5) 11 wt %; (6) 10 wt %. Inset: the dependence of the average distances between the clusters, d , on the polymer concentration in double logarithmic scale. The slope of the straight line is equal to -0.6 .

Now let us fix the content of charged units and let us consider the effect of the degree of swelling of the gel (i.e., of the polymer concentration) on the position of the intercluster peak. From Figure 3, it is seen that when the polymer concentration decreases, the clusters move farther apart, which is expected. The mean intercluster distances ($d = 2\pi/Q$) scale with polymer concentration as $d \sim C_p^{-0.6}$ (Figure 3, inset). As was shown previously,¹⁹ HM PAA gels with a-charges behave in a similar manner, but the exponent is somewhat lower ($d \sim C_p^{-0.5}$).

Thus, the general behavior of the HM polyelectrolyte gels with q- and a-charges is quite similar. However, one can observe a considerable difference between them: the positions of intercluster peaks on the SANS curves of the gels with q-charges are shifted toward wide angles (i.e., shorter spacing) as compared to those of the gels with the same content of a-charges (Figure 4). The shift is quite significant. For instance, in the sample with 2 mol % charged units, the peak displaces from 0.022 \AA^{-1} (intercluster distance 286 Å) for a-charges to 0.044 \AA^{-1} (intercluster distance 143 Å) for q-charges.

If we compare the SANS curves at the lowest charge content under study (1 wt %), we observe (Figure 5) that the scattering curve of the gel with q-charges has two structure peaks corresponding to interdomain (55 Å) and intercluster (286 Å) distances, while the scattering curve of the gel with the same content (1 mol %) of a-charges contains only one peak corresponding to interdomain distances (55 Å). Nevertheless, the last curve demonstrates much stronger scattering at low angles in comparison with the uncharged gel (cf. curves 1 and 2 in Figure 5), which may be due to the presence of clusters. This allows us to suggest that probably the intercluster peak for this gel is located in a low-angle area out of the Q -range under study, that is, at lower angles than the corresponding peak for the gel with q-charges.

The same tendency (i.e., the shift of the intercluster peak toward wide angles for the gels with q-charges) remains valid also for the gels at other degrees of swelling, which is evident from Figure 6. The direction of the observed shift of the scattering peak is consistent with theoretical predictions,²⁵ which are based on the assumption that a-charges are able to screen more effectively the electrostatic repulsion in comparison with q-charges. In the present system, the reduced electrostatic repulsion in a-gel is responsible for less efficient breaking of the clusters at charging.

In general, one can suggest that the dimensions of hydrophobic clusters in microphase-separated gel are

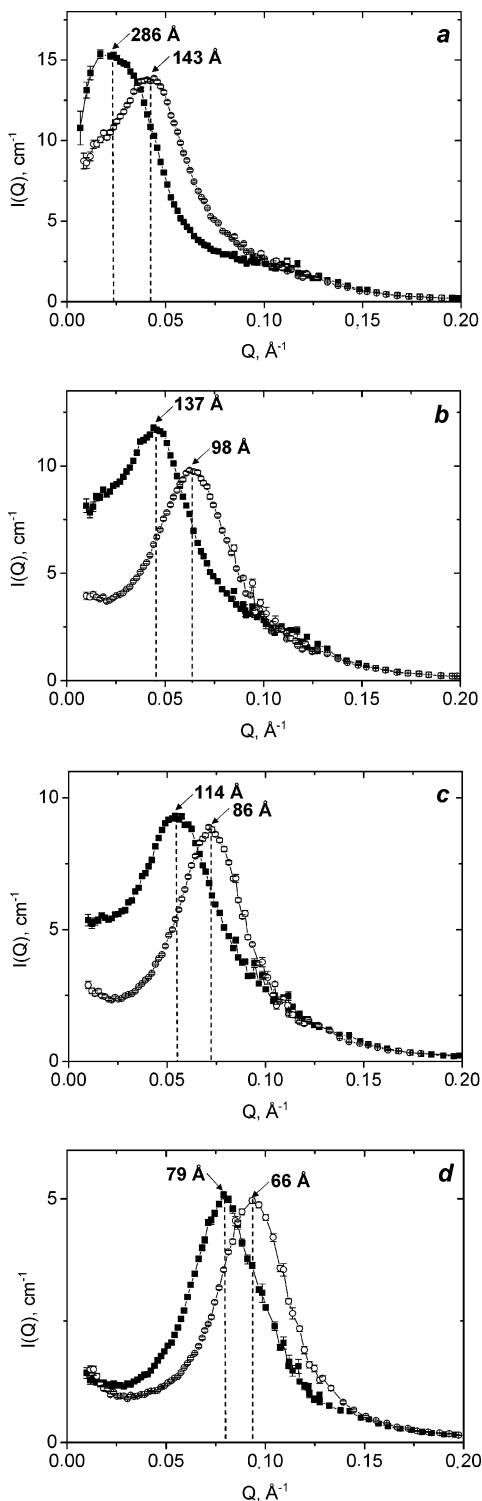


Figure 4. SANS profiles for HM PAA C12-20 gels with different contents of annealed (filled squares) and quenched (open circles) charged groups: (a) 2 mol %; (b) 4 mol %; (c) 6 mol %; (d) 20 mol %. The polymer concentration is equal to 33 wt % in all cases. The intercluster distances, d ($d = 2\pi/Q$), corresponding to peak maxima are indicated in the figures.

governed by a balance between the following counteracting driving forces. On one hand, the tendency to decrease the contact of hydrophobic domains with water favors the growth of the clusters in size (i.e., the hydrophobic domains prefer to stay in the interior of clusters rather than on their shell in contact with water). On the other hand, the charged units like to reside in a water medium, that is, on the surface of clusters or on the chains connecting

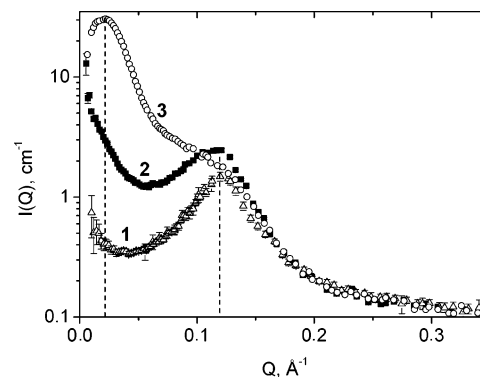


Figure 5. SANS profiles for HM PAA C12-20 gels without charges (1) and with 1 mol % annealed (2) and quenched (3) charged groups. The polymer concentration is equal to 33 wt % in all cases.

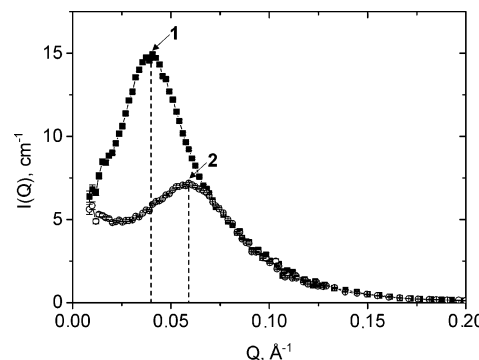


Figure 6. SANS profiles for HM PAA C12-20 gels with 20 mol % (1) annealed and (2) quenched charged groups. The polymer concentration is equal to 18.5 wt % in both cases.

different clusters. As the similarly charged groups repel each other, this induces the growth of the interface between clusters and water, which is achieved by the breaking of big clusters into many smaller ones. In other words, the electrostatic repulsion between the charged units in the shell of the clusters counteracts the growth of hydrophobic clusters. In the gel with α -charges, this last contribution is reduced because charged units can migrate farther from each other, thus decreasing their mutual repulsion, which allows one to keep a larger size of the clusters.

One can suggest that the effect of the mobility of charges should depend on the content of charged units in the system. Indeed, when only a few charges are present, it does not really matter whether they are quenched or annealed. On the other hand, the same is true for highly charged polyelectrolyte. Therefore, one can expect that the difference between q - and α -systems should pass through a maximum at increasing charge content. From Figure 4, it is seen that the experimental data obtained correspond to the descending branch of this dependence; that is, the difference in peak positions between q - and α -gels decreases with increasing content of charged units.

Let us estimate the mean aggregation number of clusters at different contents of charged units in q - and α -gels. To do it carefully, it is necessary to take into account the possibility of the disruption of some of the hydrophobic aggregates with the passage of a part of hydrophobic groups to water medium, when the electrostatic repulsion between similarly charged units becomes too strong. The amount of hydrophobic tails still residing in the aggregates can be estimated by ^{13}C NMR spectroscopy using the technique elaborated by Iliopoulos et al.³² It was

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Table 1. Intercluster Distances d and Aggregation Numbers of Clusters for the Gels with Different Content of Annealed and Quenched Charged Units^a

content of charged units (%)	annealed charges			quenched charges		
	spacing, d (Å)	av no. of n -dodecyl tails in one cluster, N	av no. of domains in one cluster, n	spacing, d (Å)	av no. of n -dodecyl tails in one cluster, N	av no. of domains in one cluster, n
1	b			286	8.9×10^3	180
2	286	8.9×10^3	180	143	1.3×10^3	26
4	137	980	20	98	360	7
6	114	560	11	86	240	5
20	79	190	4	66	110	2

^a The polymer concentration is 33 wt % in all samples. ^b The peak position is out of the studied range of Q .

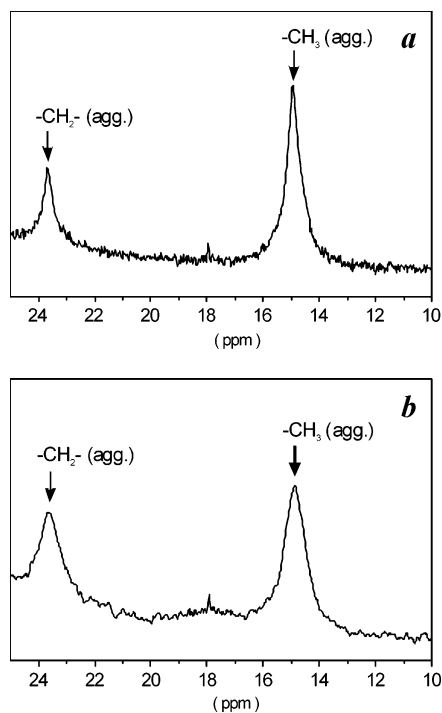


Figure 7. The NMR spectra of HM PAA C12-20 gels containing 20 mol % (a) annealed and (b) quenched charges. The polymer concentration is equal to 11 wt % in both cases.

shown³² that in HM PAA the NMR bands of CH_2 and CH_3 groups of the n -alkyl side chains are split due to slow exchange between the free and aggregated states of these groups. In particular, the bands at 14.5 and 14.8 ppm were shown to be due to free and aggregated terminal CH_3 groups, while the bands at 23.1 and 23.5 ppm were ascribed to free and aggregated penultimate CH_2 groups of n -alkyl tails, respectively.³²

Using this technique, the hydrophobic aggregation of n -alkyl side chains was studied in the C12-20 gels with a- and q-charges. For this purpose, the gel samples with the maximum amount of charged units under study (20 mol %) were used. The NMR spectra obtained are depicted in Figure 7. It is seen that on both spectra only peaks inherent to aggregated groups (at 14.8 and 23.5 ppm) are present. Thus, the NMR data unambiguously show that the incorporation of 20 mol % charged units does not lead to disruption of the hydrophobic aggregates. This observation is consistent with the results previously obtained in ref 29, where it was demonstrated that 20 mol % a-charges does not disrupt the aggregates in less hydrophobic C8-20 gel. Therefore, one can suggest that the microphase separation arises in order to keep all hydrophobic domains from disruption at the gel charging.

Taking into account that all hydrophobic tails in the gels under study are aggregated, let us estimate the number of hydrophobic domains included in one cluster,

n . The position of the intercluster peak defines a characteristic distance between neighboring clusters, $d = 2\pi/Q$. Assuming in a first approximation a locally simple cubic arrangement (other local cubic arrangements would yield comparable results) of the clusters in the gel volume, one can calculate the volume of one cell as d^3 . From the concentration of hydrophobic units in the gel, C (in monomol/L), it is possible to estimate the number of n -dodecyl tails per one unit cell as $N = N_A C d^3$, where N_A is Avogadro's number.

The value of N is actually the number of n -dodecyl tails per one cluster, because in a simple cubic lattice one cell contains only one cluster. To roughly estimate the number of domains, n , included in one cluster as $n = N/N_{\text{dom}}$, the value of the aggregation number of one hydrophobic domain, N_{dom} , was supposed to be equal to 50 like in C12-20 gels³³ with 20 mol % a-charges. It should be noted that the close value of the aggregation number of domains was obtained for aqueous solutions of linear HM PAA C12-15 with 85 mol % q-charges.³⁴

The data obtained for the gels with different contents of charged units are presented in Table 1. From Table 1, it is seen that the aggregation number of clusters decreases with an increase in the content of charged units for the gels with both a- and q-charges. As was mentioned above, this phenomenon is governed by the enhancement of the electrostatic repulsion between similarly charged units on the surface of the cluster at the increase of the content of charged groups.

Let us compare the aggregation numbers of clusters for the gels with a- and q-charges at the same content of charged units. From Table 1, it is seen that the aggregation numbers of clusters in the gels with a-charges are larger than those of clusters in the gels with q-charges. Since in both gels the total number of aggregated hydrophobic tails is the same, this indicates that the gels with q-charges contain a higher amount of smaller clusters as compared to the gels with a-charges. As was discussed above, the smaller size of clusters in the gels with q-charges can be due to stronger electrostatic repulsion in the corona of the hydrophobic clusters, while in the gels with a-charges a part of the charged units can move from the corona to the gel chains, connecting different hydrophobic clusters together. Thus, the fixing of the charged group position on the polymer backbone is analogous to the effective increase of the degree of charging.

The results obtained closely resemble the findings²⁸ for aqueous solutions of linear NIPAM–MADAP copolymers with a- and q-charges. Although the SANS profiles of these solutions do not contain any structure peaks, the strong scattering at low angles indicates a larger size of microphase-separated structure in the copolymer with

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a-charges. This suggestion is also supported by the observation of higher turbidity of these samples.^{24,28}

The similarity of the effect of charge migration on the microphase separation in linear and cross-linked polymer samples with different chemical compositions indicates that the observed phenomena have general character; that is, they are inherent to various polymeric systems independently on their structure.

Conclusions

The mobility of charges exerts a dramatic effect on the microphase separation in ion-containing gels. At an equal content of charged units, the gels with q-charges behave

like more charged ones and they bear hydrophobic clusters of smaller size. Therefore, the possibility of charge migration should be taken into account, when designing the nanostructure of microphase-separated polymeric systems.

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