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ORIGINAL CONTRIBUTION

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Microphase separation of cationic poly(*N*-isopropylacrylamide) copolymers in water: Effect of the migration of charges

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Abstract The structures of aqueous copolymer solutions have been examined through small angle neutron scattering. The copolymers contained mostly *N*-isopropylacrylamide (NIPAM) monomers. Poly(NIPAM) solutions have a lower critical solution temperature (LCST), above which the macromolecules separate from water. A small fraction of ionizable *N*,*N*-[(dimethylamino) propyl] methacrylamide (MADAP) monomers was introduced into the macromolecules. This had dramatic consequences on the solution behavior at temperatures above the LCST of PNIPAM, where phase separation would have been expected for the homopolymer. When all MADAP monomers were ionized, it was found that the solutions resisted the phase separation. At short spatial scales, the chains were collapsed but at large scales they formed branched aggregates that did not separate out of water. When only half of the MADAP monomers are ionized, the electrical charges were able to redistribute themselves along the chains. In this case, the rise in temperature caused a microphase separation where the electrical charges were relocated on a fraction of the chains that remained in solution.The other chains (or section of chains) formed large nodules of a polymer rich phase.

Introduction

The introduction of ionized groups onto a polymer chain raises its solubility in water. This effect is due to the release of counter-ions in the solution, since a phase separation would lead to a large loss in their translational entropy. Consequently, under poor solvent conditions, weakly charged polyelectrolytes may undergo a microphase separation rather than a macroscopic phase separation [1, 2]. This theoretical prediction has been verified experimentally through light scattering [3].

In the present paper we consider the case of polymer chains with either fixed or migrating charges. These polymers are obtained by introducing a certain number of ionizable monomers along the chains and ionizing all or only part of them by varying pH. When these monomers are completely ionized, the electrical charges remain fixed along the chain, making phase separation unfavorable. On the other hand, when they are partly ionized, the charges may migrate. In this case one may expect the charged units and the corresponding counterions to remain in water while the other units segregate out of water. Thus, the effect of migration of charges should lead to different structures. The polymer studied here is a statistical copolymer of *N*-isopropylacrylamide (NIPAM) and N,*N*-[(dimethylamino) propyl] methacrylamide (MADAP).

Poly(*N*-isopropylacrylamide) (PNIPAM) is a nonionic water-soluble polymer that exhibits an inverse solubility behavior: when heated above the lower critical solution temperature (LCST) of about 32 °C, it precipitates out of water [4]. This polymer has attracted much theoretical interest since it has a well-defined transition from coil to globule [5]. Moreover, there are numerous practical applications for this collapse transition [6, 7], including biological uses since it occurs near body temperature. For some of these uses, the LCST has been shifted by the addition of comonomers to the PNIPAM chains. For instance, introducing 40% hydrophilic acrylamide units in the chain shifts the LCST to 75 °C [8] and introducing 10% sodium acrylate (AA) brings it above 100 °C [9].

In this work we have used the MADAP weak base as ionizable comonomer; the introduction of weak electrolytes in the macromolecules makes it possible to switch from chains with migrating charges (incomplete neutralization) to chains with localized charges (full neutralization). Specifically, two copolymers that have the same overall ionization have been compared. In the first one (cop 5–100), the mole fraction of MADAP units was only 5% but all of them were ionized. In the other one (cop 10–50), the mole fraction of MADAP was 10% but only half of them were ionized. These copolymers had the same overall ionization but very different association behaviors at high temperature. These copolymers have been studied previously through turbidimetry [10] and further measurements were performed in the present study. As an example, the turbidity behavior of 2 wt.% solutions of NIPAM-MADAP copolymers with localized charges (cop 5–100) and migrating charges (cop 10–50) is presented in Fig. 1 (see [10] for experimental details).

These data clearly evidence the huge effect of the localization of charges for a given ionization degree ($i = 0.05$) of the polymer chains. When the charges are localized (cop 5–100), the solution does not exhibit any turbidity below 45 °C and beyond this temperature it only shows a minor effect. When the charges can migrate (cop 10–50), the turbidity starts to increase around 37 °C and rises much more rapidly towards a much higher value than in the case of localized charges. However, it is important to note that in both cases no separation in two well-defined phases is observed by this method. The large differences in turbidity between the two copolymers suggest two different structural evolutions upon the temperature increase. In order to determine these structures, we performed small angle neutron scattering experiments (SANS) on the copolymer solutions at temperatures below and above the LCST of pure PNIPAM. The results, and the structural analysis, are reported here.

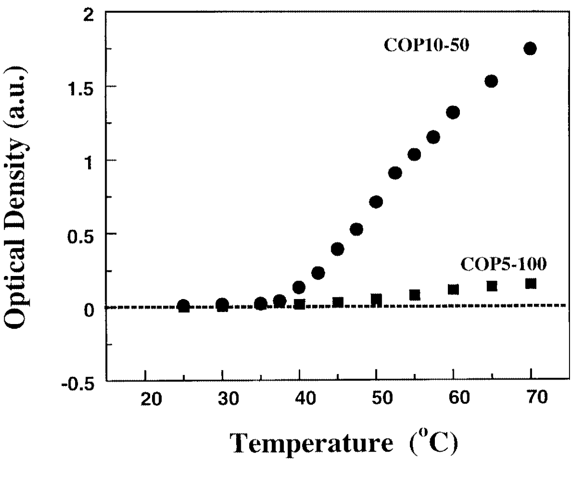

Fig. 1. Turbidity curves of 2 wt. % copolymer solutions. cop 10–50: copolymer whose fraction of MADAP units that were charged is equal to 0.5 (migrating charges) and whose ionization degree is $i = 0.05$ (●); cop 5–100: copolymer whose fraction of MADAP units that were charged is equal to 1 (localized charges) and whose ionization degree is $i = 0.05$ (■)

Materials and Methods

Materials

Copolymer synthesis

The NIPAM/MADAP copolymers were synthesized through radical polymerization in water at 29 °C, using the redox couple ammonium peroxydisulfate/sodium metabisulfite as initiator. Monomers and initiators were obtained from Aldrich. Before the initiation, the pH of the polymerization mixture was set to ~6 by addition of HCl. The reaction was allowed to proceed for 24 h. At the end of the reaction, the copolymer was transformed to the basic form by addition of sodium hydroxide, dialyzed against water and finally freeze-dried. The composition of the copolymers was estimated by potentiometric titration with HCl and by ^{13}C NMR spectroscopy. The monomer distribution was found to be rather random with a slight preference for isolated MADAP units. A detailed study of the synthesis and characterization of these copolymers is given elsewhere [11]. To prepare the solutions at the desired concentration and ionization degree, the appropriate volume of a solution of HCl 0.100 M was added to a part of the stock solution and diluted up to the desired concentration. The measurements were performed at least 24 h after mixing.

Solution properties

The intrinsic viscosities, $[\eta]$, of the non-ionized copolymers (amine form) were measured at 20 °C in 0.5 M $LiNO_3$ solution. The molar masses, M_w, were estimated from the relation: $[\eta] = 0.047\ M_w^{0.61}$ (see Table 1). This relation has been established for PNIPAM [12] and therefore only provides a rough estimation of the molar mass of the copolymers. However, the influence of MADAP units on $[\eta]$ is not expected to be strong because of the non-ionized form of the chains and the relatively high ionic strength.

The ionized copolymers can be considered as weakly charged polyelectrolytes. Indeed, there is a threshold in charge density, i_0, above which the counter-ions begin to condense around the chains. According to Manning [13], this limit is expressed as the ratio of the monomer size, a, to the Bjerrum length, L_B. In our case a~2.5 Å and L_B is equal to 7.16 Å in water at 25 °C giving a condensation limit $i_0 = a/L_B = 0.35$. The value of i of our samples being 0.05, we may consider that the counterions are not condensed on the polymer backbones.

The overlap concentration C* of the copolymer solutions can be estimated using the relation $C^* \sim 1/[\eta]$, leading to C*~0.45–0.5% wt. However, this relation is only valid for the non-ionized form of the copolymer. The introduction of charges tends to stretch the

Table 1. Copolymer properties

Sample	Fraction of MADAP units in the chain	Fraction of MADAP units ionized	M_w[a]	$[\eta]$[b] ($cm^3\ g^{-1}$)
cop 5–100	0.05	1	1.04×10^6	220
cop 10–50	0.1	0.5	9.2×10^5	204

[a] Determined for the non-ionic form of the copolymer
[b] Measured with the non-ionic form of the copolymer in 0.5 M $LiNO_3$

polymer chains and therefore causes a decrease in C*. In the present study, the copolymer concentration was fixed at 2% wt. Therefore, for both copolymers, the chains were in the semi-dilute regime where the configurations of neighboring chains overlap. The characteristic distance is the distance between neighboring chains, ξ. Since the copolymers are weakly charged polyelectrolytes, ξ may be estimated according to the relation established for charged rods [14], which is $\xi = a \times C_p^{-1/2}$ where a is now the length of the statistical unit. Accordingly, for 2% wt. copolymer solutions, $\xi \approx 50$ Å.

At shorter distances ($r < \xi$), the correlations between monomers are mainly intrachain, but at larger distances ($r > \xi$) interchain correlations become important. In this range of distances, the repulsions between charged chains will oppose fluctuations in polymer concentration, and the solution will appear uniform.

At very large distances, however, the effect of electrostatic repulsions must be limited by the presence of free ions, i.e. ions that are not counterions of the charged groups on the polyelectrolytes. Those free ions originate from the acid (HCl) that was used to ionize the copolymers. The concentration of free ions is equal to 8.6×10^{-3} M for cop 5–100 and 8.4×10^{-3} M for cop 10–50 leading to a Debye screening length, κ^{-1}, equal to 30 Å which is comparable to the value estimated for ξ.

Accordingly, the polymer concentration and the free ion concentration determine three ranges for the behavior of fluctuations in monomer concentration:

- At $r < \xi$, the monomer – monomer correlations are the same as in an isolated chain.
- At $\xi < r <$ a few κ^{-1}, they are controlled by electrostatic repulsions between neighboring chains, which tend to suppress fluctuations in monomer concentration.
- At $\kappa^{-1} \ll r$, they become the same as in a semi dilute solution of uncharged chains.

Table 1 shows the properties of the copolymer solutions.

Methods

Small angle neutron scattering

Scattering curves result from interferences between neutron rays scattered by the nuclei in the sample. The experiment consists in measuring the scattered intensity, I, as a function of the scattering vector, q, which depends on the scattering angle θ and on the wavelength λ of the incident neutrons:

$$q = (4\pi/\lambda)\sin(\theta/2) \qquad (1)$$

From $I(q)$ some geometrical parameters characterizing the macromolecules in solution can be deduced. In dilute solutions, polymer chains are well separated and experience intramolecular segmental interactions. In this case the chain can be described by a form factor. When the concentration is increased up to the semi-dilute regime, the chains overlap and it is more appropriate to describe the system using the screening length, ξ, described above. Thus, three regions of the scattering curve have to be distinguished [15]:

Region A:

> For q values such that $q\xi > 1$, subchain configurations (i.e. within a blob) are investigated. In this region, the scattered intensity decays as a $q^{-\mu}$ power law. The value of the exponent, μ, depends on the shape of the objects: $\mu = 1$ for rod like chains and $\mu = 1.67$ for flexible polymer chains in good solvent.

Region B:

> In the intermediate regime where $q\xi \sim 1$, correlations between neighboring chains are observed. For repelling chains, the scattered intensity will exhibit a peak at a q value corresponding to the inverse of the interchain distance ξ, and a depression at lower q values.

Region C:

> At low q values, the scattered intensity is determined by large-scale fluctuations of the polymer concentration. At these large distances ($r >> \kappa^{-1}$), electrostatic repulsions are screened by the free ions. If the macromolecules are not associated, then the intensity must be the same as for a semi dilute solution of uncharged macromolecules. If they associate, then the intensity is enhanced.

In the limit where the associated macromolecules form permanent aggregates, the value of the intensity scattered at $q \to 0$ yields the number of macromolecules per aggregate and the shape of the decay at larger q values yields the size of the aggregates.

As an example, regions A, B and C are indicated on Fig. 2.

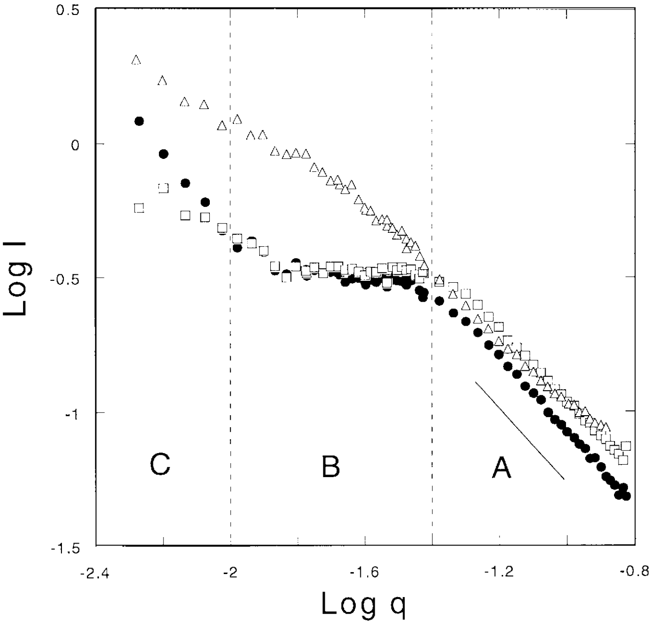

Fig. 2. SANS curves of the copolymer solutions at T = 20 °C. cop 5–100 (●); cop 10–50 (□); PNIPAM (△). The *continuous line* has a slope –1.4

Instruments

The small angle neutron scattering (SANS) experiments were performed on the instruments D11 and D22 at ILL, Grenoble, and on the instrument PAXE at LLB, Saclay. Protonated polymer was dissolved in D_2O. The spectra were obtained at room temperature (20 °C), and at temperatures above the LCST of pure PNIPAM (40, 60, and 70 °C).

Results

At 20 °C

The scattering curves for all copolymer solutions at 20 °C are shown in Fig. 2. For comparison, the scattering from a solution of the PNIPAM homopolymer is also shown. The main features of these scattering curves are as follows.

High q behavior (Region A)

At high q values (above 0.04 $Å^{-1}$) the copolymer solutions give the same scattering as solutions of pure PNIPAM. All the scattering curves are power laws in this range, and the exponent is typical of swollen chains ($q^{-1.4}$). Accordingly, the single chain conformations, at spatial scales of the order of 10 to 100 Å, are similar to those of PNIPAM. Hence, the presence of a few electrostatic charges does not cause appreciable stretching of the chains at this scale.

Intermediate q values (Region B)

In the intermediate range of q, the scattered intensities are depressed with respect to those of PNIPAM. This depression originates from destructive interferences between rays scattered by neighboring chains, as electrostatic repulsions suppress fluctuations in polymer concentration in this range of distances.

Low q behavior (Region C)

At low q values (below 0.01 $Å^{-1}$), the scattering of the copolymers increases toward the intensities of pure PNIPAM solutions. This strong scattering originates from concentration fluctuations at spatial scales larger than 650 Å, where the electrostatic repulsions are screened by free ions ($r \gg \kappa^{-1}$).

At 40 °C

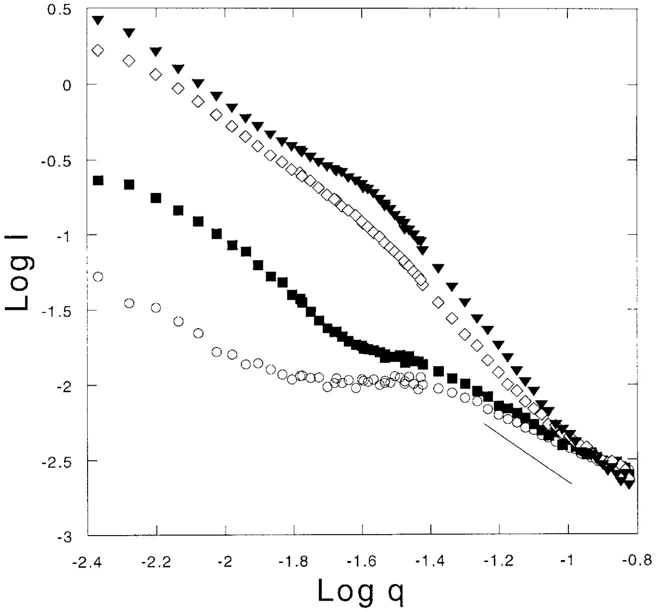

Fig. 3. Effect of temperature on the SANS curves of cop 5–100 (localized charges): 20 °C (○); 40 °C (■); 60 °C (◇); 70 °C (▼). The *continuous line* has a slope –1.6

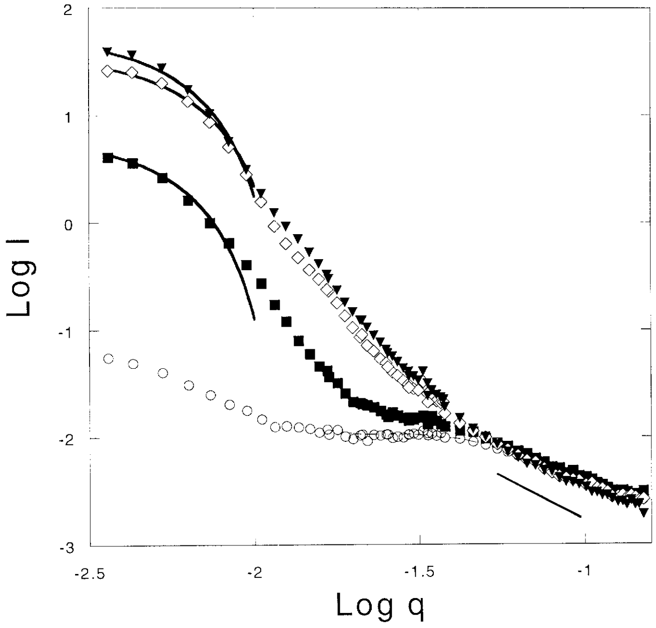

Fig. 4. Effect of temperature on the SANS curves of cop 10–50 (non localized charges): 20 °C (○); 40 °C (■); 60 °C (◇); 70 °C (▼). The *continuous line* has a slope –1.6. The *curved lines* are fits using the scattering function of spheres (see Table 2)

The effects of temperature on the scattering curves of each copolymer are shown in Figs. 3 and 4. These effects are obviously quite large, with huge increases in the intensities scattered at low q, indicating strong concentration fluctuations.

High q behavior

At high q, the scattering curves are still the same for both copolymers, and they have remained close to the scattering measured at 20 °C. They are power laws, with an exponent –1.6, which is typical of swollen chains. This is remarkable, since PNIPAM homopolymer chains at this temperature would have collapsed.

Intermediate q values

At intermediate q values, the depression that was observed at the lower temperature has now vanished, indicating that concentration fluctuations in this range of distances are no longer suppressed. Since the electrostatic repulsions that oppose concentration fluctuations are still present, there must be other forces that promote these fluctuations.

Low q behavior

At low q, the magnitude of the scattering depends on the fraction of MADAP monomers that are ionized. The copolymer where only half of those monomers are ionized (cop 10–50, Fig. 4) give intensities that are more than ten times higher compared with the copolymer where all these monomers are ionized (cop 5–100, Fig. 3). For the partly ionized copolymers, the strong low q scattering decays as q^{-4}, indicating that large dense objects of a polymer rich phase have been formed. This is reminiscent of the behavior of PNIPAM homopolymer solutions brought above the LCST, where the same q^{-4} decay has been observed [16]. Thus, some segregation of PNIPAM chains occurs, but it is not full phase separation.

For the fully ionized copolymer, the decay of the low q scattering is $q^{-1.6}$, indicating that the copolymer chains have associated to form structures that are still branched chains swollen by the solvent.

At 60 and 70 °C

At high temperature, the scattering depends on the nature of the copolymers, in ways that are different at high q and low q values.

High q behavior

In this range, the shape of the decay has changed for the copolymer with few MADAP monomers (cop 5–100). The slope is –3 at 70 °C, indicating that the macromolecules are collapsed. Similar observations were made with other copolymers that also had a low fraction of MADAP.

For the copolymer that has more MADAP (cop 10–50), the slope is only –1.8, indicating that the chains have remained swollen.

Low q behavior

In this range, the scattering varies mostly with the fraction of MADAP monomers that have been ionized (Fig. 5). Copolymers in which only half of the MADAP monomers have been ionized (cop 10–50) give a very intense scattering. The low q part of this scattering follows the form factor of spheres (i.e. globular aggregates). The average number of macromolecules in each globule is given by the ratio of the intensity scattered at q→0 by these objects to the intensity scattered by a single macromolecule. Accordingly, at 70 °C each globule is made of 500 macromolecules lumped in a small volume. The average radius extracted from the fit by the form factor of spheres is in the range 340–390 Å (Fig. 4 and Table 2). The concentration of PNIPAM in each globule can be calculated from these data: it is 50%. This confirms that the segregated objects (the globules) are indeed dense PNIPAM phase [17]. Since the overall concentration of polymer in the sample was 2% wt., the volume fraction occupied by these globules must be less than 4%. The average distance between globules may

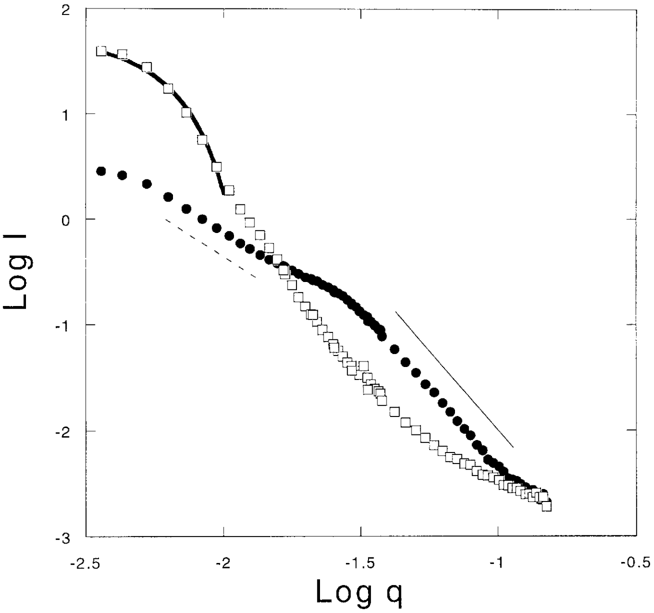

Fig. 5. SANS curves of the copolymer solutions at T = 70 °C: cop 5–100 (●); cop10–50 (□). The *continuous line* has a slope –3. The *dashed line* has a slope –1.7. The *curved line* is a fit using the scattering function of spheres (see Table 2)

Table 2. Size and mass of the aggregates present in 2% wt. solutions of cop 10–50. The sizes were obtained from a fit of the scattering curves at low q using the form factor of spheres (see Figs. 4 and 5). The mass was extracted from the intensity values at q→0, calibrated by the intensity for a dilute solution of polymer of known mass

Temperature (°C)	Mass (g/mol)	Mean radius (Å)
40	5×10^7	375
60	3.2×10^8	340
70	4.9×10^8	360

then be estimated assuming a cubic lattice: it is larger than 1600 Å.

Copolymers in which all the MADAP monomers have been ionized give a less intense scattering, which is characteristic of branched aggregates. These objects have not acquired as much mass as those formed from the other copolymers. Indeed, the mass per object is only 50 times larger than that of a single macromolecule. Therefore these aggregates are probably still full of water.

Discussion

The copolymers used in this work contain either 90 or 95% NIPAM monomers. Aqueous solutions of pure PNIPAM have a LCST at 32 °C, where they separate into a polymer-rich phase and a polymer-poor phase. At higher temperatures (40–70 °C), the phase separation is nearly complete, i.e. most of the polymer is in the polymer-rich phase [4]. Yet in this range of temperatures the copolymers produced neither a separation of macroscopic phases, nor the separation of macroscopic domains of one phase dispersed in the other. Instead, they evolved through limited segregation processes that lead to various microphase segregated structures. The aim of this discussion is to relate the observed structures to the characteristics of the copolymers.

Temperatures immediately above the LCST of PNIPAM

At temperatures up to 40 °C (and even 50 °C, data not shown), most chains remain swollen in water (cf. the low decay exponent –1.6 of the high q scattering in Figs. 3 and 4). This is a consequence of the presence of MADAP monomers in the chains, which resist dehydration. However, there is a tendency for interchain association, evidenced by the increase in the magnitude of the low q scattering. This association originates from the insolubility of NIPAM sequences. It has different consequences, depending on whether all MADAP monomers are ionized (localized charges) or only some of them (non-localized charges).

In copolymer solutions where all MADAP groups are ionized (cop 5–100, Fig. 3), the intensity scattered at low q increases by one order of magnitude with respect to low temperature, but the shape of the scattering curve (exponent –1.6) remains characteristic of loose aggregates. Thus, the association of PNIPAM sequences does not succeed in forming domains of a polymer-rich phase, even though the temperature is above the LCST of PNIPAM. The forces that prevent this segregation must be the electrostatic repulsions of the charged MADAP groups, which prevent any large-scale fluctuations in the polymer concentration.

In copolymer solutions where only half of the MADAP groups are ionized (cop 10–50, Fig. 4), the intensity at low q has increased much more (two orders of magnitude), and the shape of the scattering curve is characteristic of dense globules (See fit of the data at low q by the scattering function of spheres on Fig. 4). Since these globules are quite large (radius around 375 Å, see Table 2) they must contain, besides PNIPAM sequences, some MADAP monomers as well. Since only half of the MADAP monomers are ionized, the monomers that are trapped in the globules must have transferred their charges to monomers that remain outside the globules.

In both cases, localized or migrating charges, the microscopic structures determined by neutron scattering are in full agreement with the turbidity measurements (Fig. 1 and reference 10). Indeed, for copolymers that form only loose aggregates (cop 5–100, localized charges), only low values of turbidity are obtained. Conversely, for copolymers that form hairy polymer-rich particles of size around 375 Å (cop 10–50, migrating charges) the solution exhibits a large increase in turbidity.

Temperatures much above the LCST of PNIPAM

At higher temperatures, the macromolecules of the copolymer with few MADAP monomers (cop 5–100) have collapsed (cf. the steeper decay of the high q scattering). This collapse is a consequence of the high free energy cost of keeping NIPAM monomers in water. There is also increased interchain association, evidenced by the very strong scattering at low q. The structures that result from this segregation are the same as those that were formed at lower temperatures, but they have collected more polymer (with a saturation of the association beyond 60 °C).

In copolymer solutions where all MADAP groups are ionized, we find that the chains have associated to form branched aggregates (q^{-3} slope at high q in Fig. 5). Remarkably, this aggregation has still not proceeded to form large domains of a polymer rich phase (the exponent of the low q scattering is –1.7, still characteristic of branched aggregates). Thus, the electrostatic repulsions between charged MADAP groups prevent large-scale fluctuations in the polymer concentration.

In copolymer solutions where only half of the MADAP groups are ionized, we find that the dense globules of polymer rich phase, already formed at 40 °C, have now collected much more polymer (see fits by the scattering function of spheres in Figs. 4 and 5). These chains must have transferred their charges to those chains that remain in water. Thus, hairy particles with a dense inner core are obtained. Since the average ionization is one half of all MADAP groups, it follows that the dense globules may contain about half of all the comonomer mass; further transfer of polymer to these globules is blocked by the electrostatic charges, that can no longer be transferred away.

At this point, it is instructive to compare the types of microphase-separated structures that are obtained with ionic vs. non-ionic copolymers. Similar experiments have been performed with poly(*N*-isopropylacrylamide-*co*-acrylamide) copolymers containing 40% monomer units of AM [18]. The solutions of these copolymers have a LCST in the vicinity of 75 °C [8]. At temperatures slightly below the LCST, they undergo a microphase separation where the macromolecules segregate their hydrophobic monomers in polymer-rich globules, while the hydrophilic monomers remain in short sequences bound to the nodules. In the present case, this formation of hairy globules is also observed for polymers that have 5% migrating charges, but it is blocked if the charges are localized along the chains. This shows the enormous effect of ionized groups on copolymer structures: a very small fraction of such group can block the segregation processes at an early stage, because further segregation would require the accumulation of such charges in the volume or at the surface of the polymer rich globules.

Conclusions

The structures formed by the copolymer solutions depend on the localization of electrostatic charges on the macromolecules.

If the charges cannot be transferred between different sites, they initially oppose the collapse that would be favored by NIPAM sequences. When the free energy cost of keeping NIPAM in water becomes too high, all chains collapse. However, this collapse cannot produce large domains, since the charged groups are localized at random locations along the chains, and they repel each other. These constraints impose the formation of branched aggregates that have a very large surface area, so that all the charged groups remain in water or at water/NIPAM interfaces.

If the charges can be transferred between different sites, then the second microphase separation is observed. Some chains lose their charges and separate out of the aqueous phase to form dense globules of a polymer rich phase. The other chains collect all the charges and remain in the aqueous medium. Presumably, some macromolecules have one section in the globules and another section in the aqueous phase, thereby acting as amphiphiles and determining the size and surface area of the globules.

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