Influence of Migrating Ionic Groups on the Solubility of Polyelectrolytes: Phase Behavior of Ionic Poly(*N*-isopropylacrylamide) Copolymers in Water

G. Bokias,[†,⊥] V. V. Vasilevskaya,[*,‡] I. Iliopoulos,[†] D. Hourdet,[†] and A. R. Khokhlov[§]

Laboratoire de Physico-chimie Macromoléculaire, UMR 7615, ESPCI-CNRS-UPMC, 10 rue Vauquelin, 75231 Paris Cedex 05, France; Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova ul.28, Moscow 117823, Russia; and Physics Department, Moscow State University, Vorob'evu gory, Moscow 119899, Russia

Received March 7, 2000; Revised Manuscript Received July 31, 2000

ABSTRACT: The influence of the migration of charges bound to polymer chains on the solubility of the charged polymer is studied theoretically and experimentally. It is found that, due to the migration of charges, the solubility of such a polymer is lower than the solubility of a polyelectrolyte having the same fraction of nonmigrating charged groups. It is shown that the solubility of a copolymer with an ionizable component depends on the ratio of the degree of ionization i to the fraction x of monomer units B able to be ionized. If this ratio equals unity ($i = x$), the solubility of the copolymer increases with an increase in the fraction of monomer units B. When the fraction x of monomer units B is much higher than the actual degree of ionization i, the ions bound to the polymer chains can be easily transferred from one chain to another in an optimum way so that to minimize the loss in translational entropy of the counterions. As a result, demixing of the polymer solution for $i \neq x$ occurs at lower values of the polymer concentration ϕ than in the case of a polymer with $i = x$; the corresponding value of ϕ is still higher than the demixing concentration for electroneutral polymer. The theoretical results are supported experimentally by a study of the solubility of copolymers of *N*-isopropylacrylamide, NIPAM, with *N*,*N*-[(dimethylamino)propyl]-methacrylamide, MADAP, with different degrees of ionization. It is found that the migration of ions bound to the polymer chains has a significant influence on the solubility of such copolymers. Because of an increase in the hydrophilicity of the copolymers with increasing fraction of MADAP units, the dependence of the solubility of these copolymers on the MADAP fraction has a complex nonmonotonic character.

1. Introduction

It is known that the solubility of polymer molecules in aqueous media can be significantly improved by introducing charged units into the polymer chains.[1,2] The physical reason for this solubility enhancement is connected to the presence of counterions that compensate the total charge of the polymer chains. The counterions move freely in the solution and, owing to their high translational entropy, try to occupy the whole volume of the system. This leads to an increase of polymer solubility, since the motion of the polymer chains depends on the motion of their counterions (the condition of total electroneutrality), and therefore, the phase demixing should cause a huge loss in translational entropy (see Figure 1).

This type of solubility enhancement was predicted theoretically and observed experimentally for the melt and solution of two different polymers[1] and studied later experimentally in ref 3. In the present paper we extend our model[1] to the case of polymer chains with migrating charges. This situation is realized when the degree of ionization of a copolymer is lower than the fraction of monomer units potentially able to be ionized. For example, let us consider a copolymer containing an acidic monomer with carboxylic COOH groups. By neutralization (i.e., adding base), the COOH groups belonging to this polymer are gradually charged (i.e., converted to COO^- form). For intermediate degrees of neutralization, the COO^- and COOH groups coexist in the chain, and, therefore, the hydrogen ions can migrate along the chain. Theoretically, this effect is equivalent to the migration of charged groups along the chain and from one chain to another.

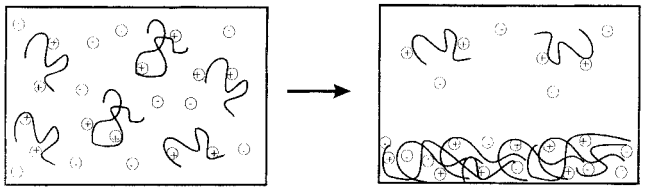


Figure 1. Schematic illustration of phase demixing in polyelectrolyte solution. Phase demixing leads to a significant loss of translational entropy of counterions. The chains in the supernatant and in the precipitant have the same charge density as in the one-phase mixture (two charges per chain).

Under the conditions of phase separation, the charged groups can also migrate between the two phases (precipitant phase and supernatant phase). Therefore, it should be a tendency for the charged units and the corresponding counterions to remain in the supernatant phase, which normally occupies a much larger volume than the precipitant (see Figure 2). This means that the loss in translational entropy of counterions, caused by the polymer precipitation, becomes relatively small.

[†] Laboratoire de Physico-chimie Macromoléculaire.
[‡] Russian Academy of Sciences.
[§] Moscow State University.
[⊥] Present address: Department of Chemical Engineering, University of Patras, GR-26500 Patras, Greece.
* To whom correspondence should be addressed.

10.1021/ma000413k CCC: $19.00
Published on Web 12/02/2000

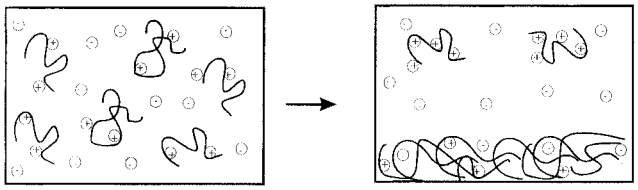


Figure 2. Schematic illustration of phase demixing in solution of polyelectrolyte with migrating charges. To diminish entropy loss of counterions, the charge density of the chains in the supernatant has been increased (four charges per chain) and in the precipitant decreased (one charge per chain) as compared to the case of homogeneous solution.

Thus, the effect of migration of charges along the polymer chains can lead to the worsening of polymer solubility in comparison to the solubility of a polymer for which all the ionizable units are actually ionized.

To shed light on this problem, we develop here a simple theory and perform experiments on the influence of migration of ions on the solubility of polymer molecules. In our study, we investigate copolymers of *N*-isopropylacrylamide, NIPAM, and *N*,*N*-[(dimethylamino)propyl]methacrylamide, MADAP.

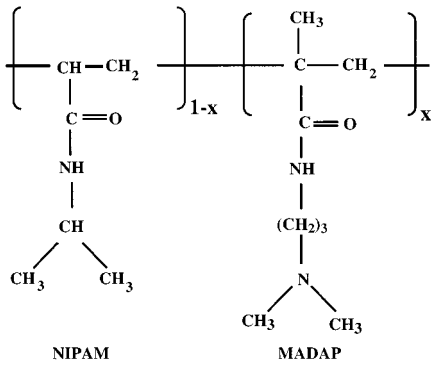
Poly(*N*-isopropylacrylamide), PNIPAM, is a water-soluble polymer characterized by an inverse solubility behavior in aqueous solution. That behavior is attributed to the delicate balance between the hydrophilic properties of the amide groups and the hydrophobic character of the isopropyl moieties.[4] When the temperature exceeds ~32−34 °C, i.e., the lower critical solution temperature (LCST) of this polymer, the aqueous PNIPAM solution separates into two phases.[4,5] This phase transition, accompanied by a large increase in solution turbidity, is abrupt, well-defined, and accomplished within a narrow temperature range.[6−8] The polymer-rich phase contains most of the polymer, while the PNIPAM concentration is very low in the water-rich phase.[5] Behind the fundamental interest, this inverse solubility behavior is expected to be useful for technological applications in various fields (such as in biological or photosensitive systems).[4]

To shift the LCST to lower or higher values, copolymers of NIPAM with more hydrophobic or more hydrophilic comonomers have been synthesized.[6,8−16] Concerning nonionic random copolymers of NIPAM, the characteristics of the phase transition (abrupt and well-defined) are preserved,[6] even for copolymers containing a relatively high fraction of hydrophilic nonionic units.[6,10] For instance, the LCST is shifted to ~55 °C for a copolymer containing 20 mol % acrylamide units.[6]

Among the ionic polymeric systems containing NIPAM,[8,11−23] the most studied are the copolymers or gels with acrylic acid, AA (in its salt form).[8,11,12,15,16,18−21] In this case, replacing ~10 mol % of the NIPAM units by acrylic acid salt suffices to shift the LCST to temperatures higher than 100 °C.[8,12,15] For lower ionic compositions, the formation of stable colloidal particles at temperatures higher than the LCST has been reported.[13−16,23]

The advantage when using weak electrolytes as comonomers, such as AA, is that the polymer chain can be charged at will, from 0 (nonionic form) up to the completely charged form of the comonomer, by simple neutralization. However, for the NIPAM/AA copolymers, the situation is more complex due to the formation of hydrogen bonds between the amide group and the acid form of the AA units.[8,15,24] This type of association is well-known in mixtures of the two homopolymers.[25,26]

Scheme 1. Chemical Structure of the NIPAM Copolymers Used in This Study



To avoid such hydrogen-bonding effects, we use a weak base, *N*,*N*-[(dimethylamino)propyl]methacrylamide, MADAP, as ionizable comonomer instead of AA. The chemical structure of the copolymers, prepared by radical copolymerization in water, is illustrated in Scheme 1. The fraction *x* of MADAP units varies from 0 (homopolymer PNIPAM) to 0.25. Their phase behavior in aqueous solution has been followed by a turbidimetric method, based on the scattering of a light beam of a wavelength 500 nm at 90°. The whole ionization range of the MADAP units has been explored: from the nonionic basic form to the completely ionized chloride salt form. All the qualitative considerations outlined in the beginning of this paper remain valid for the NIPAM/MADAP copolymers. The only difference is that the effective charge able to migrate along the chain is positive rather than negative.

The paper is organized as follows. In the next section we will derive the free energy of the solution of a polymer with migrating charges and calculate the spinodal of such solution with respect to its phase separation. Section 3 contains the experimental data on the solubility of NIPAM/MADAM copolymers with different fractions of MADAM units and different degrees of ionization. The comparison of the obtained experimental data with the theoretical results is given in the discussion section 4. Conclusions are formulated in section 5.

2. Theoretical Part

Free Energy. Let us consider the solution of a copolymer containing two different types of monomer units A and B. Monomer units B can be ionized, either completely or partially. At intermediate degrees of ionization, the charges associated with the polymer chains can move along the chain and from one chain to another. The counterions, which compensate the total charge of the polymer chains, can move freely in the solution.

The connection of this theoretical model with the experimental system described above is the following: NIPAM corresponds to A monomer units; MADAP corresponds to B monomer units; the positively charged ions of hydrogen connected with the amino groups of MADAP units are the migrating charges; the negatively charged Cl^- ions are the counterions.

Let *P* be the degree of polymerization of the copolymer, *x* the fraction of monomer units B (ratio of the number of monomer units B to the total number of chain

units), and i the degree of ionization, i.e., the ratio of the total number of charged monomer units to the total number of chain units. In this way, i denotes also the linear charge density of the polymer chain, and the following relation is fulfilled: $x \geq i$.

The free energy F of the solution of a polymer with migrating charges can be presented as a sum of three contributions: the free energy of interaction F_{int}, the free energy F_{tr-en} from the translational entropy of freely moving counterions, and the entropy contribution F_{tr-mig} of migrating ions which can translate from one polymer chain to another:

$$F = F_{int} + F_{tr-en} + F_{tr-mig} \quad (1)$$

Of course, direct electrostatic interactions between charged species should be also taken into account. However, the direct electrostatic contribution to the free energy is always negligible in comparison with the free energy due to the translational entropy of counterions.[27]

The free energy F_{int} of polymer−solvent interaction and entropy of intermixing can be written in the framework of the Flory−Huggins approximation[28] as

$$\frac{F_{int}}{T} = \frac{V}{a^3}\left[\frac{\phi}{P}\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right] \quad (2)$$

Here V is the total volume of the solution, T is the temperature in energetical units, a is the elementary spacing in the Flory−Huggins model, ϕ is the volume fraction of the polymer, and χ is the Flory−Huggins parameter.

The contribution F_{tr-en} due to the translational motion of the counterions is

$$\frac{F_{tr-en}}{T} = Ni\ln(i\phi) \quad (3)$$

Here N is the total number of monomer units in solution ($N = V\phi/a^3$), and therefore Ni is the total number of counterions, while $i\phi$ is the volume fraction of counterion units.

The contribution F_{tr-mig}, accounting for the entropy due to the possible translation of the total number Ni of migrating ions over the total number Nx of possible sites (equal to the total number of monomer units B) potentially able to host the migrating charges, can be presented as

$$F_{tr-mig} = -T\ln S$$

$$S = \frac{(Nx)!}{(Ni)!(Nx-Ni)!} \quad (4)$$

From eqs 3 and 4 and using the Stirling approximation ($\ln(k!) \sim k\ln k$), we obtain the following expression for the free energy of ions bound to the polymer chains and the freely moving counterions:

$$\frac{F_{tr-en} + F_{tr-mig}}{T} = Ni\ln i^2\phi + N(x-i)\ln(x-i) - Nx\ln x \quad (5)$$

Solubility of Polymer with Charges Unable To Migrate. First, let us consider the case $x = i$, corresponding to the situation when the number of charged units is exactly equal to the number of monomer units B. The number of possible positions for the charges along the polymer chains is exactly equal to the number of charges; i.e., there is no possibility for the charge translation from one chain to another, and therefore the corresponding contribution to the free energy is equal to zero: $F_{tr-mig} = 0$. As a result, the condition of electroneutrality makes the motion of counterions directly coupled with the motion of the polymer chain.

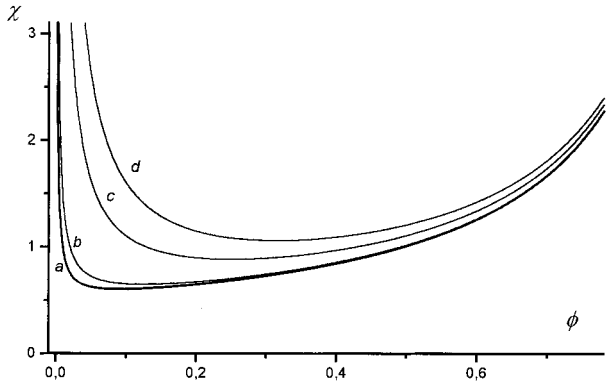


Figure 3. Spinodal curves for the solution of charged polymer for degree of polymerization $P = 100$ at $x = i$ and $i = 0$ (a), 0.01 (b), 0.1 (c), and 0.2 (d).

The free energy $f^{x=i}$ of the solution (per unit of volume) can be written as the sum of the free energy of interaction and the free energy due to the translational entropy of the counterions (neglecting the contributions which depend linearly on ϕ):

$$\frac{f^{x=i}}{T} = \frac{F}{TV}a^3 = \frac{\phi}{P}\ln\phi + \phi i\ln\phi i + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \quad (6)$$

One can see that, mathematically, the expression for the free energy (eq 6) coincides with the expression for the free energy of the solution of a similar electroneutral polymer[29] with a lower effective degree of a polymerization, i.e., $P_{eff} = P/(iP + 1)$. Therefore, the compatibility of the mixture is expected to increase.

The spinodal curve with respect to the phase separation for such a solution is determined by equating the second derivative of the free energy $f^{x=i}$ to zero:[29]

$$\partial^2 f^{x=i}/\partial\phi^2 = 0 \quad (7)$$

The results of the numerical calculation according to eq 7 are shown in Figure 3 for $P = 100$ and for different values of the fraction of charged monomer units, i. One can see that, by increasing i, the solubility of the polymer improves. The physical reason for such an effect is clear: due to the condition of electroneutrality, the translation of a part of freely moving counterions to the precipitate (together with the corresponding polymer chains) leads to an extremely high loss in their translational entropy. It should be noted that the effect of compatibility enhancement by introduction of a low fraction of charged units into the chain was first described theoretically in ref 1.

Solubility of Polymer with Migrating Charges. Let us consider now the general case: $x > i$. In this case, the free energy F depends not only on the polymer concentration ϕ but also on the total number $N_z = Ni$ of charged units and, therefore, on the total number N of monomer units in the system, as well as on the total

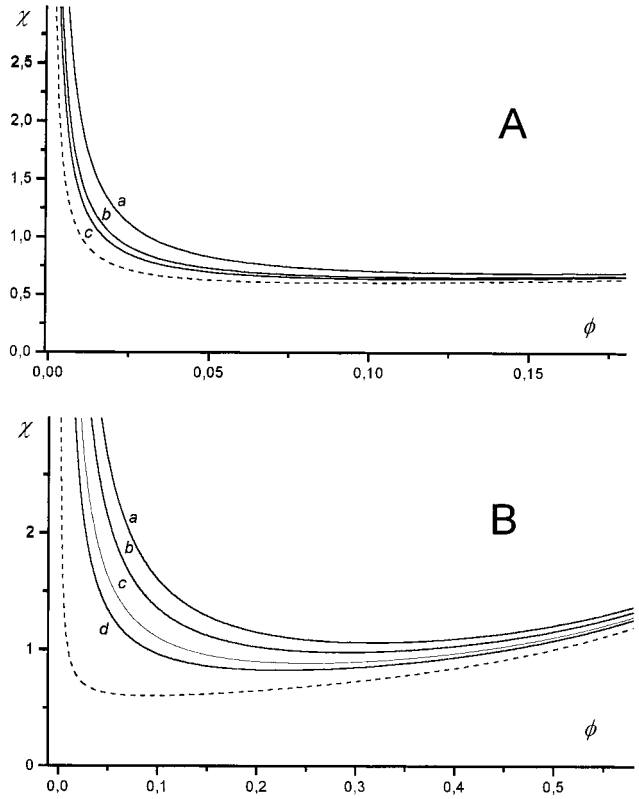


Figure 4. Spinodal curves of solution of copolymer with component able to ionization for $P = 100$, degree of ionization $i = 0.01$, and $x = 0.01$ (a), 0.02 (b), and 1.0 (c) **(A)**; degree of ionization $i = 0.1$ and $x = 0.1$ (a), 0.12 (b), 0.25 (c), and 1.0 (d) **(B)**. Dashed lines represent the spinodal curves for corresponding electroneutral polymer.

volume V. For such a system, the spinodal curve can be calculated according to equation[30]

$$\det\begin{vmatrix} \dfrac{\partial^2 F(V,N,N_z)}{\partial^2 V} & \dfrac{\partial^2 F(V,N,N_z)}{\partial V\,\partial N} & \dfrac{\partial^2 F(V,N,N_z)}{\partial V\,\partial N_z} \\ \dfrac{\partial^2 F(V,N,N_z)}{\partial V\,\partial N} & \dfrac{\partial^2 F(V,N,N_z)}{\partial^2 N} & \dfrac{\partial^2 F(V,N,N_z)}{\partial N\,\partial N_z} \\ \dfrac{\partial^2 F(V,N,N_z)}{\partial V\,\partial N_z} & \dfrac{\partial^2 F(V,N,N_z)}{\partial N\,\partial N_z} & \dfrac{\partial^2 F(V,N,N_z)}{\partial^2 N_z} \end{vmatrix} = 0 \quad (8)$$

After simple calculations, eq 8 can be rewritten as

$$\det\begin{vmatrix} \dfrac{\phi^2}{P} + \dfrac{\phi^2}{1-\phi} - \phi^2 + 2\chi\phi^3 + 2i\phi^2 & -\dfrac{\phi}{P} - \dfrac{\phi^2}{1-\phi} + 2\chi\phi^2 & -2\phi \\ -\dfrac{\phi}{P} - \dfrac{\phi^2}{1-\phi} + 2\chi\phi^2 & \dfrac{1}{P} + \dfrac{\phi}{1-\phi} - 2\chi\phi + \dfrac{x^2}{x-i} - x & -\dfrac{x}{x-i} \\ -2\phi & -\dfrac{x}{x-i} & \dfrac{2}{i} + \dfrac{1}{x-i} \end{vmatrix} = 0 \quad (9)$$

Figure 4 presents the spinodal curves calculated from eq 9 for a solution of a polymer with migrating charges: $i = 0.01$ (A), $i = 0.1$ (B), and $x > i$. One can see that, by increasing x, the region corresponding to the phase demixing becomes wider, and the phase separation occurs at lower concentrations of polymer ϕ.

The physical reason for this effect can be explained as follows. In the course of the phase separation the migrating charges can redistribute due to the excess of sites available for the bound ions. As a result, in the diluted supernatant phase, they occupy almost all the available sites ($i_{dil} \sim x_{dil}$), while the fraction of charged units in the concentrated phase becomes much lower than the average over the whole volume: $i_{conc} \ll i$. In other words, there is a tendency for the concentrations of the charged units in the coexisting phases to be approximately equal to each other. In this case, the translational entropy of the counterions reaches a maximum. As a result of such a redistribution of the charged monomer units, the phase separation leads to much smaller loss in translational entropy of counterions in comparison with the case $i = x$. The higher the value of the x/i ratio, the lower the loss of translational entropy of counterions resulting from the phase separation. However, even at $x \gg i$, the spinodal curve for a solution of polymer with migrating charges still deviates from the spinodal curve of the corresponding electroneutral polymer solution (dashed lines in Figure 4), since further redistribution of the migrating charges can lead to loss in the combinatory entropy associated with these charges.

Thus, from the theoretical consideration, we can draw the following conclusions. The solubility of a copolymer with an ionizable component depends essentially on the ratio of the degree of ionization i to the fraction x of the monomer units B able to be ionized. If this ratio is equal to unity ($i = x$), the solubility of the polymer improves with the increase of the fraction of monomer units B. The reason is that the demixing in such solution leads to significant loss in translational entropy of freely moving counterions. In the case, when the fraction of monomer units B is much higher than the degree of ionization, the co-ions can be easily transferred from one chain to another in an optimum way so as to minimize the loss in translational entropy of the counterions. As a result, the demixing of a polymer solution for $i \neq x$ occurs at lower values of polymer concentration ϕ than in the case of a polymer with $i = x$, these values being still higher than the demixing concentration of electroneutral polymer.

Table 1. Characteristics of the NIPAM/MADAP Copolymers Used in This Study

notation	x^a (^{13}C NMR)	x^a (potentiometric titration)	$[\eta]^b$ (cm^3/g)
PNIPAM	0	0	330
cop5	0.05	0.054	220
cop10	0.1	0.104	204
cop25	0.26	0.25	260

[a] x is the molar fraction of MADAP units of the copolymer. [b] $[\eta]$ is measured in a 0.5 M $LiNO_3$ aqueous solution at 20 °C. The copolymers were in the uncharged basic form.

3. Experimental Section

Polymers. The homopolymer, PNIPAM,[31] and the NIPAM/MADAP copolymers were synthesized by radical polymerization in water at 29 °C, using the redox couple ammonium peroxydisulfate/sodium metabisulfite as initiator. Monomers and initiators were products of 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 (~90% conversion). 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. In Table 1, some of the characteristics of the polymers used in this study are presented. Under the used polymerization conditions, the reactivity ratios of the two monomers are found to be very similar ($r_{NIPAM} = 0.62$ and $r_{MADAP} = 0.59$). Therefore, no significant composition drift is expected for the present

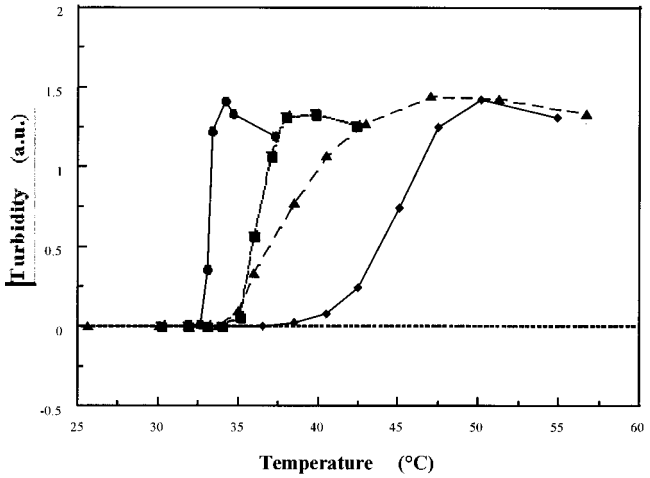


Figure 5. Influence of the temperature on the turbidity of the aqueous solutions of PNIPAM (●) and NIPAM/MADAP copolymers at their nonionic basic form: (■) cop5, (▲) cop10, and (◆) cop25. $c = 0.01$ g/cm^3.

copolymers. A detailed study of the synthesis and characterization of these copolymers will be given elsewhere.[32] A copolymer annotated, for instance, cop10 is a NIPAM/MADAP copolymer with $x = 0.10$; i.e., it contains 10 mol % MADAP units.

Turbidimetry. The intensity of a light beam at a wavelength 500 nm, scattered by the polymer solution at 90°, was measured on a spectrophotometer SPF-500C (SLM AMINCO), equipped with a thermostated cell and magnetic stirring. The apparatus settings were kept constant in all the experiments. Temperature changes were made manually and the solutions were thermostated for at least 15 min under stirring at the desired temperature before performing the measurements.

Sample Preparation. First, concentrated stock solutions of the various polymers in water were prepared. The final solutions were obtained from the stock solutions after adjustment of the ionization degree (addition of 0.1 M HCl) and further dilution with water. The measurements were performed at least 24 h after preparation of the samples. Water was purified with a Millipore system, combining inverse osmosis membrane (Milli-R) and ion-exchange resins (Milli-Q).

Results. Figure 5 presents typical turbidity curves for the homopolymer PNIPAM and the three NIPAM/MADAP copolymers in the nonionic form, at a concentration $c = 0.01$ g/cm^3. The aqueous solution of PNIPAM turns turbid very sharply at 33 °C. When the MADAP content in the copolymers increases, the corresponding turbidity curves move to higher temperatures, so that for cop25 the onset of the turbidity (assigned as the cloud point of cop25 at this concentration) is at ∼40 °C. This increase of the cloud point, from 33 °C for the PNIPAM to 40 °C for cop25, was expected since the MADAP units are more hydrophilic than NIPAM. For comparison, we note that the cloud point of a copolymer containing 10 mol % acrylamide is already shifted to ∼45 °C. The relatively low increase of the cloud point in our copolymers shows that the MADAP units are not as hydrophilic as the acrylamide. Indeed, the homopolymer PMADAP, in the nonionic form, presents a cloud point at ∼80 °C.[33] Note finally that, although the turbidity levels off at the same value for all the systems, the transition for the copolymers is not as sharp as for PNIPAM. This is more evident for cop25 and is probably due to the presence of a small fraction of charges onto the polymer chain, resulting from the self-ionization of MADAP, which is a weak base. The contribution of self-ionization to the behavior of these copolymers becomes negligible as soon as they are partially neutralized by HCl.

The influence of the introduction of charges to the polymer chain is demonstrated in Figure 6, where the turbidity behavior of cop5 at various ionization degrees, *i*, is presented

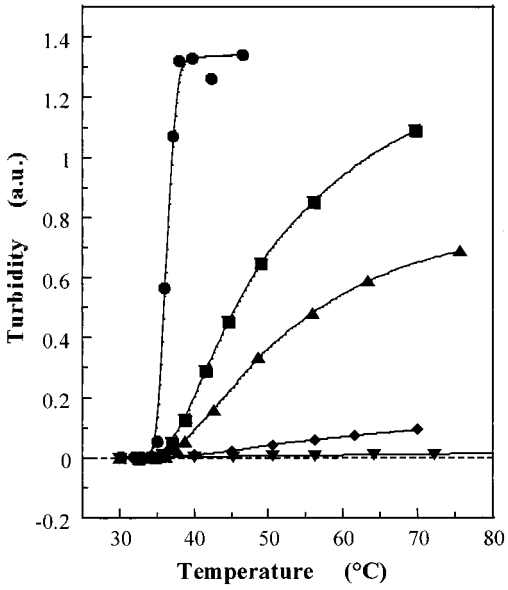


Figure 6. Turbidimetric behavior of the cop5 at various degrees of ionization, *i*: (●) $i = 0$, (■) $i = 0.0125$, (▲) $i = 0.025$, (◆) $i = 0.035$, and (▼) $i = 0.05$. $c = 0.01$ g/cm^3.

($c = 0.01$ g/cm^3). As the charge content increases by gradual neutralization, the corresponding solutions become less and less turbid. Moreover, the higher the value of *i*, the more gradual the increase in turbidity as a function of temperature. Finally, the fully neutralized sample, $i = 0.05$, is macroscopically homogeneous (no turbidity) in the entire temperature range studied. Similar results with increasing *i* were obtained for cop10 and cop25 (not shown here).

It is worthy to note that in all cases, even if the copolymers are slightly charged, the system does not separate into two well-defined phases but, rather, is stabilized in the form of a colloidal suspension: droplets of the polymer-rich phase are dispersed in the water-rich phase. These colloidal suspensions are stable, and no changes in the turbidity or in the appearance of the solutions were observed after testing them for several days at the appropriate temperature. The stabilization in the form of colloidal particles has often been observed when the NIPAM chain contains a small fraction of charged units.[13,16,23]

In Figure 7a the turbidimetric behavior of cop10 and cop25 at $i = 0.10$ is presented, while Figure 7b presents similar results for the three copolymers at $i = 0.05$. In all cases, the polymer concentration is 0.01 g/cm^3. It is obvious that the tendency for phase separation increases as the MADAP content in the copolymer increases. Indeed, as shown in Figure 7a, the MADAP-richer cop25 clearly phase-separates at ∼55 °C, whereas cop10 (containing only 10 mol % MADAP units) does not phase-separate in the temperature range studied. Similar conclusions can be drawn from Figure 7b where all the copolymers bear 5 mol % cationic charges. The copolymers that are richer in MADAP units, i.e., cop10 and cop25, phase-separate at ∼36 and ∼50 °C, respectively. On the contrary, the solution of cop5 does not turn turbid in the temperature range studied. As seen in Figure 7b, although the cloud point of cop25 is above that of cop10, the slope of the turbidity curve of cop25 is much higher, so that above ∼70 °C the solution of cop25 turns more turbid than the solution of cop10. All these observations suggest that, when the charge density is kept constant, the higher the hydrophilic content (MADAP) of the copolymers, the easier and more efficient the tendency to phase-separate from an aqueous solution.

The experimental results presented above were obtained at a constant polymer concentration 0.01 g/cm^3. To get a more complete view of the phase behavior of our copolymers, we established their "phase diagrams", i.e., the cloud point as a function of the polymer concentration for several ionization degrees.

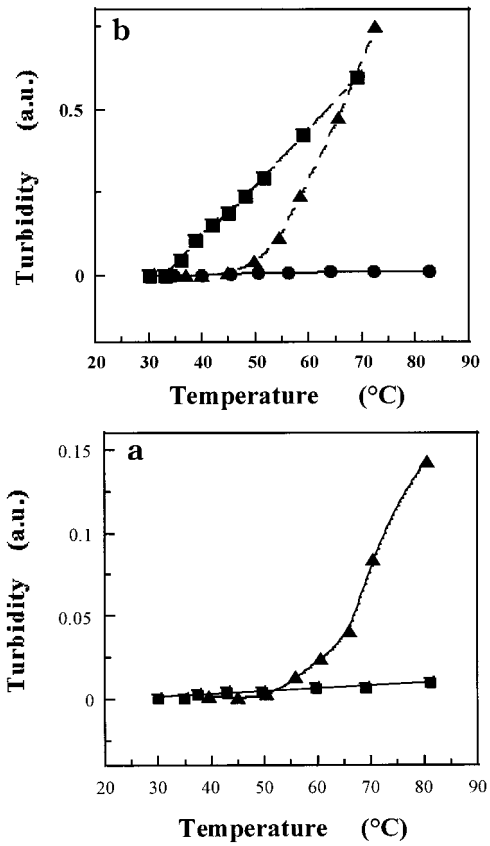


Figure 7. Comparison of the turbidimetric behavior of the NIPAM/MADAP copolymers, containing the same charge content, *i*: (a) $i = 0.10$ and (b) $i = 0.05$. (●) cop5, (■) cop10, and (▲) cop25. $c = 0.01$ g/cm^3.

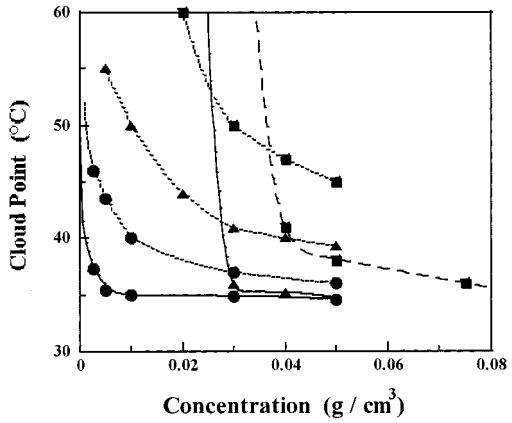


Figure 8. "Phase diagrams" of the NIPAM/MADAP copolymers at various degrees of ionization, *i*. Solid lines: cop5 ((●) $i = 0$ and (▲) $i = 0.05$). Dashed line: cop10 ((■) $i = 0.10$). Dotted lines: cop25 ((●) $i = 0$, (▲) $i = 0.05$, and (■) $i = 0.125$).

In Figure 8, the results concerning cop5 and cop25 at $i = 0$ (uncharged form) and $i = 0.05$ (the ionization is full for cop5 and partial for cop25) are plotted. For comparison, we have also presented the data for cop10 at $i = 0.10$ and for cop25 at $i = 0.125$. The phase diagrams of cop5 and cop25, in the uncharged form ($i = 0$), look rather similar and still keep the general features of the phase diagram of the homopolymer PNIPAM (not shown here).[5] They are rather flat over a broad concentration range, and only when the polymer concentration is very low does the phase-separation temperature increase rapidly. The curve of cop25 lies above that of the cop5, a result attributed to the higher fraction of hydrophilic (MADAP) units.

4. Discussion

The influence of the charged units on the solubility of these copolymers, at least as seen by the turbidity of the solutions, supports the theoretical predictions of the previous section. As predicted by theory, and shown in Figure 3, when the copolymers are fully charged ($i = x$), their solubility significantly increases with increasing x. Indeed, cop5 in the fully charged form ($i = 0.050$) does not exhibit any phase separation for concentrations lower than ~0.03 g/cm^3, whereas in the uncharged form ($i = 0$) it presents a cloud point at concentrations 1 order of magnitude lower. The increase of the solubility by complete neutralization is even more evident for cop10 at $i = 0.10$; the phase separation occurs only for concentrations higher than ~0.04 g/cm^3 (no measurable turbidity at $c = 0.03$ g/cm^3); see Figure 8. Finally, cop25 at $i = 0.25$ does not present any turbidity in the entire concentration and temperature range studied.

Even more interesting is the behavior of the copolymers when they are only partially ionized. For instance, increasing i from 0 to 0.05 has less effect on the phase diagram of cop25 than for cop5. Moreover, at $c = 0.02$ g/cm^3, cop5 ($i = 0.05$) does not exhibit any measurable turbidity while cop25 ($i = 0.125$) still shows a cloud point (Figure 8). A similar conclusion can be drawn when comparing cop25 ($i = 0.125$) and cop10 ($i = 0.10$).

The experimental observations reported in Figures 7 and 8 support the theoretical predictions on the phase behavior of partially ionized copolymers presented in Figure 4 (charge migration effect). The effect of charge migration is very clear in Figure 7b. When $i = x$ (cop5), no charge migration is possible and the sample remains clear over the temperature range studied. On the other hand, the copolymer with the highest fraction of MADAP units (cop25) exhibits the most pronounced tendency to phase separation since now the charge migration is highly facilitated ($x - i = 0.20$) and the slope of the turbidity curve is rather steep. Finally, cop10 exhibits an intermediate behavior with a turbidity curve of smoother slope ($x - i = 0.05$). Of course, cop25 is the most hydrophilic, and that explains why the turbidity appears at higher temperature (~50 °C) compared to cop10 (~36 °C).

Comparing the phase diagrams of cop25 and cop5 at $i = 0.05$ (Figure 8) and the theoretical curves of Figure 4, one can note that the experimental curves intersect each other, i.e., at constant values of i, by increasing x, the region of instability widens at low temperatures, whereas it becomes smaller at higher temperatures. However, the theory presented above shows that, due to the effect of the migration of charges, the region of phase demixing should widen with increasing x for all the values of parameter χ. The reason for this discrepancy is that, for the specific experimental system studied, the introduction of ionizable groups not only leads to the migration effect but also changes the polymer/solvent interaction (i.e., the system becomes more hydrophilic).

For the theoretical accounting for this effect, we have introduced the following dependence of excluded-volume interaction (i.e., parameter χ) on the polymer composition x.

$$\chi = \chi_1 x + \chi_2(1 - x) \qquad (10)$$

In eq 10 the parameter χ_1 describes the excluded-volume interaction of monomer units able to be ionized. (In

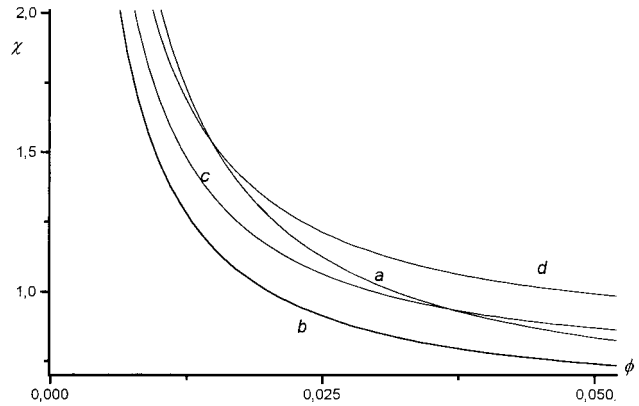


Figure 9. Spinodal curves for the solution of charged copolymer with comonomer units having different affinity to the solvent for $\chi_1 = 0$, $P = 100$, $i = 0.01$, and $x = 0.01$ (a), 0.05 (b), 0.2 (c), and 0.3 (d).

terms of our theoretical consideration, these are monomer units B, whereas experimentally these are the monomer units of MADAP.) The parameter χ_2 is responsible for excluded-volume interaction of monomer units A (i.e., in our experiments the thermosensitive units of NIPAM). It is natural to suppose, to a first approximation, that by changing the temperature, the interaction parameter χ_2 of the thermosensitive NIPAM monomer is changed, whereas the interaction parameter χ_1 is kept constant. Since MADAP is a hydrophilic polymer, it is natural to assume that the value of parameter χ_1 is at least less than 0.5. In our calculations (see below), for simplicity, we have chosen the value $\chi_1 = 0$.

The results obtained under these assumptions are presented in Figure 9. One can see that, in this case, the region of phase demixing changes in a complex manner with the change of parameter x. At low values of x, the region of phase demixing becomes wider with increase of x, due to the effect of migration of charges described above. However, with a further increase of parameter x, the field of phase separation becomes narrower once again. This is because the polymer becomes more hydrophilic as a whole, due to the increase of the fraction x of ionizable groups. Comparing the curves a and c−d in Figure 9, one can see that the curves intersect each other in accordance with the experimental data shown in Figure 8. Thus, the experimental data presented above can be qualitatively described, if one takes into account the proper balance between the polyelectrolyte effect, the charge migration, and the change of the excluded-volume interaction.

5. Conclusions

In the present paper we have shown that the phase behavior of weakly charged polyelectrolytes depends essentially on whether the position of the charged units along the chain is fixed or whether the charges can migrate within the chain and between the different chains. The possibility of such migration diminishes the effect of compatibility enhancement caused by the translational entropy of the counterions, i.e., weakens the stability toward the precipitation of the polymer chains. This theoretical result is in full accordance with the experimental data (turbidimetry) obtained for the solutions of copolymers of NIPAM (thermosensitive monomer) and MADAP (ionizable monomer).

Acknowledgment. This work was supported by the European Union under the Marie Curie Research Training Grant ERBFMBICT960831 for the postdoctoral stay of G. Bokias in Paris, by Program "University of Russia−Fundamental Research" (Grant 5261), by Russian Foundation for Basic Research (Grant 98-03-33336), and by NATO linkage (Grant PST.CLG 975359).

References and Notes

(1) Vasilevskaya, V. V.; Starodubtzev, S. G.; Khokhlov, A. R. *Vysokomol. Soed.* **1987**, *29B*, 930.
(2) Grosberg, A. Yu.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; AIP Press: New York, 1994.
(3) Philippova, O. E.; Starodubtzev, S. G. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 421.
(4) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(5) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2*, 1441.
(6) Priest, J. H.; Murray, S. L.; Nelson, R. J.; Hoffman, A. S. *ACS Symp. Ser.* **1987**, *350*, 275.
(7) Schild, H. G.; Tirrell, D. A. *J. Phys. Chem.* **1990**, *94*, 4352.
(8) Chen, G.; Hoffman, A. S. *Macromol. Rapid Commun.* **1995**, *16*, 175.
(9) Chiklis, C. K.; Grasshoff, J. M. *J. Polym. Sci., Part A-2* **1970**, *3*, 1617.
(10) Taylor, L. D.; Cerankowski, L. D. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2551.
(11) Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *Macromolecules* **1993**, *26*, 2496.
(12) Chen, G.; Hoffman, A. S. *Nature* **1995**, *373*, 49.
(13) Deng, Y.; Pelton, R. *Macromolecules* **1995**, *28*, 4617.
(14) Shibayama, M.; Tanaka, T. *J. Chem. Phys.* **1995**, *102*, 9392.
(15) Yoo, M. K.; Sung, Y. K.; Cho, C. S.; Lee, Y. M. *Polymer* **1997**, *38*, 2759.
(16) Qiu, X.; Kwan, C. M. S.; Wu, C. *Macromolecules* **1997**, *30*, 6090.
(17) Kitano, H.; Yan, C.; Nakamura, K. *Makromol. Chem.* **1991**, *192*, 2915.
(18) Beltran, S.; Baker, J. P.; Hooper, H. H.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* **1991**, *24*, 549.
(19) Shibayama, M.; Tanaka, T. *J. Chem. Phys.* **1992**, *97*, 6842.
(20) Yu, H.; Grainger, D. *Macromolecules* **1994**, *27*, 4554.
(21) Shibayama, M.; Fujikawa, Y.; Nomura, S. *Macromolecules* **1996**, *29*, 6535.
(22) Matsukata, M.; Hirata, M.; Gong, J. P.; Osada, Y.; Sakurai, Y.; Okano, T. *Colloid Polym. Sci.* **1998**, *276*, 11.
(23) Hahn, M.; Gornitz, E.; Dautzenberg, H. *Macromolecules* **1998**, *31*, 5616.
(24) Jones, M. S. *Eur. Polym. J.* **1999**, *35*, 795.
(25) Staikos, G.; Bokias, G.; Karayanni, K. *Polym. Int.* **1996**, *41*, 345.
(26) Nonaka, T.; Yoda, T.; Kurihara, S. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1998**, *36*, 3097.
(27) Khokhlov, A. R.; Starodubtzev, S. G.; Vasilevskaya, V. V. *Adv. Polym. Sci.* **1993**, *109*, 123.
(28) Flory, P. G. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(29) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(30) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Nauka: Moscow, 1986.
(31) Bokias, G.; Durand, A.; Hourdet, D. *Macromol. Chem. Phys.* **1998**, *199*, 1387.
(32) Bokias, G.; Hourdet, D., manuscript in preparation.
(33) Bokias, G., unpublished results.

MA000413K