**Macromolecules**
ARTICLE

*Macromolecules* **2010**, *43*, 6871–6876 **6871**
DOI: 10.1021/ma1003562

# Unusual Phase Behavior of the Mixture of Poly(acrylic acid) and Poly(diallyldimethylammonium chloride) in Acidic Media

**Ekaterina A. Litmanovich,* Elena V. Chernikova, Georgi V. Stoychev, and Svetlana O. Zakharchenko**

*Department of Polymer Science, Faculty of Chemistry, Lomonosov Moscow State University, Leninskie gory, 119991, Moscow, Russian Federation*

*Received February 16, 2010; Revised Manuscript Received July 10, 2010*

ABSTRACT: A new type of temperature-sensitive polymer systems based on mixtures of poly(acrylic acid) (PAA) and poly(diallyldimethylammonium chloride) (PDADMAC) in strongly acidic aqueous medium is described. The mixtures exhibit reversible separation into two liquid phases upon a decrease in temperature. The phase separation is induced by the intermolecular binding between PAA and PDADMAC due to ion−dipole interactions between protonated carboxylic groups of PAA and quaternary nitrogen atoms of PDADMAC. Molecular and hydrodynamic characteristics of the interpolymer complexes are probed by static and dynamic light scattering.

## Introduction

Recent interest of the research community to temperature-responsive polymers has been largely due to promising potential applications of these systems in separation, biosensor, and membrane technologies. Current approaches to engineering of micro- and nanoscale smart, temperature-triggered polymer systems for biomedicine and bioengineering often involve individual water-soluble polymers (poly(*N*-isopropyl acrylamide) being the most well-known example) or mixtures of polymers such as PEG and polyvinyl alcohol and others.[1] In the case of the mixtures, phase separation is induced because of increased polymer incompatibility, and each phase is enriched by one of the components. The common feature of all reported temperature-sensitive polymer systems is that they all have lower critical solution temperature (LCST); that is, phase separation is induced by heat. Temperature-responsive polymer mixtures with upper critical solution temperature (UCST) are well known for the nonpolar polymers in nonpolar solvents (e.g., polystyrene in cyclohexane). However the aqueous polymers solutions with UCST are more rarely reported. In particular, the occurrence of UCST has been confirmed in water−salt solutions of poly(acrylic acid) (PAA) in acidic medium. Therefore, it was shown[2] that the critical salt concentration, which induces the phase separation, enhanced with increasing temperature. Similar features have also been observed[3] for aqueous solutions of copolymers of AA and NIPAM. The most extensively studied are the aqueous solutions of mixtures of un-ionized PAA and polyacrylamide[4−10] or poly(dimethyl acrylamide)[11] as well as semi-interpenetrating polymer networks of PAA and polyacrylamide.[12,13] The temperature responsivity of such systems is induced by the formation of hydrogen bonds between carboxylic and amide groups at low temperatures. For synthetic ionized macromolecules, water generally is a good solvent, and changes in temperature usually do not lead to phase separation. The same concerns interpolyelectrolyte complexes (IPEC) composed of linear oppositely charged polyelectrolytes.[14−19] Indeed, because of the weak dependence of the energy of intermolecular salt bonds on temperature, phase separation has usually been induced by an increase in concentration of low molecular salt, and the phase diagrams for IPEC are traditionally presented as salt concentration versus IPEC concentration. In the case of complementary pairs of polyelectrolytes (sodium polystyrene sulfonate−poly(trimethylbenzylvinyl ammonium) chloride,[20] sodium polyacrylate−polyethyleneimine,[14] and other systems[15,21−23]), phase separation in IPEC occurs via a salt-induced disproportionation mechanism when a water-insoluble polyelectrolyte complex of equimolar composition is included in a precipitating phase and a nonstoichiometric complex remains in solution.

While being relatively insensitive to temperature variation, ionic pairing within IPEC is strongly affected by pH variations and at extreme pH values where one of the IPEC components might become completely un-ionized (in acidic media in the case of weak polyacids and in alkaline media in the case of weak polybases), in some cases leading to IPEC dissociation. However other types of interchain interactions (hydrophobic,[24] dipole−dipole,[25,26] and ion−dipole interactions[27]) might come in effect under these conditions, sometimes resulting in interesting temperature -responsive behavior of solutions of the polyelectrolyte complexes. For example, solutions of sulfobetaine polymers were found to have both UCST[26,27] and LCST as well as “apparent inverted” UCST.[25] As a whole, this process still remains poorly explored.

Here we study mixtures of PAA and poly(diallyldimethylammonium chloride) (PDADMAC) exposed to extremely acidic environments, where PAA is completely protonated and the formation of ionic pairing between PAA and PDADMAC is suppressed, and find that the onset of ion−dipole interactions between PDADMAC/PAA interpolymer complex results in temperature-dependent, UCST-type behavior of the polyelectrolyte mixture.

## Experimental Section

**Materials and Sample Preparation.** PAA has been synthesized using the procedure that we previously developed.[28,29] In brief, solution of free-radical initiator azo-bis-isobutyronitrile ($10^{-3}$ mol/L) and a RAFT agent dibenzyltrithiocarbonate (synthesized as described in ref 18, $4 \times 10^{-3}$ mol/L) in 20 mL of freshly

---

*Corresponding author. E-mail: elit@genebee.msu.ru.

distilled monomer *tert*-butyl acrylate was prepared. The reaction mixture was poured in an ampule, degassed to $5 \times 10^{-3}$ mmHg pressure using four freeze–vacuum–thaw cycles, and sealed under vacuum. The ampule was immersed for 8 h in an oil bath thermostatted at 60 °C. After polymerization, the reaction mixture was cooled in liquid nitrogen and diluted with benzene. The polymer was extracted by lyophilization from benzene and analyzed by SEC (number degree of polymerization of 1000 and polydispersity index equal to 1.3) and $^1$H NMR (in $CDCl_3$, $\delta$: 1.38 ($CH_3$), 1.78 and 2.17 ($CH_2$), 2.52 (CH)). The product was then subjected to hydrolysis in acidic medium with concentrated hydrochloric acid, which did not affect the trithiocarbonate group located in the middle of the polymer chain and therefore had no effect on the molecular weight of the polymer.[28] The polymer was then dissolved in 1,4-dioxane, and concentrated HCl was added on stirring. The reaction mixture was immersed for 24 h in an oil bath thermostatted at 85 °C. The solvents were then evaporated under vacuum, the polymer residue was collected and dissolved in distilled water, and dialysis against distilled water was performed for 1 week, followed by freeze-drying. The completeness of the hydrolysis was confirmed by $^1$H NMR (in $(CD_3)_2SO$, $\delta$: 1.75 and 2.20 ($CH_2$), 3.50 (CH), 12.22 (COOH)). The final characteristics of PAA were the following: $M_w = 94\,000$, $M_w/M_n = 1.3$.

PDADMAC with $M_w = 400\,000$ was purchased as a 34% water solution from CPS Chem. Comp.

The required concentration of HCl in PDADMAC solutions was achieved by the addition of a calculated amount of 1 M HCl to the stock polymer solution. Polymer mixtures containing desired concentration of HCl were then prepared by mixing stock PDADMAC solutions with PAA solutions containing the same concentration of HCl. The polymer mixtures were stirred for several days prior to their use. Here we use HCl concentration instead of pH because high polyelectrolyte concentrations might result in considerable changes in the activity of low-molecular-weight ions, including counterions. The composition of the mixtures *z* is defined as the molar ratio of PDADMAC to PAA repeating units. All other reagents were of analytical grade and obtained from commercial sources.

**Static Light Scattering.** All measurements were performed on a "Photocor Complex" photometer (Photocor Instruments). A 10 mW He–Ne laser ($\lambda = 633$ nm) was used as a light source. The refractive index increments were measured on a Chromatix KMX16 refractometer (Germany) with 5 mW He–Ne laser light source ($\lambda = 633$ nm). Solvents and polymer solutions were filtered using 0.45 $\mu$m Millipore filters.

Measurements of the average scattering intensity were done at angles from 30 to 150° in 0.05 M HCl at 25–40 °C. The molecular weight ($M_w$), the gyration radii ($R_g$), and the second viral coefficient ($A_2$) were determined from Zimm's plot. The concentrations of the solutions used for Zimm's approximation were 0.6, 1.3, 2.8, and 4.9 g $L^{-1}$ for PAA/PDADMAC mixtures and 0.25, 0.5, 1.0, and 2.0 g $L^{-1}$ for PDADMAC.

We have carried out the critical opalescence measurements by cooling the solution with a 0.5 °C step. Prior to each measurement, all samples were incubated at a preset temperature for 12 min. The measurements have been conducted after the scattering intensity has reached the constant value. It is a standard procedure[30−32] for measuring the critical opalescence.

**Dynamic Light Scattering.** The time correlation function of the scattered light intensity fluctuatuion $g_2(\tau)$ was measured by digital real-time 288 channel multi-tau correlator Photocor-FC, equipped with pseudocrosscorrelative photon counter (Photocor Instruments). Data processing was performed using DynaLS software by the following equation

$$g^{(2)}(\tau) = B + \beta \exp(-2\Gamma\tau)$$

where *B* is the baseline of the correlation function at infinite delay, $\beta$ is the correlation function amplitude at zero delay, $\tau$ is the delay time, and $\Gamma$ is the decay rate.

Correlation functions were then used to determine *z*-mean values of diffusion coefficient using cumulant analysis. The distribution by diffusion coefficients in the program DynaLS is calculated using the combination of regularization procedure and Pike's eigenfunctions. Hydrodynamic radii of the particles were then calculated using the Stokes–Einstein equation

$$R_h = \frac{kT}{6\pi\eta_0 D}$$

where $R_h$ is the hydrodynamic radius, *k* is the Boltzmann constant, *T* is temperature, $\eta_0$ is the viscosity of the solvent, and *D* is the diffusion coefficient.

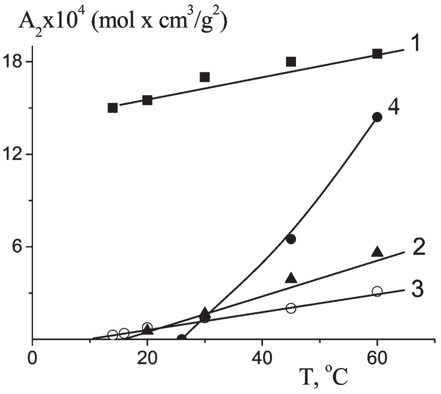


**Figure 1.** Second virial coefficient $A_2$ as a function of the temperature for solutions of: (1) PDADMAC in 0.1 M HCl, (2) PAA in 0.2 M HCl, (3) PAA in 0.1 M HCl, and (4) mixture of PDADMAC and PAA ($z = 1$) in 0.1 M HCl.

## Results and Discussion

Prior to studying the phase behavior of the investigated polymer mixtures, we explored the effects of temperature and HCl concentration on solutions of PAA and PDADMAC.

**1. Effect of HCl concentration and Temperature on the Solvent Quality.** *Static Light Scattering*. Figure 1 summarizes static light scattering measurements with PDADMAC and PAA solutions exposed to different temperatures. Positive values of $A_2$ denote that 0.1 M HCl is a good solvent (like water) for PDADMAC in a wide temperature range from 12 to 60 °C. Such a behavior is typical for aqueous polyelectrolyte solutions, where the major contribution to the free energy of mixing is due to the entropy of low-molecular-weight counterions. The slight growth of $A_2$ with temperature increase is probably due to increased entropy of counterions at higher temperatures.

In the case of PAA solutions, $A_2$ temperature dependence was measured for two HCl concentrations of 0.1 and 0.2 M (Figure 1, curves 2 and 3). As in the case of PDADMAC, positive values for $A_2$ are also observed, indicating that HCl is a good solvent for PAA. However, in contrast with the polycation solutions, values of $A_2$ are lower, as is expected for unionized polyacids. Another important observation is that as compared with PDADMAC, PAA solutions exhibit a somewhat stronger decrease in $A_2$ (i.e., deterioration of the quality of the solvent) at lower temperatures. This is consistent with the formation of hydrogen bonds between the protonated groups of PAA under acidic conditions[33−36] and with the increased number of such bonds at lower temperatures. The linear extrapolation of the data for PAA in 0.1 and

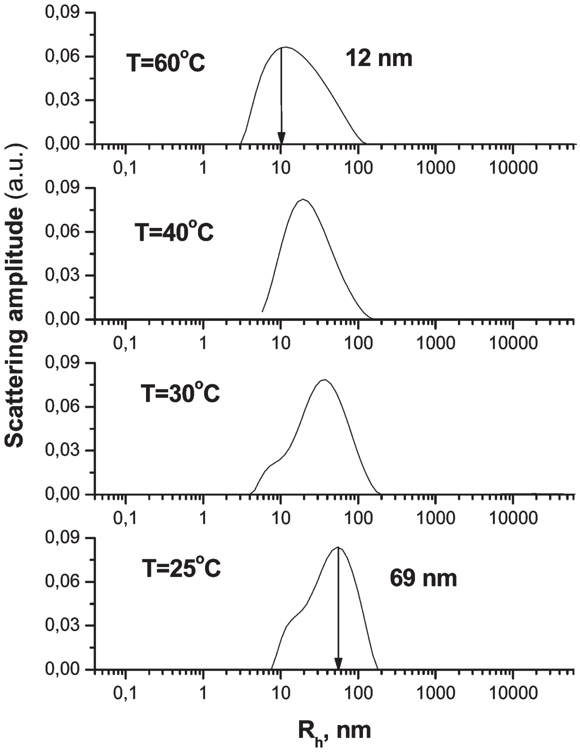


**Figure 2.** Particle size distributions for mixture with $z = 0.18$, [HCl] = 0.05 M.

0.2 M HCl solutions gave $\theta$ temperatures of 10 and 15 °C, respectively.

In the case of PDADMAC/PAA mixtures, much stronger dependence of the quality of the solvent on temperature is observed (Figure 1, curve 4). The $A_2$ value falls drastically and reaches zero value at a temperature value significantly higher than $\theta$ temperatures for PAA solutions. Such dependence is indicative of an UCST behavior of polymer mixtures. We then explored the phase behavior of PDADMAC/PAA mixtures when homogeneous solutions were prepared at a high temperature (60 °C) and cooled at a lower temperature.

*Dynamic Light Scattering*. The particle size distributions in PDADMAC/PAA mixture with concentration equal to 1.23 g/L in 0.05 M HCl at different temperatures are presented in Figure 2. In homogeneous solutions at 60 °C, the apparent hydrodynamic radius of the particles is 12 nm. The apparent size of PAA and PDADMAC coils under the same conditions are 11 and 18 nm, respectively. These data indicate that at high temperature, solution probably contains the unbound macromolecules of PAA and PDADMAC. The small difference in the size of the coils does not allow us to obtain separate peaks for the components of the mixture by means of dynamic light scattering. Significant changes in the hydrodynamic size occur upon cooling. At 25 °C, the apparent particle size increases to 69 nm; that is, a size is much larger than that of individual PAA or PDADMAC coils. Because such an increase does not occur in solutions of individual polymer components, we suggest that complexation between PAA and PDADMAC macromolecules occurs. The driving force of such binding probably involves ion–dipole interactions between carboxylic groups of PAA and quaternary nitrogen atoms of the polycation. It should be noted that the variation of particle size distribution is reversible: the rise of the temperature from 25 to 60 °C is accompanied by decrease in the apparent particle size from 69 to 12 nm.

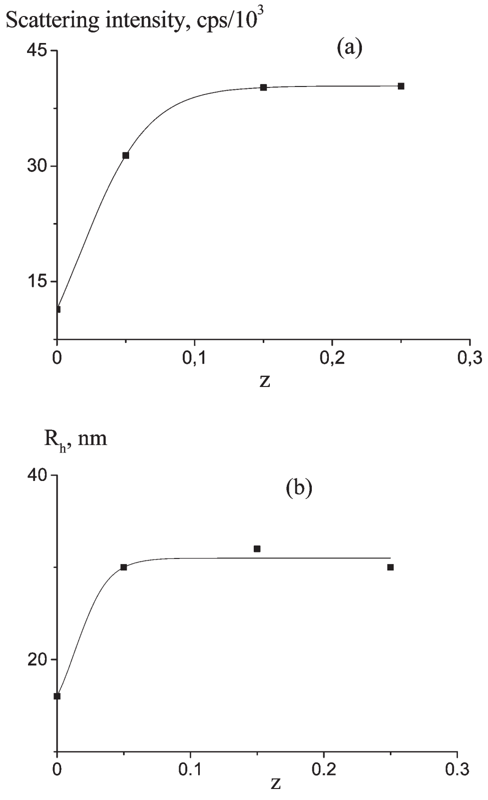


**Figure 3.** Effect of the composition of PDADMAC/PAA mixture (a) on the average scattering intensity and (b) on the hydrodynamic radius of the particles; concentration 2 g/L, [HCl] = 0.01 M, $T = 20$ °C, angle $\theta = 90°$.

To determine the molecular mass characteristics of the particles of interpolymer complex (IPC), we were then seeking to select precisely the appropriate mixture composition. If an IPC of a certain composition is formed, mixing the components in ratio different from that of the IPC will result in disproportionation. In this case, particles of both the complex and the excessive component will be present in the system. An optimal composition to perform light scattering measurements should be equal or close to the composition of the complex.

**2. Choosing the Mixture Composition.** Figure 3 shows the average scattering intensity and the hydrodynamic radii of the IPC particles as a function of the composition of the PDADMAC/PAA mixture.

At $0 \le z \le 0.15$, the scattering intensity significantly increases with increased content of PDADMAC and limits off at higher relative concentration of the polycation. The limiting value of the IPC particles of 30 nm is significantly larger than those of the individual components. Whereas these results do not provide information on the composition of the complex, we conclude that (a) aggregates, most probably PDADMAC/PAA IPC particles, are formed with the composition of $z > 0.15$ and (b) the concentration of the polycation does not affect the light scattering results for mixture compositions from $z = 0.15$ to 0.30. On the basis of these conclusions, we chose a "working" composition of the mixtures $z = 0.18$. While having virtually no influence on the results, the slight excess of polycation (compared with the composition of the complex) assures us that all PAA molecules will be bound within IPC.

**Table 1. Static and Dynamic Light Scattering Results for Mixtures in 0.05 M HCl; $z = 0.18$**

| $T$, °C | $M_w/10^5$ | $R_g$, nm | $R_h$, nm | $R_g/R_h$ | $A_2 \times 10^4$, mol × cm$^3$/g$^2$ |
|---|---|---|---|---|---|
| 40 | 3.5 | 35 | 20 | 1.75 | 12.2 |
| 30 | 13 | 45 | 37 | 1.22 | 3.85 |
| 25 | 16 | 73 | 64 | 1.14 | 3.55 |

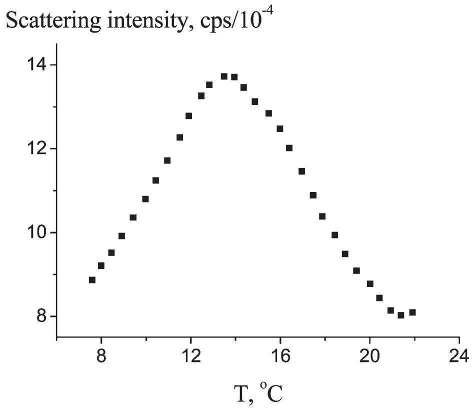


**Figure 4.** Scattering intensity versus temperature; $z = 0.18$, [HCl] = 0.05 M.

*Static Light Scattering*. The molecular weights, gyration radii, and the second virial coefficients for the particles were determined by static light scattering. The results are presented in Table 1. An important trend is that as the temperature is lowered and $A_2$ decreases (as also observed in Figure 1 for PDADMAC/PAA mixture of a different composition), both $M_w$ and $R_g$ consistently increase.

Further lowering of temperature is accompanied by the appearance of the critical opalescence (the abrupt growth of scattering intensity nearby the spinodal). Figure 4 shows a typical temperature dependence of scattering intensity in PDADMAC/PAA mixture with $z = 0.18$. A decrease in temperature below 25 °C results in the onset solution turbidity. A rapid increase in solution turbidity occurs in a narrow interval of temperature as the system approaches the spinodal temperature, indicated by the maximum in Figure 4. At even further cooling below 14 °C, microphase solution layering occurs, resulting in a decrease in the intensity of scattered light. We found that the onset of solution turbidity below 25 °C resulted in errors in determination of the molecular weight of the IPC particles. Therefore, we consider 25 °C to be the lowest temperature at which the accurate values for the molecular weight of the particles in mixtures in 0.05 M HCl can be acquired. Table 1 shows that the $M_w$ of the particles was $1.6 \times 10^6$ at 25 °C. This value may correspond to possible compositions of IPC: $z = 0.15$ (1 molecule of PDADMAC and 13 molecules of PAA), $z = 0.47$ (2 molecules of PDADMAC and 8 molecules of PAA), and $z = 1.52$ (3 molecules of PDADMAC and 4 molecules of PAA). Having in mind the previous results (see Choosing the Mixture Composition section) and the five-fold excess of the monomeric units concentration of PDADMAC in the initial mixtures comparing to PAA concentration, we conclude that the composition of the IPC form in these conditions is $z = 0.15$.

A spinodal of a ternary system represents a surface in ternary coordinates: concentration of PAA, concentration of PDADMAC, and temperature. Measurements at the fixed composition of the mixture give a section of the surface. Spinodals at $z = 0.18$ are presented in Figure 5. The temperature of phase separation increases with the increase in HCl concentration.

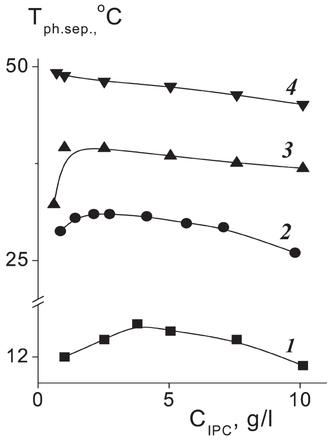


**Figure 5.** Spinodals for mixtures with $z = 0.18$ at different HCl concentrations: (1) 0.05, (2) 0.10, (3) 0.15, and (4) 0.20 M.

**Table 2. Composition of the Phases**

| $T$, °C | [HCl], mol/L | $Z_{\text{dil}}$ | $Z_{\text{conc}}$ |
|---|---|---|---|
| 8 | 0.075 | 0.41 | 0.14 |
|  | 0.10 | 0.44 | 0.13 |
|  | 0.15 | 0.48 | 0.15 |
|  | 0.20 | 0.50 | 0.13 |
| 14 | 0.10 | 0.33 | 0.13 |
| 19 | 0.10 | 0.22 | 0.13 |

**3. Composition of Phases.** Phase separation in PDADMAC/PAA mixtures results in the formation of two liquid phases. To determine the composition of the phases, we have performed titration of the separated phases in PDADMAC/PAA mixtures in 1:1 (by volume) water–acetone media. The use of water–acetone media was essential because it prevented precipitation of polymers, otherwise occurring when using water as a solvent in the titration experiment.

For calculation of the composition of the phases from the titration data, we first experimentally confirmed that hydrochloric acid is evenly distributed between both phases. Indeed, our measurements showed that phases exhibit equal pH values.

We then assumed that an increase in pH promotes the formation of ionic pairs between PAA and PDADMAC, leading to the formation of the IPC of equimolar composition. In this reaction, additional quantities of HCl are released in the solution. The total amount of HCl released in the course of the ionic pairs formation is equal to the number of functional groups of the polyelectrolyte that are present in the deficient amount in the system, that is, of that of the polycation. The released HCl is titrated along with the HCl originally added to the solution. In this case, two jumps in pH should be observed during titration, the first one corresponding to the total amount of initially added HCl and the amount of the polycation and the second one corresponding to the amount of the free PAA so that both the PAA and PDADMAC concentrations can be evaluated. Prior to applying this procedure to PDADMAC/PAA mixture, we checked its consistency using model systems containing known quantities of the components. The relative deviation in the determination of the concentrations and the compositions ($\Delta z/z$) was < 5% (data not shown). This procedure enabled us to determine the composition of the coexisting, that is, diluted ($Z_{\text{dil}}$) and concentrated ($Z_{\text{conc}}$) phases at different temperatures and HCl concentrations (Table 2).

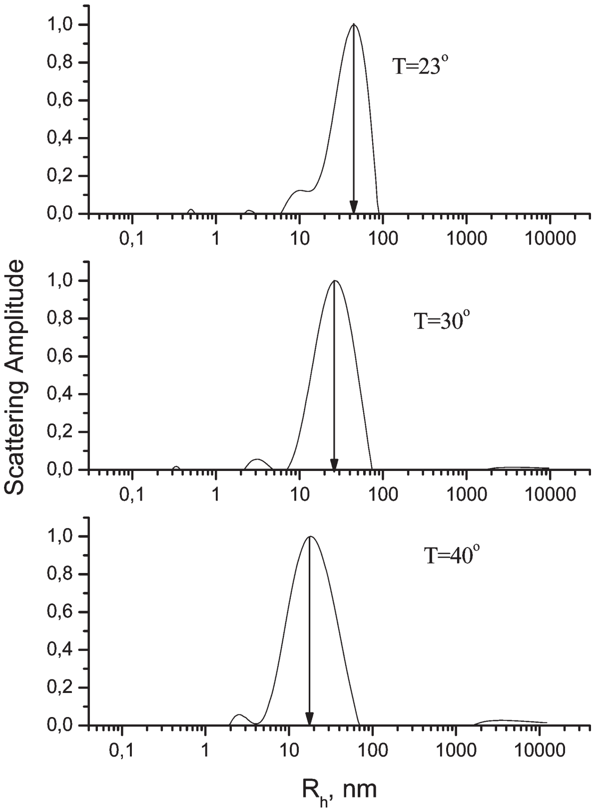


**Figure 6.** Particle size distribution for diluted phase at $z = 0.18$, $T_{\text{ph.sep.}} = 23$ °C.

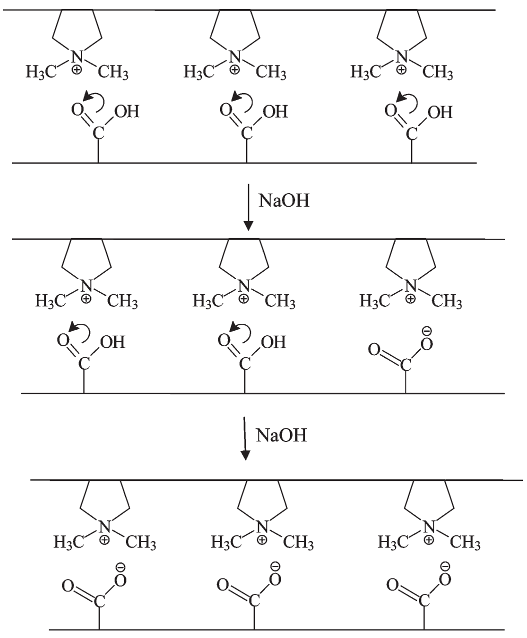
Importantly, the composition of the concentrated phase with $z = 0.13$ to 0.15 is independent of both HCl concentration and temperature. The polymer components ratio in the concentrated phase in the PDADMAC/PAA system corresponds to 13−15 molecules of PAA per 1 molecule of the polycation, which is close to the composition of aggregates formed in homogeneous solutions of PDADMAC/PAA mixtures. There, the concentrated phase consists mostly of PDADMAC/PAA complex of certain composition.

It is unusual that IPC formed contains a noticeable excess of PAA. However the similar complexes of 5:1 and 3:1 compositions have already been described for the aqueous solutions of the mixtures of polycarboxylic acids with 5,6-ionene bromide[37] and poly-*N*-ethyl-4-vinylpyridinium bromide.[38] The formation of the complexes of such a composition can be explained by strong folding of the chains of nonionized PAA owing to intrachain H-bonding. As a result, in the reaction with polycation, only the fragments of the PAA chains participate; the rest of the fragments of PAA macromolecules remain unbound with polycation.

The diluted phase might contain either unbound individual components or IPC. To determine the state of the components in the diluted phase, we have carried out the following experiment. The solution of the mixture at $z = 0.18$ has been kept at 23 °C during 1 month; the separation in two transparent liquid phases occurred. Then, the diluted phase was carefully separated, and it was then investigated under various temperatures by means of DLS.

Figure 6 shows the DLS data for the diluted phase in PDADMAC/PAA system at different temperatures. For measurements performed at 23 °C, the hydrodynamic size of the particles of $R_h = 45$ nm is significantly higher than the size of both individual components of the mixture. This suggests that the diluted phase contains a PDADMAC/PAA IPC and possibly additional free polycation because the ratio of polycation to PAA in the diluted phase is higher than that in the IPC. An increase in temperature leads to dissociation of IPC, and when temperature is raised to 40 °C, the particle size ($R_h = 18$ nm) becomes close to the size of individual macromolecules.

**Scheme 1. Schematic Representation of the Transition between the Two Types of IPCs (the Fragments of PAA Bound with Polycation Are Shown)**



The fact that the composition of the concentrated phase appeared to be independent of the concentration of hydrochloric acid was quite unexpected. Indeed, it is well known that at pH 4 and higher PAA forms insoluble stoichiometric complexes with polycations,[14] and we would expect that with a decrease in HCl concentration, the composition of the IPC and thus the composition of the concentrated phase would increase and reach $z = 1$ at pH 4 (i.e., in $10^{-4}$ M HCl solutions). Nothing of the kind was observed, so we assumed that in a narrow range of concentrations of HCl, there occurred a transition from the IPCs stabilized by ion−dipole interactions to a more traditional type of IPCs stabilized by intermolecular ionic pairing. To confirm our hypothesis, we have conducted experiments illustrated in Figure 7.

Specifically, a mixture with $z = 0.18$ was first dialyzed in 0.01 HCl. The solution remained transparent, with no signs of precipitation or phase separation (Figure 7, left). The concentration of HCl in the external solvent was then lowered to $8 \times 10^{-3}$ mol/L. The solution became opaque but did not show precipitation of PDADMAC/PAA IPC (Figure 7, middle). Temperature sensitivity of the PDADMAC/PAA mixture was retained, and the turbid solution could be reversibly turned transparent by heating from 20 to 60 °C. However, further decrease in HCl concentration led to the formation of white precipitate, which could not be dissolved upon heating. Therefore, the transition between the two types of complexes stabilized by ion−dipole and ion−ion interactions occurred at HCl concentration equal to $5 \times 10^{-3}$ M, as shown in Scheme 1.

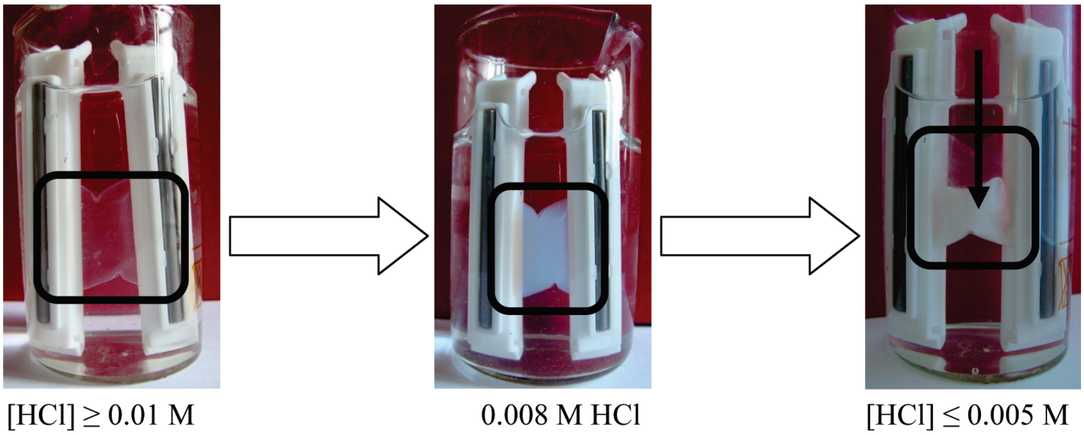


**Figure 7.** Precipitation in the PDADMAC/PAA system induced by lowering the concentration of HCl. $T$ = 20 °C.

## Conclusions

Here we present the first report on the formation of IPC between a weak polyacid and a strong polybase under conditions when carboxylic groups are fully protonated and ionic pairing between the polyacid and the polycation does not occur. We show that at high temperatures (~60−70 °C) the PDADMAC/PAA system represents as a mixture of noninteracting polymers whose unlimited compatibility originates from the high entropy of polycation counterions. Upon lowering the temperature, the ion−dipole interactions between the carboxylic groups of PAA and the functional groups of PDADMAC occur, resulting in the formation of the IPC complex enriched with PAA. Binding of a larger number of PAA macromolecules within IPC probably becomes possible because of additional intramolecular hydrogen bonding (or formation of dimers of carboxylic groups) within PAA chains.

Lowering the solution temperature strengthens both ion−dipole and hydrogen bonding interactions within IPCs, eventually resulting in phase separation of IPCs within a concentrated phase. Importantly, the acidic PDADMAC/PAA mixture reported here shows a completely reversible UCST-type transition, which is rare to find with other polymer systems. Therefore, the mixtures of PAA and polycations in acidic media can be referred to as a new type of equilibrium temperature-responsive polymer systems.

**Acknowledgment.** This work was supported by the Russian Basic Research Foundation (project no. 08-03-00445).

**Supporting Information Available:** Refractive index increments, Zimm plots, correlation functions for the mixture at $z$ = 0.18 in 0.05 M HCl, angular-dependent DLS measurements, and titration data for PAA and mixtures of different compositions. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Kumar, A.; Srivastava, A.; Galaev, I.Yu.; Mattiason, B. *Prog. Polym. Sci.* **2007**, *32*, 1205.
(2) Ikegami, A.; Imai, N. *J. Polym. Sci.* **1962**, *56*, 133.
(3) Bokias, G.; Staikos, G.; Iliopoulos, I. *Polymer* **2000**, *41*, 7399.
(4) Truong, N. D.; Galin, J. C.; Francois, J.; Pham, Q. T. *Polymer* **1986**, *27*, 459.
(5) Truong, N. D.; Galin, J. C.; Francois, J.; Pham, Q. T. *Polymer* **1986**, *27*, 467.
(6) Sivadasan, K.; Somasundaran, P.; Turro, N. J. *Colloid Polym. Sci.* **1991**, *269*, 131.
(7) Sivadasan, K.; Somasundaran, P. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 911.
(8) Garces, F. O.; Sivadasan, K.; Somasundaran, P.; Turro, N. J. *Macromolecules* **1994**, *27*, 272.
(9) Abe, K.; Koide, M.; Tsuchida, E. *Macromolecules* **1977**, *10*, 1259.
(10) Yang, S. Y.; Lee, D.; Cohen, R. E.; Rubner, M. F. *Langmuir* **2004**, *20*, 5978.
(11) Wang, Y.; Morawetz, H. *Macromolecules* **1989**, *22*, 164.
(12) Owens, D. E.; Jian, Y.; Fang, J. E.; Slaughter, B. V.; Chen, Y. H.; Peppas, N. A. *Macromolecules* **2007**, *40*, 7306.
(13) Aoki, T.; Kawashima, M.; Katono, H.; Sakurai, Y. *Macromolecules* **1994**, *27*, 947.
(14) Kabanov, V. A.; Zezin, A. B. *Pure Appl. Chem.* **1984**, *56*, 343.
(15) Kabanov, V. A. In *Macromolecular Complexes in Chemistry and Biology*; Dubin, P., Bock, J., Davies, R. M., Schulz, D. N., Thies, C., Eds.; Springer-Verlag: Berlin, 1994; pp 151−174.
(16) Tsuchida, E.; Osada, Y.; Ohno, H. *J. Macromol. Sci.* **1980**, *B17*, 683.
(17) Philipp, B.; Dautzenberg, H.; Linow, K. J.; Koetz, J.; Dawydoff, E. *Prog. Polym. Sci.* **1989**, *14*, 91.
(18) Webster, L.; Huglin, M. B. *Eur. Polym. J.* **1997**, *33*, 1173.
(19) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.
(20) Tsuchida, E.; Osada, Y.; Sanada, K. *J. Polym. Sci.* **1972**, *10*, 3397.
(21) Deng, S. M.; Li, X. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1997**, *A34*, 695.
(22) Webster, L.; Huglin, M. B. *Eur. Polym. J.* **1997**, *33*, 1173.
(23) Dragan, S.; Cristea, M.; Luca, C.; Simionescu, B. C. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3485.
(24) Petrak, K. *J. Bioact. Compat. Polym.* **1986**, *1*, 202.
(25) Schulz, D. N.; Peiffer, D. G.; Agarwa, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L.; Handwerker, B.; Garner, R. T. *Polymer* **1986**, *27*, 1734.
(26) McCormick, C. L.; Salazar, L. C. *Polymer* **1992**, *33*, 4617.
(27) Nedelcheva, A. N.; Novakov, C. P.; Miloshev, S. M.; Berlinova, I. V. *Polymer* **2005**, *46*, 2059.
(28) Chernikova, E. V.; Terpugova, P. S.; Garina, E. S.; Golubev, V. B. *Vysokomol. Soedin., Ser. A* **2007**, *49*, 108.
(29) Chernikova, E. V.; Terpugova, P. S.; Trifilov, M. Yu.; Garina, E. S.; Golubev, V. B.; Sivtsov, E. V. *Vysokomol. Soedin., Ser. A* **2009**, *51*, 658.
(30) Anisimov, M. A.; Kostko, A. F.; Sengers, J. V. *Phys. Rev. E* **2002**, *65*, 051805.
(31) Jacob, J.; Anisimov, M. A.; Sengers, J. V.; Dechabo, V.; Yudin, I. K.; Gammon, R. W. *Appl. Opt.* **2001**, *40*, 4160.
(32) Yudin, I. K.; Nikolaenko, G. L.; Kosov, V. I.; Agayan, V. A.; Anisimov, M. A.; Sengers, J. V. *Int. J. Thermophys.* **1997**, *18*, 1237.
(33) Smitha, B.; Sridhar, S.; Khan, A. A. *Macromolecules* **2004**, *37*, 2233.
(34) Mori, H.; Lanzendorfer, M. G.; Muller, A. H. E.; Klee, J. E. *Langmuir* **2004**, *20*, 1934.
(35) Mori, H.; Muller, A. H. E.; Klee, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 3712.
(36) Yoo, M. H.; Sung, Y. K.; Cho, C. S.; Lee, Y. M. *Polymer* **1997**, *38*, 2759.
(37) Gulyaeva, Z. G.; Poletaeva, O. A.; Kalachev, A. A.; Kasaikin, V. A.; Zezin, A. B. *Vysokomol. Soedin., Ser. A* **1976**, *18*, 2800.
(38) Izumrudov, V. A.; Kasaikin, V. A.; Ermakova, L. N.; Zezin, A. B. *Vysokomol. Soedin., Ser. A* **1978**, *20*, 400.