Behavior of Poly(*N*-vinylcaprolactam-*co*-methacrylic acid) Macromolecules in Aqueous Solution: Interplay between Coulombic and Hydrophobic Interaction

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ABSTRACT: Dynamic light scattering measurements have been performed for aqueous solutions of linear copolymer of *N*-vinylcaprolactam (VCa) and methacrylic acid (MA) with variable composition (i.e., charge degree of polymer chain). The swelling behavior of macromolecules was investigated as a function of both the solution pH value and fraction of methacrylic acid groups. It was shown that these copolymers are thermosensitive, and intermacromolecular aggregation takes place at the temperature increase. They exhibit compositionally dependent swelling behavior as a function of both pH and temperature. The behavior of studied copolymer was explained by the partial formation of ion pairs. The dependence of hydrodynamic diameter on pH of the solution is nonmonotonic. In acidic media at room temperatures we observed the intermolecular aggregation of copolymers accompanied by a sharp increase of the light scattering intensity. In alkaline media intermacromolecular aggregation is observed at higher temperatures. The effect of oppositely charged surfactant (cationic cetylpyridinium chloride, CPC) on the swelling behavior of PVCa−MA macromolecules was investigated under various conditions of pH and temperature. The association of PVCa−MA macromolecules was demonstrated to be a function of pH and CPC concentration. The equilibrium size of copolymer−CPC aggregates was found. It was shown that the size of intermacromolecular aggregates containing copolymers and CPC depends only weakly on the variation of ambient conditions (pH, surfactant, or copolymer concentration). The effect of temperature on the stability of copolymer/surfactant complexes was studied. This result is compared with recent theoretical predictions.

Introduction

In recent years "smart" polymers and gels have been the objects of intensive studies. The effect of temperature on the conformational state of polymers is one of the actual problems in this field. The importance of the problem is due to both the theoretical and practical aspects. In particular, the temperature effect on biopolymers is directly connected with the functioning of living systems. The thermoshrinking behavior of polymers in solution normally reflects the hydrophobic−hydrophilic balance of polymer chains.[1,2] The hydrophobic interactions between polymer groups, which are the major driving force for phase separation, are enhanced at elevated temperatures due to a decrease in the structuring of water around hydrophobic groups.[3] The coil−globule transition in such linear polymers is an entropy-driven phenomenon.[4−6] Above the critical temperature these hydrophobic interactions become dominant and lead to the collapse of polymer chains.

Incorporation of hydrophilic/charged comonomers reduces the amount of hydrophobic groups and increases the polymer hydrophilicity due to the strong interactions between water and charged or hydrophilic groups on the polymer. This leads to an increased lower critical solution temperature (LCST). The swelling behavior of charged copolymers is a result of the competing forces of repulsive electrostatic interaction between the ions on the copolymers and attractive forces between the hydrophobic segments. The competitive balance among these interactions depends on the temperature and the degree of ionization that defines the thermoshrinking behavior of polymer chains.

Poly(*N*-isopropylacrylamide) (NIPA) occupies a central position in the studies of thermoshrinking polymers.[7] In most cases the effect of ionic groups on the swelling behavior of NIPA was studied for hydrogels.[1,2,8−11] It was shown that the introduction of ionic groups into NIPA gel, both anionic (copolymer with acrylic acid[8,9]) and cationic,[2] leads to increase of the critical temperature. The changes in LCST caused by the incorporation of ionic groups was connected with the changes in overall hydrophilicity of the polymer.[3] The LCST can be shifted in these ionic gels by changing the pH and ionic strength, giving greater flexibility in tailoring properties for particular applications.[10−14] The comparison of the behavior of linear anionic copolymer and gel based on NIPA in the presence of cationic surfactant was demonstrated in ref 15. It was shown that a plot of the swelling ratio vs the degree of binding gives a curve around which all the experimental points scatter, showing that the swelling ratio is uniquely determined by surfactant binding, irrespective of the copolymer composition. Another new system based on linear PNIPA containing as much as 10 mol % 2-carboxyisopropylacrylamide units[15] exhibits a sensitive phase transition in response to small temperature changes, but these LCST were ionic groups content and pH independent.[16]

Another representative of thermosensitive polymers is poly(*N*-vinylcaprolactam) (PVCa). Earlier we studied[17] the effect of ionic surfactant on the behavior of neutral PVCa. The influence of attraction of the as-

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sociating groups and the repulsion of the chains due to Coulombic interactions of adsorbed ionic surfactant molecules on the mechanism of the inter- or intramacromolecular aggregation of neutral PVCa macromolecules was investigated. In this case both charged and associating groups were able to migrate along the polymer chains, as a result of the complex formation between amide groups of PVCa and surfactants. It was shown that the formation of the intermacromolecular aggregates requires significant gain in association energy to overcome the Coulombic energy of repulsion of the chain charges as well as translational entropy losses due to the inhomogeneous distribution of counterions.[17]

The present paper is a continuation of a previous study where mainly complex formation between VCa monomer units, ionic surfactant, and a neutral water-soluble organic compound, pyrogallol, where the effect of migrating charges was treated.[17] Here we report the swelling behavior of copolymers of *N*-vinylcaprolactam (VCa) and methacrylic acid (MA) with a variable fraction of charged groups. This paper focuses on the investigation of the interplay between hydrophobic and Coulombic interactions for the polyelectrolyte thermosensitive macromolecules when charges of polymer chains are fixed. In this case the degree of ionization of polymer chain affects the solubility and conformational properties of macromolecules. The special attention will be dedicated to the interaction between thermosensitive polyelectrolyte and oppositely charged surfactant. The purpose of this publication is to analyze (a) the temperature dependencies of the swelling behavior as a function of pH of the medium and (b) the stability for PVCa–MA copolymers in the presence of cationic surfactant CPC with respect to intermacromolecular aggregation. The phase diagram of polymer solution as a function of the amount of charged and associating groups reflects for this case the interplay between Coulombic and hydrophobic interaction and its effect on the conformational state of macromolecules.

Experimental Section

Materials. *N*-Vinylcaprolactam (VCa) (BASF) and methacrylic acid (MA) (Fluka) were distilled under reduced pressure. 2,2′-Azobis(2-methylpropionitrile) (Fluka) and cetylpyridinium chloride (CPC) (Aldrich) were used without further purification.

Copolymerization. The polymer was prepared by free-radical copolymerization of VCa in benzene solution. The initiator was 2,2′-azobis(2-methylpropionitrile).

The copolymers were prepared by free-radical copolymerization of VCa and MA in ethanol solutions.

Monomer solutions were prepared shortly before use by the addition of specified amounts of monomers, initiator, and solvent. The initial content for monomers was 50 vol %, and the initiator concentration was 0.001 wt %. The MA content was 0, 10, and 20 mol %; we will define those copolymers as PVCa, PVCa-MA$_{10}$, and PVCa-MA$_{20}$, respectively. The polymerization at 30° C was carried out in ampules in an argon atmosphere for 96 h.

After the reaction, the copolymers were precipitated into diethyl ether, decanted, and dried at 50 °C. Then the synthesized polymers were fractionated by standard solvent/nonsolvent techniques.

Potentiometric Measurements. Measurements were carried out using a pH-meter DELTA 350 (Mettler, Germany) with an accuracy of 0.002. The calibration of the device was made before each measurement using the standard buffer solutions. All measurements were conducted at 20 °C.

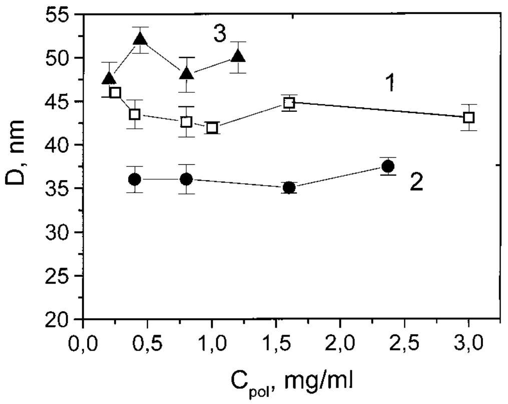

Figure 1. Dependence of hydrodynamic diameter (*D*) of PVCa (1), PVCa–MA$_{10}$ (2), and PVCa–MA$_{20}$ (3) macromolecules as a function of polymer concentration. $T = 20$ °C.

The fraction of methacrylic units in PVCa–MA copolymers was determined from the results of routine titration of 1 wt % aqueous solutions of polymer. The solutions were prepared in 0.1 M NaOH. Polymer solutions were titrated with 0.1 M HCl solution up to pH value of 3.0. From the amount of HCl taken by a system between two distinct inflection points the content of carboxylic groups in the copolymer was calculated. The fraction of carboxylic groups is 12% for PVCa–MA$_{10}$ and 18% for PVCa–MA$_{20}$.

Preparation of Solution. The copolymers were dissolved in 0.1 M NaOH solution (deionized water was used, which was purified by an Elgastat UHQ-PS purification system). After the copolymer dissolution pH media was adjusted to required value by addition of 0.1 M HCl. The polymer–surfactant solutions were prepared by dissolving a desired amount of the surfactant in aqueous polymer solutions. The polymer–surfactant solutions were prepared at least 1 day before the dynamic light scattering measurements.

Dynamic Light Scattering. Dynamic light scattering (DSL) measurements were performed with a Brookhaven Instruments BI-200SM goniometer and a BI-9000 digital correlator. The light source was Spectra Physics model 127 helium/neon laser (633 nm, 35 mW). Time correlation functions were analyzed using a second-order cumulant fit.

The intensity–intensity time correlation functions $g_2(t,q)$ in the self-beating mode were measured at a scattering angle 90° as a function of temperature. The temperature ranged from 20 to 60 °C. At each temperature the sample was allowed to equilibrate 30 min before the measurements. The equilibrium state was controlled by following the intensity of scattered light as a function of time.

Before use the solutions were filtered through Millipore membranes with 0.22 μm pore size.

Static light scattering measurements (Zimm method) were used for the determination of M_w. Data obtained for PVCa, PVCa-MA$_{10}$, and PVCa-MA$_{20}$ are $M_w = 1.5 \times 10^6$, 6.4×10^5, and 2.9×10^6 g/mol, respectively.

The light scattering measurements were conducted using 0.1 M NaOH and 0.1 M NaCl solutions. In these solvents the measured Zimm plots are similar to those observed for uncharged polymers.

Results and Discussion

Figure 1 shows the dependencies of hydrodynamic diameter for neutral (1) and charged (2) PVCa macromolecules as a function of polymer concentration at 20 °C. DLS measurements were performed in 0.1 M NaOH solution. The straight lines connecting experimental points should be regarded just as a guide for the eye (here and below). There is no concentration dependence of hydrodynamic diameter. This fact indicates that the studied polymer concentrations were below overlap concentration C^*.[18]

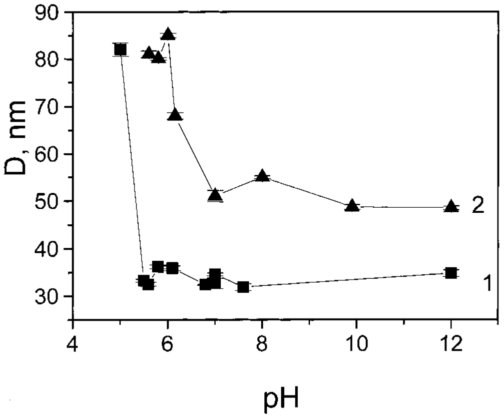

Figure 2. Dependence of hydrodynamic diameter (*D*) of PVCa$-$MA$_{10}$ (1) and PMCa$-$MA$_{20}$ (2) macromolecules as a function of pH of the solution. $T = 20$ °C.

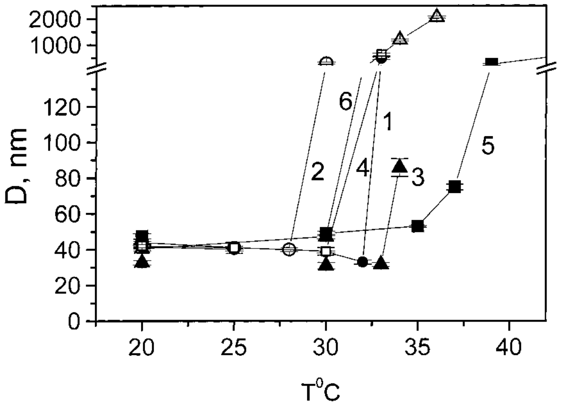

Figure 3. Temperature dependence of hydrodynamic diameter of PVCa (1, 2), PVCa$-$MA$_{10}$ (3, 4), and PVCa$-$MA$_{20}$ (5, 6) macromolecules at different values of pH of the solution. pH is 7 (1, 3, and 5) and 12 (2, 4, and 6).

The swelling behavior of both studied copolymers as a function of pH of the solution is shown in Figure 2. The pH dependence is adjusted by addition of NaOH or HCl. It can be seen that in acidic medium the value of hydrodynamic diameter diverges which is the indication of intermacromolecular association. The cloud point is pH 4.9 for PVCa$-$MA$_{10}$ and 5.6 for PVCa$-$MA$_{20}$.

Temperature Effect. Figure 3 illustrates the temperature dependencies of hydrodynamic diameter of PVCa (curves 1, 2) and PVCa$-$MA$_{10}$ (curves 3, 4), and PVCa-MA$_{20}$ (curves 5, 6) macromolecules for different values of pH of the medium. All studied polymers demonstrate their thermosensitive swelling behavior with critical points below 40 °C. The temperature increase leads to polymer aggregation that is accompanied by the relaxation time increase. The aggregation of macromolecules is observed as a sharp increase of the scattered light intensity. At elevated temperatures it is difficult to characterize the particle sizes. Above LCTS the polymer is water-insoluble and tends to form large aggregates due to the hydrophobic association of globules.

The introduction of charged methacrylate groups in PVCa macromolecule generally leads to the increase of the temperature of intermacromolecules aggregation (which will be called critical temperature, T_{cr}) in comparison with homopolymer at the same alkaline pH values (see Figure 3, curves 1, 3, 5 and 2, 4, 6). The observed effect of ionic groups on the thermosensitive behavior of PVCa is similar to that discussed for charged NIPA copolymers.[7-9]

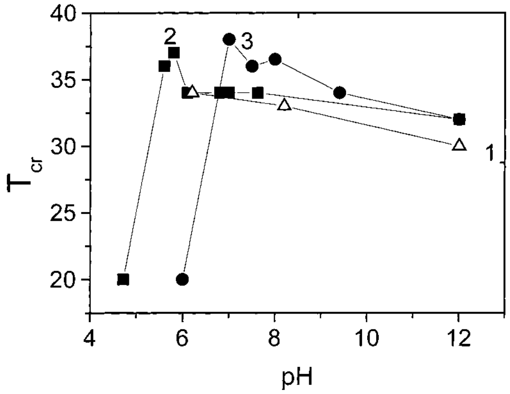

Figure 4. Dependence of critical temperature on pH of the solution for PVCa (1), PVCa$-$MA$_{10}$ (2), and PVCa$-$MA$_{20}$ (3).

Figure 4 shows the temperature of the intermacromolecules aggregation (T_{cr}) of neutral polymer (curve 1), PVCa$-$MA$_{10}$ (curve 2), and PVCa$-$MA$_{20}$ (curve 3) as a function pH of the solution. For all studied macromolecules (neutral polymer as well as charged copolymers) the change of pH from 6 up to (the decrease in curve 3 starts at pH $>$ 7) 12 leads to the decrease of the temperature of intermacromolecular aggregation, T_{cr}, which in principle may be connected with (1) electrostatic screening of charges of polymer chains in strongly alkaline solutions and (2) the enhancement of hydrophobic interactions in alkaline solutions. However, it should be noted that the pH dependence is adjusted by addition of HCl to initial 0.1 N solution of NaOH. It means that the electrolyte concentration does not change, and consequently electrostatic screening is also unchanged. On the other hand, in ref 19 it was shown the effect of NaCl and NaOH on the Gibbs energy of transfer of hydrophobic groups from their hydrophobic environment to water. Thus, the increase of the hydrophobic interactions in alkaline medium should be the main cause of the slight shrinking of PVCa$-$MA macromolecules with the increase of fraction of OH$^-$ in electrolyte solution.

At pH values below 5.5 in the case of PVCa$-$MA$_{10}$ and at pH $<$ 7 in the case of PVCa$-$MA$_{20}$ intermacromolecular aggregation is observed at room temperature. The slight maximum for T_{cr} value is observed at pH $=$ 5.8 for PVCa$-$MA$_{10}$ and at pH $=$ 7 for PVCa$-$MA$_{20}$ that is correlated with the minimum value of the hydrodynamic diameter (see Figures 2 and 4). Probably, at these values of pH of solution the degree of charge of polymer chains is enough to prevent the formation of intermacromolecular aggregates but not enough to destroy still relatively compact conformation of macromolecules.

One of the most striking and counterintuitive features shown in Figure 4 corresponds to the region around pH $\sim$ 6. One can see that in this region the critical temperature of PVCa$-$MA$_{10}$ ($T_{cr} = 37$) is significantly higher than the critical temperature of PVCa$-$MA$_{20}$ ($T_{cr} = 20$); i.e., for these values of pH the increase of the fraction of charged monomer units in the chain enhances the intermolecular aggregation.

To understand the reason for such unusual behavior, an additional experimental fact should be described. Let us suppose that after a temperature increase with the formation of large aggregates we lower the temperature and return to initial conditions. Then the behavior of

PVCa−MA_{20} copolymers will be different from that of PVCa homopolymer and PVCa−MA_{10} copolymer. In the latter case the decrease of temperature leads to the destruction of intermacromolecular aggregates formed upon the temperature increase; therefore, after cooling the hydrodynamic diameter of particles returns to the value observed before heating. In the case of PVCa−MA_{20} aggregates the reversibility of swelling of macromolecules depends on pH of the solution. In this case at pH <8 macroaggregates are not broken after temperature decrease for a few days which demonstrates their stability. Taking into account that the studied copolymer varies in the fraction of ionic groups the stability of PVCa−MA_{20} aggregates may be explained by additional ionic interactions. From our previous experience[20−22] this normally means that the aggregates are induced not only by hydrophobic but also by the much stronger ionic interactions leading to ion pairs formation.

The origin of these interactions can be understood as follows. The Na^+ counterions either can be in the free state (polyelectrolyte regime) or form ion pairs with methacrylic acid groups (ionomer regime).[23] For aqueous media most of counterions are normally considered to be free, while the intensive ion pairs formation is characteristic for somewhat less polar solvents.[23−25] However, this is the case for hydrophilic polymers (such as poly(acrylic acid)). For hydrophobic polymers, such as poly(styrenesulfonate) and poly(acrylamide-*co*-sodium-2-acrylamido-2-methylpropanesulfonate) the effect connected with ion pairs was definitely observed even for water solutions.[25,26] In a sense, this is quite understandable since the local dielectric constant around a hydrophobic polymer should be much lower than that of pure water. The unusual behavior of the PVCa−MA_{20} copolymer reported above can well be explained by the fact that at low enough values of pH most of the Na^+ counterions are actually forming ion pairs with the charges on the polymer chain, and these ion pairs attract to each other leading to the enhancement of aggregation. The multiplets formed by aggregated ion pairs are normally not easy to redissolve[20] which corresponds to the effect described in the previous paragraph. So, in the case of PVCa−MA_{20} attractive forces stabilized aggregates are both of hydrophobic interaction and ionomeric multiplets while the temperature decrease leads to the weak of hydrophobic interaction and does not effect on the ionomeric multiplets formed which stabilize formed aggregates. As for the PVCa−MA_{10} copolymer, the concentration of ionic groups for this case is probably not high enough to induce formation of ionomeric multiplets (cf. refs 20, 21, and 28). In this case at the decrease of temperature hydrophobic interactions are weakened, and consequently the attractive force (in the case of PVCa−MA_{10} it is only hydrophobic interactions) is also decreased which leads to the aggregates destruction and reversibility of macromolecules swelling.

Effect of Cetylpyridinium Chloride. Since the thermoshrinking transition of PVCa macromolecules in aqueous solutions is caused by hydrophobic interactions, we can control the temperature-induced shrinking of macromolecules by addition of surfactants to the solution. In this case the critical hydrophobic/hydrophilic balance can be easily varied.[29−31] In the present paper we consider the interaction of negatively charged groups of polymer chains and oppositely charged surfactant, CPC. In the case of copolymers of PVCa−MA the driving force for the complex formation between ionic surfactants and oppositely charged copolymer is the strong Coulomb attraction between opposite charges as well as the aggregation of hydrophobic tails of surfactants. Earlier it was shown that phase separation, surfactant micelle formation, and collapse of macromolecules can be the result of interaction between polyelectrolyte and oppositely charged surfactant.[32−34]

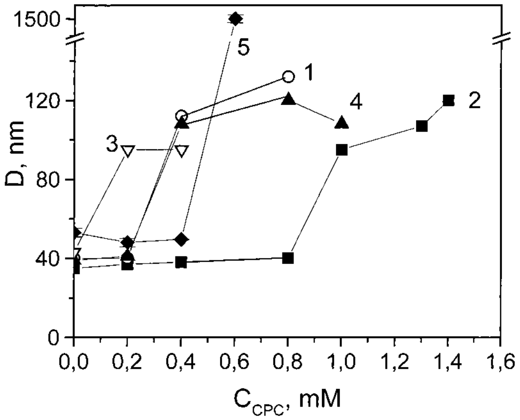

Figure 5. Dependencies of hydrodynamic diameter of PVCa−MA_{10} (1−4) and PVCa−MA_{20} (5) on CPC concentration. pH = 5.6 (1, 2) and 7 (3−5). T = 20 °C. Copolymer concentration is 0.4 mg/mL (1, 3) and 0.8 mg/mL (2, 4, 5).

Figure 5 demonstrates the dependencies of the hydrodynamic diameter of PVCa−MA_{10} (curves 1−4) and PVCa−MA_{20} (curves 5) as a function of CPC concentration at pH = 5.6 (curves 1, 2) and 7 (curves 3−5) and at T = 20 °C. The copolymer concentration was also varied: 0.4 mg/mL (curves 1, 3) and 0.8 mg/mL (curves 2, 4, 5). All obtained dependencies for PVCa−MA_{10} are of S-type: three distinct regions which can be described in CPC concentration dependence of the swelling of macromolecules. At first the hydrodynamic diameter is practically independent of the surfactant concentration; then the increase of CPC concentration results in the significant increase of the hydrodynamic diameter of copolymers, and finally, further increase of CPC concentration does not result in the significant change of macromolecule size. The increase of CPC concentration at studied values of pH leads to the increase of hydrodynamic diameter at the temperatures below the critical temperature that can be connected with the formation of intermacromolecular aggregates induced by the enhancement of attraction energy due to hydrophobic interaction of cetyl tails of added surfactant. It can be noted that the decrease of the copolymer concentration at constant pH of the solution from 0.8 mg/mL (Figure 5, curves 2 and 4) to 0.4 mg/mL (see curves 1 and 3) and decrease of the value of pH of the medium at constant copolymer concentration from 7 (curves 3, 4) to 5.6 (see curves 1, 2) leads to the formation of macromolecular aggregates at lower CPC concentrations.

To understand the reason for such behavior, let us consider the obtained results in terms of molar ratio between added CPC and carboxy groups of copolymers ($[CPC]_{cr}/[MA]$) and ratio between added CPC and charge of polymer chain ($[CPC]_{cr}/[charge]$) taking into account that the amount of charged methacrylic groups (degree of ionization, α) is a function of pH of the medium. The values of $[CPC]_{cr}/[MA]$ and $[CPC]_{cr}/[charge]$ at which intermacromolecular aggregation takes place are pre-

Table 1. Values of $[CPC]_{cr}/[MA]$ and Size of Complexes of PVCa−MA_{10} and CPC at Different Copolymer Concentration and pH

copolymer concn	pH 5.6				pH 7			
	$[CPC]_{cr}/[MA]$	α[a]	$[CPC]_{cr}/[charge]$	D_{max}	$[CPC]_{cr}/[MA]$	α	$[CPC]_{cr}/[charge]$	D_{max}
0.4	0.6	0.04	15.8	107 ± 6	1.4	0.5	2.8	115 ± 3
0.8	0.6	0.04	15.8	110 ± 4	1.6	0.5	3.2	110 ± 7

[a] The degree of ionization of copolymers α was calculated using the following relation: $pH = pK + \log\{\alpha/(1-\alpha)\}$.

Table 2. Values of $[CPC]_{cr}/[MA]$ and Hydrodynamic Diameter of Residual Particles after Filtration D^{res} for PVCa−MA_{20}

pH	$[CPC]_{cr}/[MA]$	α	$[CPC]_{cr}/[charge]$	D^{res}, nm (after filtration)
7	0.5	0.5	1	46 ± 1.3
6.1	0.33	0.11	3	49 ± 0.7
5.8	0.7[a]	0.06	12	102 ± 2.7

[a] Intermacromolecular aggregation is observed at lower CPC concentartion.

sented in Tables 1 and 2; these values will be referred below as critical ratio. Obtained results point out that in acidic media macromolecular aggregates are formed at relatively low ratio of $[CPC]_{cr}/[MA]$.

However, the values of $[CPC]_{cr}/[charge]$ are high (see Tables 1 and 2). Taking into account low degree of ionization of macromolecules at this pH of the medium and ionic strength of solution (0.1 N NaCl), we could consider the behavior of studied copolymer in the presence of ionic surfactant in the terms of the formation of mixed polymer/surfactant micelles.[17,30] In this case the formation of such micelles is known to induce intermacromolecular aggregation.

Here it should be noted that the fraction of charged groups could be varied by two ways: changing the content of methacrylic groups and value of pH. The other important point is the decrease of concentration of CPC inducing the intermacromolecular aggregation for PVCa−MA_{20} in comparison with PVCa−MA_{10} at the same value of pH (Figure 5, curves 1 and 5, Tables 1 and 2), which is contrary to expectation. Indeed, the formation of intermacromolecular aggregates takes places if hydrophobic interactions overcome electrostatic repulsion that is higher in the case of PVCa−MA_{20}. However, here it should be remembered that in the case of the PVCa−MA_{20} copolymer the formation of ion pairs and multiples should take place, as discussed above. This can enhance the formation of intermacromolecular aggregates.

To understand this effect, we analyzed the solutions of PVCa−MA_{20} copolymers forming aggregates after their filtration through Millipore membranes with 0.22 μm pore size. It was found that hydrodynamic diameter of residual particles in the filtrated solution depends on the amount of added CPC and is practically independent of the pH value (Table 2). At pH = 7 and [CPC]/[MA] = 0.5 and pH = 6.1 and [CPC]/[MA] = 0.33 the hydrodynamic diameter (D_h) of residual particles in the filtrated solution is 46 and 49 nm, respectively,which is close to the polymer size in the CPC-free system (polymer concentration is 0.8 mg/mL). These results possibly indicate that with PVCa−MA_{20} copolymers at intermediate CPC concentration there is a coexistence of intermacromolecular aggregates and single macromolecules. This fact points out that binding of CPC by copolymer chains is cooperative, and it leads to CPC disproportionation. Indeed, at low CPC concentration only part of macromolecules forms large intermacromolecular aggregates (which results in the increase of hydrodynamic diameter) with high molar ratio between CPC molecules in the complexes and monomer unit of MA adsorbing total added CPC. In this case the formation of ion pairs and their multiples (that was noted above) increasing energy of attraction between macromolecules and enhance the aggregation of PVCa−MA_{20} macromolecules at lower surfactant concentration. Residual macromolecules exist as single chains.

Here it should be noted that studied copolymers were prepared by free-radical copolymerization, and the conversion was slightly less than 100%. In principle, for this case we expect the heterogeneity of polymers in composition. However, the observed results do not show this. Indeed, the hydrodynamic diameter of supernatant macromolecules after filtration leading to separation of polymer−surfactant aggregates is close to the size of initial macromolecules. It is unlikely that this can be the case for copolymers with different composition.

The other important feature of the formed copolymer/surfactant complexes is their size. First, at high CPC concentration the intermacromolecular aggregates of PVCa−MA_{10} with approximately the same size (~110 nm, see Figure 5 and Table 1) are formed at the different initial conditions (polymer and CPC concentration, pH). Second, in the case of PVCa−MA_{20} size of formed aggregates is significantly larger in comparison with PVCa−MA_{10}. Theoretically, it was shown that the main effect leading to the formation of optimum size clusters is a competition between energy of attraction of hydrophobic groups and energy of Coulombic interaction of charges of the clusters.[35,36] The obtained experimental data point out that the interaction of polyelectrolyte macromolecules of PVCa−MA_{10} with oppositely charged surfactant at the surfactant concentration above some critical concentration leads to the formation of stable intermacromolecule aggregates containing constant optimum amount of macromolecules. This critical surfactant concentration (or amount of added surfactant) inducing the intermacromolecular aggregation is a function of degree of charges of polymer chains; therefore, it is defined by balance of hydrophobic and Coulombic interaction. Further increase of surfactant concentration does not lead to the change of the aggregate size. In the case of PVCa−MA_{20} the larger size of aggregates could be explained by the formation of ion pairs and multiples, resulting in the agglomeration of aggregates.

The additional feature of the studied systems is that it possible to vary hydrophobic/electrostatic balance by the change of temperature. The most important and interesting point here is the temperature stability of CPC/copolymer complexes. The effect of temperature on the behavior of copolymer oppositely charged surfactant aggregates is illustrated by the temperature dependencies of hydrodynamic diameter of PVCa−MA_{10} (Figure 6) and PVCa−MA_{20} (Figure 7) macromolecules in

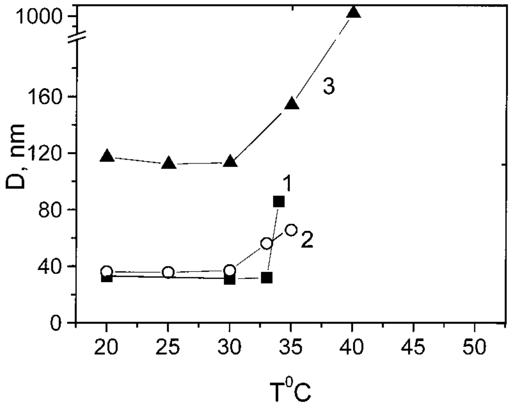

Figure 6. Temperature dependencies of hydrodynamic diameter of PVCa−MA$_{10}$ macromolecules in the presence of CPC (2, 3) at pH = 7. CPC concentration is 0.5 (2) and 1 mM (3).

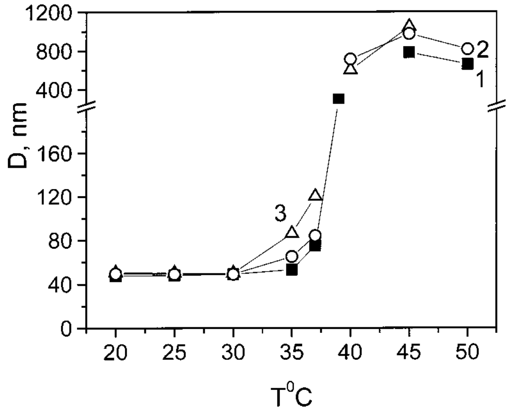

Figure 7. Temperature dependencies of hydrodynamic diameter of PVCa−MA$_{20}$ macromolecules in the presence of CPC (2, 3) at pH = 7. CPC concentration is 0.2 mM (2) and 0.4 mM (3).

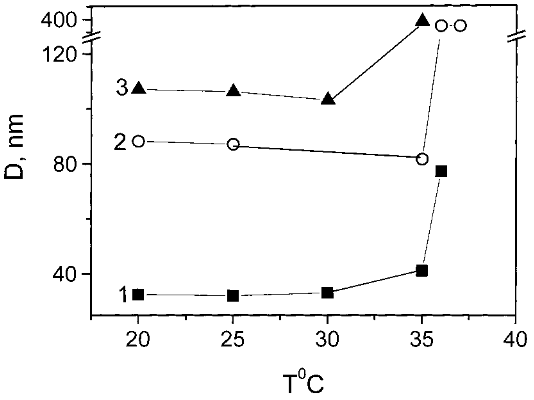

Figure 8. Temperature dependencies of hydrodynamic diameter of PVCa−MA$_{10}$ macromolecules in the presence of CPC (2, 3) at pH = 5.6. CPC concentration is 0.5 (2) and 1.3 mM (3).

the presence of CPC (curves 2, 3) at pH = 7. The temperature dependencies of hydrodynamic diameter of PVCa−MA$_{10}$ macromolecules at pH = 5.6 is shown in Figure 8. The temperature dependencies show that copolymer/surfactant clusters are stable up to 30 °C. The increase of temperature above 30 °C results in the further aggregation. In this case T_{cr} is below T_{cr} of the CPC-free system.

It should be emphasized that the size of intermacromolecular aggregates of PVCa−MA−CPC$_{20}$ at the temperature above T_{cr} does not change upon the further temperature increase (Figure 7). This fact should be compared with theoretical papers[34,35] where the possibility of existence of solution phase having stable aggregates with optimum size was shown.

Conclusions

In the present paper we studied the behavior of charged macromolecules of thermosensitive polymer in aqueous solutions and considered the copolymer behavior from the viewpoint of balance of hydrophobic and electrostatic interaction. The copolymers with different degree of macromolecular charges, different pH of the medium, and complexes of PVCa−MA with oppositely charged surfactant were used for the variation of hydrophobic/electrostatic balance. We have shown that a tailored delicate balance between hydrophobic and hydrophilic components in macromolecules provides novel thermosensitive swelling behavior in aqueous solution. In some cases (for PVCa−Ma$_{20}$ copolymers) we have found evidence supporting the hypothesis that the collapse of macromolecules leads to the formation of ions pairs which further aggregate in the multiples. This effect is analogous to mixed polyelectrolyte/ionomer behavior, previously studied by us both theoretically[28] and experimentally.[20]

The association of PVCa−MA macromolecules was demonstrated to take place as a function of pH, CPC concentration, and temperature.

One of the important results of the present work is the experimental demonstration of the formation of aggregates of finite optimum size (for which further aggregation stops) (see Figure 5, Table 2) in the solution of associating polyelectrolytes. The decrease of the degree of charging of macromolecules at a fixed value of the association energy as well as increase of the association energy at a fixed value of charged degree of macromolecules does not change significantly the size of these intermacromolecular aggregates.

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References and Notes

(1) Saito, S.; Konno, M.; Inomata, H. *Adv. Polym. Sci.* **1993**, *109*, 207−232.
(2) Beltran, S.; Baker, J. P.; Hooper, H. H.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* **1991**, *24*, 549−551.
(3) Feil, H.; Bae, Y. H.; Feijen, J.; Kim, S. W. *Macromolecules* **1993**, *26*, 2496−2500.
(4) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311.
(5) Otake, K.; Inomata, H.; Konno, M.; Saito, S. *Macromolecules* **1990**, *23*, 283−289.
(6) Meewes, M.; Ricka, J.; de Silva, M.; Nyffnengger, R.; Binkert, T. *Macromolecules* **1991**, *24*, 5811−5816.
(7) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 165−249
(8) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1987**, *87*, 1392−1395.
(9) Hirotsu, S. *J. Chem. Phys.* **1988**, *88*, 427−431.
(10) Yu, H.; Grainger, D. W. *Macromolecules* **1994**, *27*, 4554−4560.
(11) Malcolm, H. B.; Yan, L.; Velada, J. L. *Polymer* **1997**, *38*, 5785−5791.
(12) Tenhu, H.; Lowe, T. *Macromolecules* **1998**, *31*, 1590−1594.
(13) Vesterinen, E.; Tenhu, H.; Dobrodumov, A. *Polymer* **1994**, *35*, 4852−4856.
(14) Ebara, M.; Aoyagi, T.; Sakai, K.; Sakurai, Y.; Okano, T. *Macromolecules* **2000**, *33*, 8312−8316.
(15) Shirahama, K.; Sato, S.; Niino, M.; Takisawa, N. *Colloids Surf. A*: *Physicochem. Eng.* **1996**, *112*, 233−237.
(16) Aoyagi, T.; Ebara, M.; Aoyagi, T.; Sakai, K.; Sakurai, Y.; Okano, T. J. *Biomater. Sci. Polym.* **2000**, *11*, 101.

(17) Makhaeva, E. E.; Tenhu, H.; Khokhlov, A. R. *Polymer* **2000**, *26*, 9139−9145.
(18) Eisele, M.; Burchard, W. *Macromol. Chem.* **1990**, *191*, 169.
(19) Ben-Naim, A. In *Hydrophobic Interactions*; Plenum Press: New York, 1980.
(20) Starodubtzev, S. G.; Sokolov, E. L.; Khokhlov, A. R.; Chu, B. *Macromolecules* **1995**, *28*, 3930−3936.
(21) Philippova, O. E.; Sitnikova, N. L.; Demidovich, G. B.; Khokhlov, A. R. *Macromolecules* **1996**, *29*, 4642−4645.
(22) Khokhlov, A. R.; Philippova, O. E. In *Solvents and Self-Organization of Polymer*; Webber, S., Ed.; Kluwer: Dordrecht, 1996; pp 197−225.
(23) Semenov, A. N.; Nyrkova, I. A.; Khokhlov, A. R. In *Ionomers: Characterization, Theory and Applications*; Schlick, S., Ed.; CRC Press: Boca Raton, FL, 1996; pp 251−279.
(24) Khokhlov, A. R.; Dormidontova, E. E. *Usp. Fiz. Nauk* **1997**, *167*, 113−128.
(25) Khokhlov, A. R.; Kramarenko, E. Yu. *Macromolecules* **1996**, *29*, 681−685.
(26) Essafi, W.; Lafuma, F.; Williams, C. *J. Phys. II* **1995**, *5*, 1269−1275.
(27) Essafi, W.; Lafuma, F.; Williams, C. *Eur. Phys. J.* **1999**, *9*, 261−266.
(28) Philippova, O. E.; Pieper, T. G.; Sitnikova, N. L.; Starodubtsev, S. G.; Khokhlov, A. R.; Kilians, H. G. *Macromolecules* **1995**, *28*, 3925−3929.
(29) Makhaeva, E. E.; Le Thi Minh Thanh, Starodoubtsev, S. G.; Khokhlov A. R. *Macromol. Chem. Phys.* **1996**, *197*, 1973−1982.
(30) Makhaeva, E. E.; Tenhu, H.; Khokhlov, A. R. *Macromolecules* **1998**, *31*, 6112−6118.
(31) Kirsh, Yu. Ye. *Polyvinylpyrrolidone and others poly(N-vinylamides);* Nauka: Moscow, 1998.
(32) Khokhlov, A. R.; Kramarenko, E. Yu.; Makhaeva, E. E.; Starodubtsev, S. G. *Theory. Macromol. Chem. Theory Simul.* **1992**, *1*, 105−118.
(33) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1992; pp 203−276.
(34) Wasserman, A. M.; Kasaikin, V. A.; Timofeev, V. P. *Spectrochim. Acta, Part A* **1998**, *54*, 2295−2308.
(35) Potemkin, I. I.; Vasilevskaya, V. V.; Khokhlov, A. R. *J. Chem. Phys.* **1999**, *111*, 2809−2817.
(36) Vasilevskaya, V. V.; Potemkin, I. I.; Khokhlov, A. R. *Lanqmuir* **1999**, *15*, 7918−7924.

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