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# pH/Temperature control of interpolymer complexation between poly(acrylic acid) and weak polybases in aqueous solutions.

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## Abstract

The formation of inter polymer complexes (IPC) between poly(acrylic acid) (PAA) and poly(acrylamide) (PAM), poly(*N,N*-dimethylacrylamide) (PDMA), and statistical copolymers of acrylamide (AM) and *N,N*-dimethylacrylamide (DMA) has been studied as a function of pH, salt concentration and temperature (0–70 °C). The cloud points of dilute solutions were measured by turbidimetry and phase diagrams were determined as a function of temperature and pH in pure water and as a function of pH and salt concentration at room temperature. For each temperature and salt concentration a critical pH ( $\text{pH}_{\text{crit}}$ ) below which IPC are observed was defined. In the case of PAA/PAM,  $\text{pH}_{\text{crit}}$  continuously decreased with increasing temperature, from pH 3.5 at 0 °C to pH 1.9 at 60 °C (UCST-type). In the case of PAA/PDMA,  $\text{pH}_{\text{crit}}$  increased with temperature. The LCST-type behavior of the hydrogen-bonding complex formed between PAA and PDMA was attributed to the dimethyl substitution of amide groups that puts in hydrophobic interactions at high temperature. PAA and statistical copolymers P(AM-co-DMA) showed an intermediate behavior between PAA/PAM and PAA/PDMA with a continuous shift from UCST-type to LCST-type with increasing amount of DMA. This behavior can be attributed to changes in configurational entropy due to the IPC formation and (for PDMA) to the release of water molecules initially confined in hydrophobic hydration cages around DMA units. While at low salt concentration, the stability of PAA/PAM and PAA/PDMA complexes only slightly increases with the screening of ionized acrylic units, there is a sharp increase of  $\text{pH}_{\text{crit}}$  at high salt concentration in relation with the weakening of the solvent quality. In this regime, the complex formation of PAA/PDMA is greatly enhanced compared to PAA/PAM due to the interference of hydrophobic interactions.

Key-words:

Hydrogen-bonding complex

Poly(acrylic acid)

Polydimethylacrylamide

## 1. Introduction

Responsive macromolecular devices, able to adapt their properties to environmental stimuli, form today a very challenging class of materials for high tech applications in microfluidics, mechanical transducers, reversible adhesion, tissue engineering or drug delivery.<sup>1-6</sup> For a given stimulus, these materials can display responsive bulk properties, with modification of their volume (by swelling), permeability, solubility, etc., as well as responsive surfaces properties that are of fundamental importance in scientific areas such as wetting, lubrication and adhesion.

Many of these responsive materials are water-soluble or water-swellaable polymers and their responsivity is related to the presence of intermolecular interactions and/or to the formation of interpolymer complexes (IPC). In essence a modification of molecular interactions due to an external stimulus (temperature, pH, electric field, light...) triggers a modification in solubility or conformation of the polymers or triggers the formation of an IPC, which in turn results in a macroscopic change in properties. Although in some cases the correspondence between the molecular scale interactions and the macroscopic effect is obvious, in some others such as adhesion between two surfaces, the connection is much less well understood. In this case molecular interactions occur at an interface, while a change in adherence of an object on a surface is a coupling between interface and bulk property.

In order to investigate systematically that molecular/macro connection it is essential to study both molecular interactions and macroscopic effects. In this paper we report a systematic study on the effect of pH and temperature on molecular interactions in a water-soluble polymer system which can also be readily used for macroscopic adhesion tests. Since the objective is to develop a multiresponsive model system by coupling pH and temperature, the key features that have to be taken into account in the selection of polymers are typically ionizable groups (weak acidic or basic moieties), hydrogen bonding and hydrophobic interactions.

Setting hydrogen bonding as the main driving force, we selected a weak polyacid (polyacrylic acid (PAA)) as the responsive polymer. PAA is well known to form hydrogen-bonding complexes with a large number of non-ionic polybases, such as poly(ethylene oxide) (PEO), poly(acrylamide) (PAM) and its derivatives, poly(*N*-vinyl-2-pyrrolidone) (PVP), etc.<sup>7</sup> The formation of IPC is generally studied with standard methods<sup>8</sup> such as gravimetry,<sup>9</sup> potentiometry,<sup>9,10</sup> turbidimetry,<sup>11-14</sup> viscosimetry,<sup>10,14-17</sup> fluorescence study after the labeling

of one of the polymers<sup>17,18</sup> and light scattering<sup>13</sup> or more specific ones like small angle neutron scattering<sup>19</sup> and infrared<sup>13</sup> or NMR spectroscopies.<sup>20</sup>

In aqueous solution, the formation of interpolymer complexes (IPC) between PAA and a proton acceptor polymer has been shown to occur only below a critical value of pH ( $\text{pH}_{\text{crit}}$ ),<sup>11</sup> where the degree of ionization was low enough. It is generally assumed<sup>11</sup> that the value of the critical pH is an index of the complexing ability of the polymer pair: the higher the critical pH of complexation, the stronger the complex. In other words, the lower the protonation of PAA for complexation, the higher the affinity between the two polymers. The absence of complexation between isolated monomers and the relatively low measured values of critical pH of IPC led to the idea that complex formation must involve cooperative effects, such as “non-interrupted linear sequences of bonds”, described by a ladder structure<sup>9,10,12,18</sup> and at the origin of the so-called “zipper effect”.<sup>21</sup>

For the specific case of PAA, the interaction between the two polymers is almost stoichiometric but the polybase/polyacid ratio can change according to the chemical structure and steric hindrance of the polybase interacting with PAA with acid:base molar ratios of 2:3 or 1:1 proposed for PAA/PAM<sup>22</sup> up to 3:2 for PAA/PNIPAM (poly(*N*-isopropylacrylamide)) or PAA/PDEAM (poly(*N,N*-diethylacrylamide)).<sup>10,22</sup>

While in organic solvents, the strength of IPC complexes formed between PAA and proton accepting polymers mainly depends from the difference between interaction forces polymer/polymer and polymer/solvent, the situation becomes more subtle in aqueous media as hydrophobic interactions and the dissociation state of PAA must also be taken into consideration. Hydrophobic interactions which often interfere in the complexation mechanism have been reported to favor the complex formation (increase of  $\text{pH}_{\text{crit}}$ ) and to modify the temperature dependence of its stability.<sup>7</sup> For instance, while the formation of IPC between PAA and PAM is characterized by negative values of standard enthalpy and entropy that underline the formation of a hydrogen-bonded complex characterized by lower configurational entropy, the complex formation between PAA and PNIPAM is characterized by thermodynamic values of opposite sign. In that case, the gain of entropy is attributed to the release of water molecules initially confined in hydrophobic hydration cages formed around isopropyl groups of PNIPAM.<sup>23</sup>

As the complex formation between polymer pairs in aqueous solution involves material parameters, such as molar mass of the polymers, relative concentration and composition and environmental parameters such as pH, temperature or ionic strength, the formation of IPC has

been investigated under many different angles. However to the best of our knowledge, and in spite of numerous studies devoted specifically to PAA complexes, we did not find a description of the whole “temperature-pH” dependence of the complex stability. As a matter of fact, most of the studies generally focus on a single stimulus, i.e. the temperature dependence of IPC at a given pH<sup>12,13</sup> or conversely its pH dependence at a given temperature, generally room temperature.

The current study was therefore mainly focused on IPC formed in aqueous solution between PAA and two H-bonding acceptor polymers, PAM and PDMA. Working at the same relative concentration for all polymers, we established comprehensive “pH-temperature” phase diagrams for these two complexes between 0 and 70 °C and below pH 4 by using turbidimetry measurements.

## 2. Experimental part

### 2.1. *Chemicals*

Acrylamide (AM, 99%, Sigma), *N,N*-dimethylacrylamide (DMA, 99%, Aldrich), ammonium peroxydisulfate (APS, 99.5% Aldrich), sodium metabisulfite (SMB, 97%, Acros), *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99.5% Sigma-Aldrich), 4,4'-azobis(4-cyanovaleric acid) (ACVA, 75%, Aldrich), ammonium chloride (99.5% Aldrich) and 3-mercaptopropionic acid ( $\geq 99\%$  Fluka) were used as received. All organic solvents were analytical grade and water was purified with a Millipore system combining an inverse osmosis membrane (Milli RO) and ion exchange resins (Milli Q).

### 2.2. *Polymers*

Poly(acrylic acid) (**PAA**,  $M_w = 50 \text{ kg}\cdot\text{mol}^{-1}$  from Polysciences) was used as received. PAM, PDMA and their copolymers were prepared by radical polymerization following two different procedures. For PDMA and its copolymers, we modified the method previously developed by Bokias *et al.*<sup>24</sup> to control the molar mass of vinyl monomers like *N*-isopropylacrylamide and acrylic acid. Targeting polymers with molar masses of about  $30 \text{ kg}\cdot\text{mol}^{-1}$ , we set the total monomer concentration at  $1 \text{ mol}\cdot\text{L}^{-1}$ , using the red-ox initiator APS/SMB with equal concentrations of  $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ . However, since the homopolymerization of AM with persulfate initiators is known to give high molar masses and high polydispersities,<sup>25</sup> we

specifically used a chain transfer agent.<sup>26</sup> The main details of the syntheses can be summarized as follows.

*PDMA and P(AM-co-DMA).* Ammonium chloride (0.5 mmol) and the proper quantities of monomers (50 mmol in total) were dissolved in water (50 mL) and the pH of the mixture was adjusted around 5-6 with hydrochloric acid before deoxygenation with nitrogen bubbling (1 h). A 1 mL solution of SMB (0.5 mmol) and a 1 mL solution of APS (0.5 mmol) were prepared, deoxygenated, and then added to the monomer solution under nitrogen atmosphere. The reaction was allowed to proceed at room temperature during 24 h. The final solution was dialyzed against milli-Q water using a membrane with a MWCO equal to 6 to 8 kg mol<sup>-1</sup> and the polymer was finally recovered by freeze-drying.

*PAM.* 3-mercaptopropionic acid (0.18 mmol) and acrylamide (180 mmol) were initially dissolved in 1 L of water at 60 °C under nitrogen bubbling. ACVA (1.8 mmol) was separately dissolved in water (18 mL) after ionization of carboxylic units by drop-wise addition of concentrated sodium hydroxide solution. After deoxygenation the initiator solution was added into the monomer solution. The reaction was left to proceed during 1 h at 60 °C followed by 1.5 h at 50 °C. The reaction medium was then concentrated under reduced pressure, precipitated in ethanol, filtered and washed several times before drying under vacuum.

The polymers were characterized by <sup>1</sup>H NMR in D<sub>2</sub>O (Bruker, 400 MHz) and size exclusion chromatography using a Viscotek SEC system equipped with three Shodex OH Pack columns equilibrated at 25 °C in a 0.5 M solution of sodium nitrate. The absolute molar masses of the samples were determined by the three detectors in line (refractometer, viscometer and light scattering), coupled with a calibration based on poly(ethylene oxide) standards. The composition and macromolecular characteristics of P(AM-co-DMA) copolymers are given in Table 1.

We can notice that the synthesis initiated by persulfate gives rise to molar masses  $M_w$  in the range of 30 to 40 kg mol<sup>-1</sup>, as expected from the literature.<sup>24</sup> In the case of radical copolymerization of AM and DMA, McCormick *et al.*<sup>27</sup> have shown that DMA tends to react a little bit faster than AM on a growing chain, but the reaction constants remain very close to one another. Consequently, we will consider that the distribution of AM and DMA in the polymer chain is almost random. Although polymerized in the presence of thiol, the molar mass of homo-PAM is clearly higher but the polydispersity remains rather low for this type of radical polymerization.

	AM (mol%) <sup>(1)</sup>	DMA (mol%) <sup>(1)</sup>	Yield (%)	$M_w$ (kg mol <sup>-1</sup> ) <sup>(2)</sup>	$\bar{D}$ <sup>(2)</sup>
PDMA	0	100	47	30	2.0
CopAM <sub>34</sub>	34	66	69	40	2.2
CopAM <sub>52</sub>	52	48	49	29	2.0
CopAM <sub>69</sub>	69	31	58	29	2.1
PAM	100	0	54	126	1.7

**Table 1.** Composition and macromolecular characteristics of P(AM-co-DMA) copolymers.

(1) the composition was determined by <sup>1</sup>H NMR.

(2) the molar mass  $M_w$  and polydispersity index ( $\bar{D}$ ) were determined by SEC.

### 2.3. Preparation of ternary mixtures

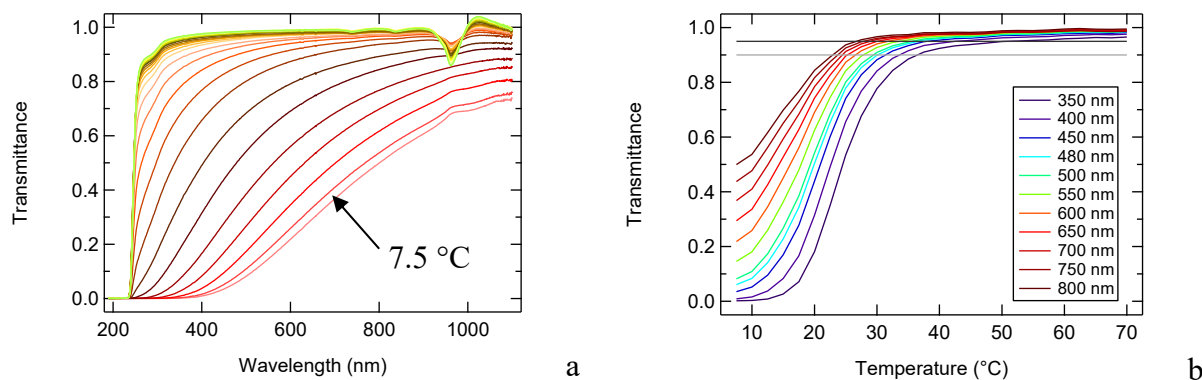
Initial solutions containing 5 wt% of polymer in pure water were prepared at least 24 h before the analysis. Then, 0.5 mL of PAA solution (proton-donor polymer) was mixed with 0.5 mL of the solution containing the proton-acceptor polymer and the resulting mixture was diluted 10 times by adding water and adjusting the pH with a small amount of concentrated NaOH or HCl solutions. For experiments exploring the influence of the ionic strength, a given amount of solid NaCl was slowly added to the previous solution and dissolved under stirring. If needed, the pH was adjusted during this procedure to avoid the formation of macro-aggregates. In the following, all the ternary systems have been studied at the same weight composition: PAA (0.25 wt%) / Polymer 2 (0.25 wt%) / water (99.5 wt%).

### 2.4. Analysis of IPC formation

Complex coacervation in ternary systems (polymer-1 / polymer-2 / solvent) gives rise to the formation of polymer aggregates that significantly impact the physical properties of the mixture. When this phase separation process remains under control of environmental conditions, the initiation of the phase transition can be readily followed by various techniques like rheology, potentiometry, light scattering (turbidimetry) or differential scanning calorimetry if enthalpy absorption or release is associated with the phase transition.<sup>7</sup> In the framework of the present study, the complex formation was studied by turbidimetry that highlights the growth of large aggregates with typical size greater than the wavelength of the light. The determination of the cloud point, that defines the transition threshold, can be made by eye but a more systematic analysis was preferred by using a UV-visible light spectrometer



(Hewlett Packard 8453) with wavelengths ranging from 200 to 1200 nm. The quartz cell (1 cm thickness) containing the ternary solution was maintained under stirring in the chamber of the spectrometer and the temperature was accurately controlled with a Peltier system. The temperature range was typically scanned from 7.5 °C to 70 °C with a heating rate of about 0.7 °C/min. As shown in Figure 1a and 1b, the transmittance of the ternary system under investigation increases with temperature, as the solubility of the complex increases, but the transmittance strongly depends on the wavelength.



**Figure 1.** Temperature dependence of the transmission spectra of a ternary mixture PAA (0.25 wt%) / CopAM<sub>69</sub> (0.25 wt%) / water (99.5 wt%) at pH 2.93. **(a)** The spectra were measured every 2.5 °C between 7.5 °C and 70 °C (from right to left). **(b)** The temperature dependence of the transmission was determined every 50 nm from 350 nm to 800 nm (left to right).

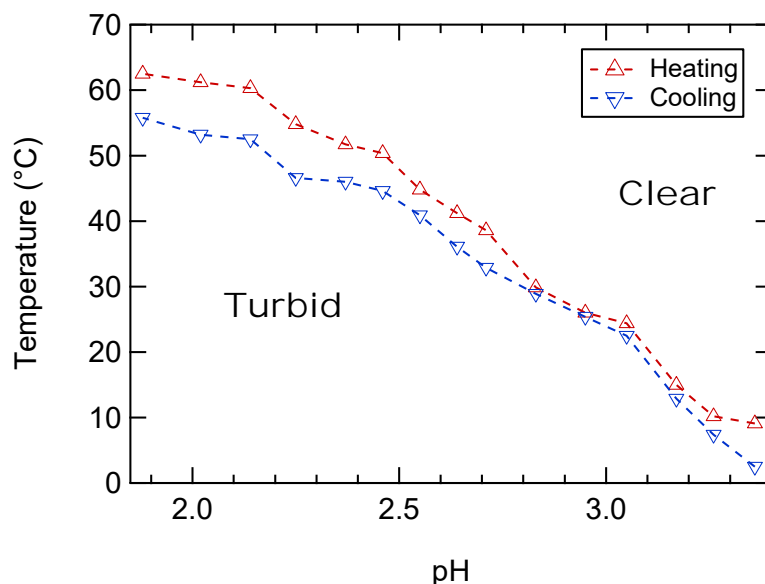
By comparing spectrometric data with those obtained by naked eye, the best agreement (within a degree) was obtained by setting the transition threshold for a transmittance value of 0.90 at 480 nm. These conditions, that have been systematically applied in this work, are typically in the spectrometric range (400-600 nm) generally considered for turbidimetry.<sup>7,12</sup>

### 3. Results and discussion

#### 3.1. *PAA/PAM phase diagram*

**Figure 2** shows the value of the transition points for the PAA/PAM IPC as a function of pH and temperature. At room temperature, PAA and PAM start to self-assemble reversibly below pH 3. However, when the temperature is changed, the pH transition zone is not sharp and it is possible to shift the association process with temperature by exploring the pH on a larger scale, typically between 1.8 and 3.4. In this range of pH, the IPC formation/dissociation can be finely tuned between 0 and 60 °C. As shown in **Figure 2**, there is a small hysteresis

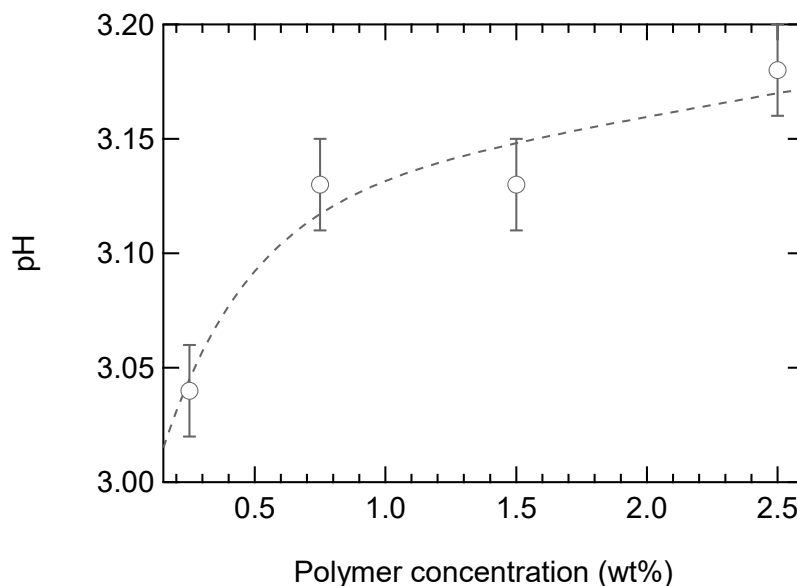
between the transition temperatures determined during heating and cooling that could be attributed to the slow dynamics of dissociation and solubilization of the two polymers with respect to the heating rate.



**Figure 2.** “pH-temperature” phase diagram of the ternary system PAA/PAM/water. Cloud points were determined during heating (Δ) or cooling (▽). The one-phase system is at high pH, in the clear domain.

Below pH 3.4, the complex formed between PAA and PAM clearly exhibits a UCST-type behavior (Upper Critical Solution Temperature) that mainly originates from hydrogen bonding between the two polymers. As shown by various authors like Staikos *et al.*<sup>23</sup> and Deng *et al.*,<sup>21</sup> the thermodynamics of formation of hydrogen-bonding complexes between PAA and PAM is an enthalpy-driven process ( $\Delta H^0 < 0$ ) with a loss of configurational entropy ( $\Delta S^0 < 0$ ). In this case hydrogen-bonding is the main factor stabilizing the IPC and its strength is weakened by increasing the temperature and/or the pH. In the absence of other additives, the thermodynamic properties of the ternary mixture PAA/PAM/water also depends on the molar mass of the polymers, their molar fraction with respect to the complex stoichiometry and their concentration. In this work, the study of IPCs was mainly carried out at low polymer concentration (0.25 wt%) in order to focus on the thermodynamic *reversibility* of the complexation while avoiding a dramatic impact of kinetics, especially for the dissolution of large aggregates. Nevertheless, we have explored more specifically for the PAA/PAM/water mixture the concentration dependence of the critical pH for complex formation ( $\text{pH}_{\text{crit}}$ ); i.e. the pH where the IPC starts to form. As shown in **Figure 3**, the critical pH slightly increases

of 0.15 units over one concentration decade; the two polymers are being added at the same weight ratio (1/1) and molar ratio (1/1) in the case of PAA/PAM.

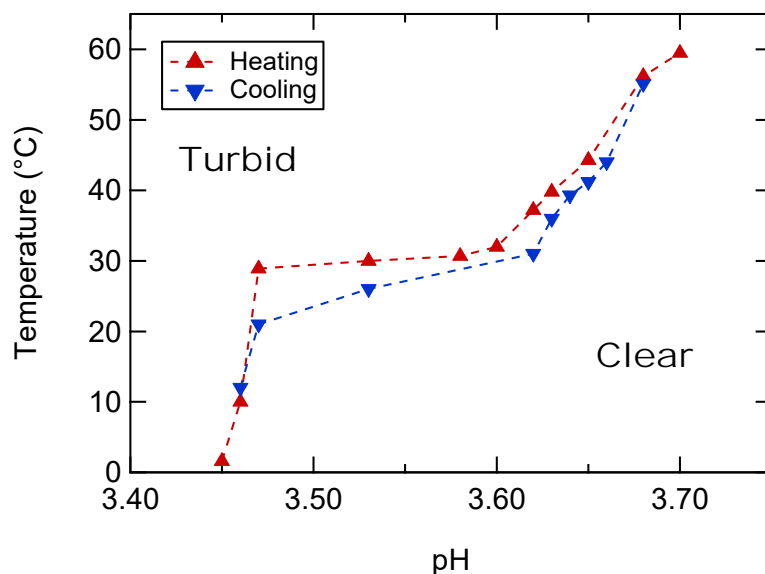


**Figure 3.** Critical pH of the IPC formation (PAA/PAM) at room temperature as a function of polymer concentration in water (PAA or PAM). The one-phase system is at high pH

As observed, the formation of IPC is favored with increasing polymer concentration since the degree of ionization of PAA is expected to decrease in such conditions. These results are in agreement with those reported by Mun *et al.*,<sup>11</sup> although they found that the critical pH of the transition increased by 0.3 unit over one concentration decade but carried out their experiments with polymers of higher molar masses.

### 3.2. PAA/PDMA phase diagram

A similar study was carried out with the ternary system PAA/PDMA/water and **Figure 4** shows the cloud points as a function of pH and temperature. At room temperature the formation of interpolymer complexes occurs at pH below 3.5 for PAA/PDMA mixtures prepared at the same relative weight concentration (0.25 wt% in water). This tendency for “PAA/PDMA” to form IPC at higher pH than PAA/PAM typically highlights the stronger complexation ability of PDMA towards PAA as already reported.<sup>12-14</sup> Moreover, contrary to PAA/PAM, the IPC formation of PAA/PDMA is favored at high temperature and there is a narrow pH range, typically between 3.45 to 3.70, where ternary mixtures turn from clear at room temperature into turbid at high temperatures.



**Figure 4.** “pH-temperature” phase diagram of the ternary system PAA/PDMA/water. Cloud points were determined while heating (▲) or cooling (▼). The one-phase system is at high pH, in the clear domain.

All these features support the idea that in addition to hydrogen-bonding, the formation of PAA/PDMA complexes in aqueous solutions is stabilized by hydrophobic interactions. Such a coupling between hydrogen bonds and hydrophobic interactions has been previously reported for various polymer pairs where one of the polymer exhibits some hydrophobic character. In these conditions, the entropic penalty due to the formation of hydrophobic cages around low polar groups of polymers is generally considered responsible for dehydration and complexation processes observed by increasing temperature ( $\Delta S^0 > 0$ ); the associated enthalpy is generally positive ( $\Delta H^0 > 0$ ).<sup>23,28</sup> This is the case for instance for poly(methacrylic acid) (PMAA) which forms stronger complexes than PAA, at higher critical pH values.<sup>29</sup> For instance, Ikawa *et al.*<sup>30</sup> and Kabanov *et al.*<sup>31</sup> have shown that the minimal critical segment length, which corresponds to the number of monomer units needed for the formation of complexes, increases with temperature for PAA/PEO and decreases for PMAA/PEO due to the increased hydrophobicity of PMAA compared to that of PAA. The formation of IPC between PAA and proton-acceptor polymers has been widely studied and it is well established that the introduction of hydrophobic comonomers into the proton-acceptor macromolecule enhances the complexation ability and the critical pH value.<sup>32</sup> The same holds for polymer pairs involving PAA and LCST polymers. In this case, IPC are formed at higher critical pH, compared to analogous polymers without LCST, and the complex itself can exhibit a LCST behavior.<sup>10,23,33</sup>

Although PDMA is water-soluble in the usual temperature range (0–100°C), it has an intermediate chemical structure between PAM, which is fully soluble in water, and poly(*N,N*-diethylacrylamide) (PDEA) that displays a LCST behavior at about 30°C.<sup>10</sup> Consequently, we can reasonably assume that PDMA is able to develop hydrophobic interactions through its methyl groups and theoretical predictions of a LCST phase transition for PDMA in water above 200 °C<sup>34</sup> support this idea. Although a LCST-type complex has been identified in the case of PAA/PDMA mixtures and grafted copolymers (PAA-*graft*-PDMA) by Aoki and coworkers,<sup>12,13</sup> the details of the temperature dependence of the complex formation as a function of pH has never been studied. As shown in **Figure 4**, the pH range where the complex formation between PAA and PDMA can be tuned with temperature is very narrow (less than 0.3 pH units over 60 °C) compared to PAA/PAM (more than 1.5 units over 60 °C). Interestingly the two systems behave similarly close to 0 °C where the two ternary systems phase separate below the same critical pH around 3.5. We can also notice that the temperature dependence of the complex PAA/PDMA is initially very weak below 20 °C and becomes larger above 20 °C and up to 60 °C. Nevertheless, as both entropy and enthalpy of complex formation may vary with the temperature, as it was shown with various polymer pairs like PAA/PEO<sup>35</sup> and PAA/PVP<sup>36</sup>, it is difficult to specifically address the temperature behavior of the complex to hydrogen bonding, hydrophobic interactions or a coupled effect. Moreover, on this specific aspect, we can mention that while most of the background originates from experiments performed on a large number of systems, there is no unifying theory taking into account distinctly the contribution of hydrogen bonds and hydrophobic forces. While UCST is readily understood in terms of intermolecular forces, interpretation of LCST generally takes into account 1) differences in thermal expansion of solvent and solute or 2) order/disorder transitions as encountered in systems capable of forming hydrogen bonds, with or without hydrophobic contribution.<sup>37</sup> In the latter case, the hydrophobic contribution could be taken into account through the introduction of a strong correlation between neighboring water molecules along the polymer chain (cooperative hydration).<sup>38</sup>

### 3.3. *Influence of ionic strength*

The stability of hydrogen-bonding complexes can be modified by adding molecules that will interfere with the interactions. While the addition of urea, a well-known competitor for hydrogen bonding, clearly destabilizes the complex formation at low pH and increases the

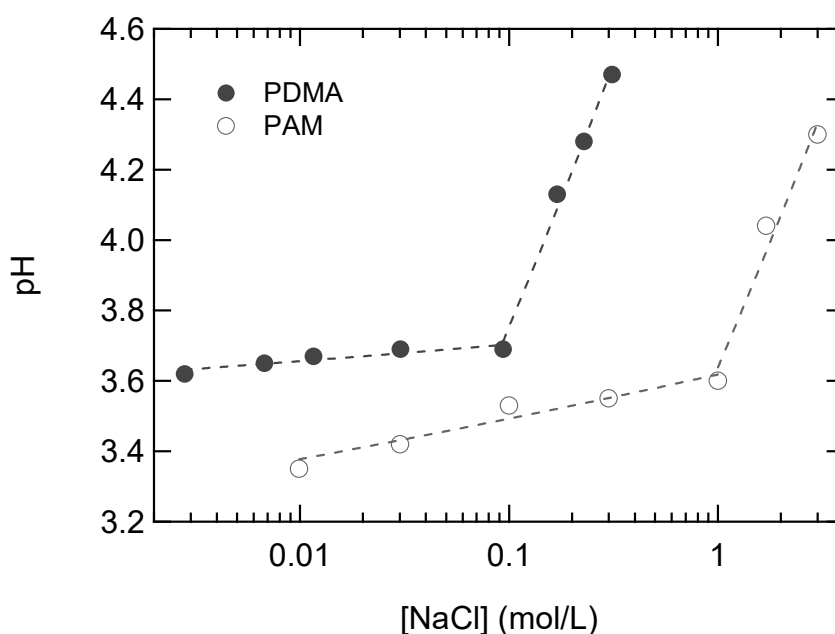
solubility of each polymer, the effect of the addition of inorganic salts could be more complex to interpret since three competing mechanisms are involved, namely:

1) an increase in the level of dissociation of the carboxylic groups of the PAA which is unfavorable for hydrogen-bonding,

2) a screening of the electrostatic repulsions between ionized residues which favors the hydrogen-bonded complex formation,

3) a decrease of the thermodynamic quality of water which strengthens interactions between polymer chains.

The influence of different concentrations of sodium chloride upon complex formation of PAA with PAM and PDMA is reported in **Figure 5**.



**Figure 5.** Salt dependence of the critical pH for hydrogen-bonding complex formation at 25 °C. All the ternary systems were studied in aqueous solutions at the same polymer concentration (0.25 wt% for each polymer): PAA/PAM (○) and PAA/PDMA (●). The one-phase system is at high pH.

Starting with the PAA/PAM complex we can notice that the addition of sodium chloride increases the critical pH and favors the formation and stability of the complex. At low salt concentration, typically below 1 mol/L, the critical pH increases only very slightly (about 0.2 units between  $10^{-2}$  and 1 mol/L) and this can be ascribed to the screening of electrostatic interactions that prevail upon dissociation of carboxylic acids. This behavior is in good agreement with the literature where IPC having a relatively low critical pH ( $pH_{crit}$  between

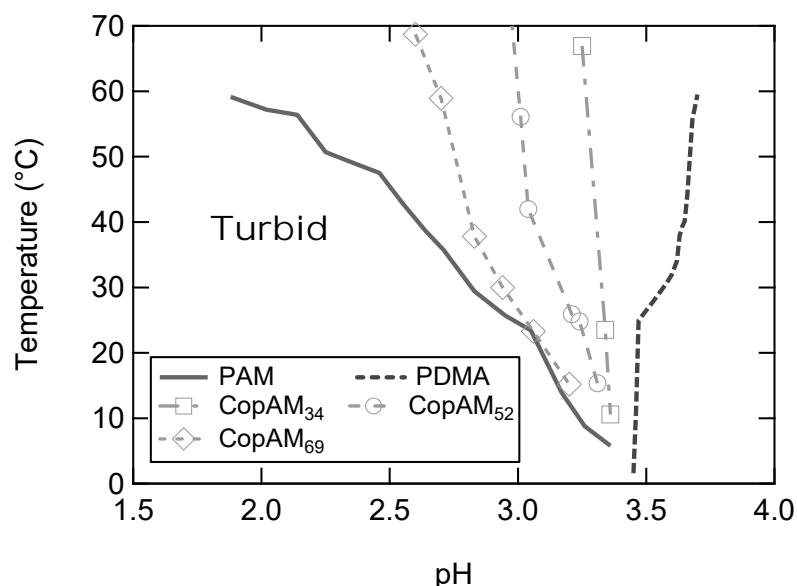
2.45 and 2.88) are known to increase their stability and  $pH_{crit}$  upon the addition of inorganic salts, while stronger complexing systems (with  $pH_{crit}$  in the range 3.66-4.85) show the opposite trend.<sup>7,39</sup> At high salt concentration (above 1 mol/L), the PAA/PAM complex displays a significant increase of the critical pH due to the weaker hydration of polymer chains (decrease of solvent quality).

In the case of PAA/PDMA, the salt dependence of the critical pH is positive at low salt concentration but much weaker than the one obtained for PAA/PAM. This result is in good agreement with the critical pH value of PAA/PDMA that is higher than PAA/PAM and we can reasonably conclude that screening and ionization effect almost compensate each other. Nevertheless, the situation becomes different at higher salt concentration where a strong increase of the critical pH is observed at about 0.1 mol/L; i.e. one decade below the two other complex. This feature can be put in line with the “hydrophobic” character of PDMA that is responsible for the LCST behavior of the PAA/PDMA complex. This hydrophobicity is expected to provide a much higher responsivity towards added molecules that will compete in the hydration process. This well-known “salting out” effect, which impacts the solubility of LCST polymers like PEO, PNIPAM and others, clearly depends from the nature of salt but becomes very significant typically for salt concentrations above 0.1 mol/L.<sup>40,41</sup>

### **3.4. Complex formation between PAA and P(AM-co-DMA) copolymers**

As the complex formation in aqueous solution between PAA/PAM and between PAA/PDMA display an opposite behavior with temperature, we investigate how random copolymers of AM and DMA behave in the presence of PAA. Such problem has been initially partly investigated in the literature by authors like Wang *et al.*<sup>18</sup> who studied at room temperature the influence of copolymer composition on complex stability. Using a dansyl label attached to PAA, they show by fluorescence spectroscopy that the density and strength of hydrogen bonded complexes formed at pH 3 with P(AM-co-DMA) increases with increasing fraction of DMA in the copolymer. Similarly, Aoki and coworkers<sup>12</sup> have shown that the stability of IPC formed between PAA and P(AM-co-DMA) increases with DMA content and that all the complexes studied exhibit a UCST-type behavior; at least for molar fraction of DMA below 27 mol%. In the same way, they also show that the swelling of interpenetrating polymer networks (IPN) composed of P(AM-co-DMA) and PAA decreases with increasing DMA content and increases with temperature. Contrary to the PAA/PAM IPN which starts to swell above 20 °C, hydrogen bonds formed between PAA and PDMA stabilizes the IPN in a

collapsed state up to 60 °C. Our results shown in **Figure 6** qualitatively confirm the previous observations and show an increased range of pH-stability for hydrogen bonding complexes as the amount of DMA in the copolymer increases, but show a more complete picture of the pH-temperature phase diagram.



**Figure 6.** “pH-temperature” phase diagram of ternary systems PAA/P(AM-co-DMA)/water. The one-phase system is at high pH.

For a given temperature, the critical pH for complexation continuously increases with DMA content. However the impact of DMA increases significantly with temperature with a common intercept at about 0°C where all the complexes behave similarly with a critical pH at about 3.5. Interestingly we can notice on **Figure 6** that the temperature dependence of the cloud point changes progressively from a UCST-type for PAA/PAM, dominated by hydrogen bonds, to a LCST-type for PAA/PDMA where hydrophobic interactions are strongly coupled to hydrogen bonds. Moreover by tuning the level of hydrophobic interactions with the DMA composition, one can control the temperature dependence of the complex formation and find stable complexes that do not respond at all to the temperature. From a thermodynamic point of view, it is possible to correlate the temperature dependence of the complex stability with the entropy change of the complex formation, which is expected to be negative for PAA/PAM and positive for PAA/PDMA; then,  $\Delta S^0$  goes through 0 for a given copolymer composition. This is almost the case for the complex formed between PAA and CopAM<sub>34</sub> that can be tuned with temperature only in an extremely narrow range of pH (about 0.1 unit over 60 °C).



As already shown with the complex formation of (co)poly(vinyl ether) with PAA, the incorporation of hydrophobic fragments into macromolecules enhances the hydrophobic stabilization of IPC in aqueous solutions which leads to an increase of the pH-stability.<sup>32</sup> While PDMA is generally considered as a hydrophilic polymer, the complex formation with PAA reveals that its hydrophobic character is strong enough to readily modify and overturn the temperature dependence of hydrogen bonding complexes formed between PAA and P(AM-*co*-DMA). Such tuning should be reflected in the level of interactions between surfaces and provide a guidance on which systems are likely to provide the broadest range of tunability.

#### **4. Conclusion**

The formation of hydrogen bonded IPC between PAA on the one hand and homopolymers of PDMA, PAM and statistical copolymers of AM and DMA on the other hand has been studied as a function of pH, salt concentration and temperature. In the case of PAA/PAM IPCs, the hydrogen-bonding complex takes place around 0°C at pH 3.5 and the critical pH for the complex formation continuously decreases with increasing temperature, up to pH 1.9 at 60 °C. This behavior, already described in the literature, is typically expected when the IPC formation is driven by hydrogen bonding in water, in which case both the enthalpy and the entropy of the complex formation are negative. Although PDMA is very soluble in water and chemically close to PAM, we have shown that methyl groups in DMA units were responsible for the opposite LCST behavior of the IPC formed with PAA. While the role of hydrophobic interactions on IPC stability in aqueous media has been well described using LCST polymers like PNIPAM or polyethers, this work clearly evidences that even weak hydrophobic contribution can strongly impact the complex formation in water and its stability. The original contribution of this work also comes from the determination of comprehensive “pH-temperature” phase diagrams of hydrogen-bonding complexes formed between PAA and statistical copolymers of AM and DMA which provide a good understanding of the impact of hydrophobic forces in hydrogen bonding complexes. Although negligible at temperature close to 0 °C, the contribution of hydrophobic interactions increases with temperature and at 60 °C the critical pH for complex formation can be shifted by about two pH units by changing the monomer composition of P(AM-*co*-DMA). Similarly, working at a fixed pH, the complex stability can be controlled with temperature as statistical copolymers display an intermediate behavior between PAM and PDMA with a continuous evolution from UCST-type to LCST-

type with increasing amount of DMA. For a molar composition close to 1AM/2DMA the complex formed with PAA has no temperature dependence. This can be explained if we assume that the loss of configurational entropy related to the IPC formation compensates the gain of entropy coming from the release of water molecules initially confined in hydrophobic hydration cages around DMA units.

Comparing PAM and PDMA complexes formed with PAA, the influence of salt is mainly significant at high salt concentration (above 0.1 mol/L) where the decrease of the solvent quality becomes noticeable, especially for PAA/PDMA which involves hydrophobic interactions. From a general point of view, this work illustrates the potentiality of IPC to design responsive devices with well controlled interactions. Based on hydrogen-bonding complexes between PAA and P(AM-co-DMA) we have defined a large “pH-temperature” playground where responsive interactions can be used to trigger responsive adhesion between macromolecular surfaces prepared with the same polymers. Such work is currently undergoing in our laboratory and will be reported elsewhere.

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