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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 interpolymer 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 (pH_{crit}) below which IPC are observed was defined. In the case of PAA/PAM, pH_{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, pH_{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 pH_{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.

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 [1–6]. 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-swellable 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.

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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 [7]. The formation of IPC is generally studied with standard methods [8] such as gravimetry [9], potentiometry [9,10], turbidimetry [11–14], viscosimetry [10,14–17], fluorescence study after the labeling of one of the polymers [17,18] and light scattering [13] or more specific ones like small angle neutron scattering [19] and infrared [13] or NMR spectroscopies [20].

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 (pH_{crit}) [11], where the degree of ionization was low enough. It is generally assumed [11] 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 [9,10,12,18] and at the origin of the so-called “zipper effect” [21].

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 [22] up to 3:2 for PAA/PNIPAM (poly(*N*-isopropylacrylamide)) or PAA/PDEAM (poly(N,N-diethylacrylamide)) [10,22].

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 pH_{crit}) and to modify the temperature dependence of its stability [7]. 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 [23].

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 [12,13] 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 peroxodisulfate (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 (≥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, $M_w = 50$ kg 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. [24] to control the molar mass of vinyl monomers like *N*-isopropylacrylamide and acrylic acid. Targeting polymers with molar masses of about 30 kg mol^{-1}, we set the total monomer concentration at 1 mol L^{-1}, using the red-ox initiator APS/SMB with equal concentrations of 10^{-2} mol L^{-1}. However, since the homopolymerization of AM with persulfate initiators is known to give high molar masses and high polydispersities [25], we specifically used a chain transfer agent [26]. The main details of the syntheses can be summarized as follows.

2.2.1. 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 hydrogen chloride 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 an MWCO equal to 6 to 8 kD and the polymer was finally recovered by freeze-drying.

2.2.2. 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 ^{1}H NMR in D_2O (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.