



# Polyampholyte hydrogels formed via electrostatic and hydrophobic interactions



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## ARTICLE INFO

### Article history:

Received 12 December 2016

Received in revised form 18 January 2017

Accepted 22 January 2017

Available online 24 January 2017

### Keywords:

Supramolecular hydrogels

Polyampholytes

Ionic interactions

Hydrophobic associations

Swelling

Mechanical properties

## ABSTRACT

We introduce here a novel strategy to produce supramolecular polyampholyte hydrogels exhibiting pH sensitivity and anti-polyelectrolyte effect. The hydrogels were synthesized by photopolymerization of N,N-dimethylacrylamide (DMA) with equimolar amounts of the ionic monomers acrylic acid (AAc) and 4-vinylpyridine (4VP) under solvent-free condition. Instead of a chemical cross-linker, stearyl methacrylate (C18) was included into the comonomer feed to create hydrophobic associations. Both the electrostatic and hydrophobic interactions produce intermolecular linkages between the polymer chains acting as physical cross-link zones that are stable in water. Polyampholyte hydrogels are in a swollen state at  $\text{pH} < 4$  and  $\text{pH} > 6$  while they undergo a swelling-to-collapse transition between these pH values by adopting a collapsed conformation over a certain range of pH including their isoelectric points. This swelling behavior is a result of the pH difference between the inside and outside of the hydrogel, as demonstrated by the theory of swelling equilibrium. Rheological measurements indicate the reversible nature of the cross-link zones with finite lifetimes. Polyampholyte hydrogels containing 80–92% water exhibit Young's moduli between 18 and 58 kPa and sustain tensile strains up to 560%, while those prepared using a chemical cross-linker are brittle in tension. Cyclic mechanical tests show a large mechanical hysteresis and the existence of reversibly and irreversibly broken bonds under large strain.

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## 1. Introduction

Polyampholytes are stimulus responsive materials containing oppositely charged functional groups. They received much attention in the past 60 years due to their biocompatibility, low toxicity, similarity to biological systems such as proteins and therefore, they have found various applications such as saline-resistant, anti-fouling and antibacterial materials [1–8]. At a high net charge density, polyampholyte molecules adopt an extended conformation in water due to the osmotic pressure of mobile counterions confined inside the polymer coil to achieve the electroneutrality. As the net charge density decreases, the conformation of the molecules changes from extended to collapsed coils because of the decrease of mobile counterion concentration and strong electrostatic attractive forces between oppositely charged segments. The addition of salt shields the electrostatic interactions in charge-balanced polyampholyte molecules leading to the expansion of polymer coils known as the anti-polyelectrolyte behavior. It was also shown that hydrophobically modified polyampholytes form intermolecular

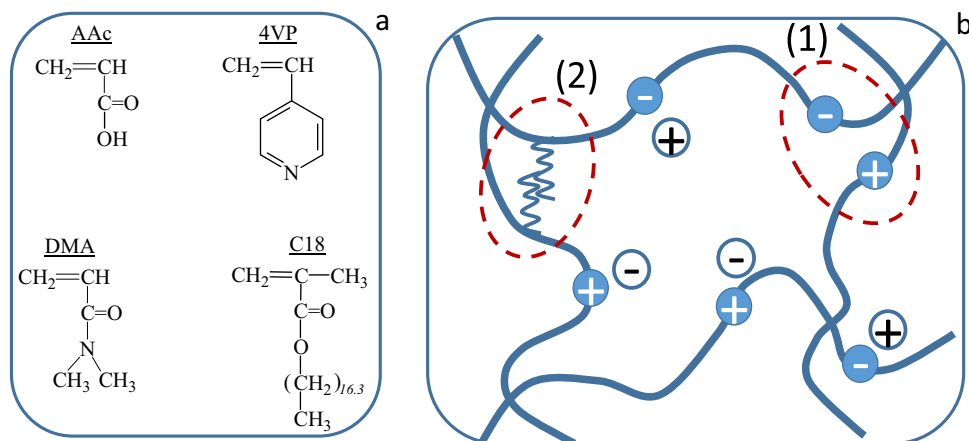
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hydrophobic associations in aqueous solutions [9–12]. Thus, they combine the properties of hydrophobically modified non-ionic polymers and polyampholytes making them effective viscosity enhancers in brine solutions.

Hydrogels mimicking the solution properties of polyampholyte molecules have been prepared by copolymerization of ionic monomers possessing cationic and anionic charges in the presence of a chemical cross-linker [13–22]. Strong polyampholyte hydrogels bearing permanent charges have a fixed net charge and therefore they exhibit pH-independent swelling behavior. Thus, the net charge of such hydrogels can only be varied by changing the comonomer ratio in the feed. In contrast, the net charge of weak polyampholyte hydrogels possessing functional groups like amines and carboxylic acids varies with the pH leading to pH-dependent swelling behavior, swelling-to-collapse transition, and anti-polyelectrolyte behavior in aqueous solutions [15,22]. Although polyampholyte hydrogels have a number of technological applications [8,19–21], they are mechanically weak materials due to the covalently cross-linked network structure, preventing dissipation of the crack energy and thus leading to their fracture under low stresses. Recently, supramolecular hydrophobically modified polyampholyte hydrogels were prepared by copolymerization of acrylamide and acrylic acid in the presence of a cationic surfmer [23]. Although pH-dependent swelling characteristics and mechanical properties of the hydrogels were not reported, they exhibit shape-memory effects and thermoplasticity. Gong et al. prepared high-toughness polyampholyte hydrogels in the absence of a chemical cross-linker by random copolymerization of oppositely charged ionic monomers at a high concentration around the zero net charge point [24,25]. It was shown that the randomness of charges leads to the formation of multiple ionic bonds with a wide distribution of strengths. While the strong bonds act as permanent cross-links, the weak bonds acting as reversible sacrificial bonds easily fracture under a low stress and hence, dissipate energy to prevent crack propagation [24]. Although the hydrogels exhibit a high mechanical strength, they do not display typical swelling characteristics of polyampholyte hydrogels due to their low water contents, e.g., 52–61 wt%, and the presence of strong electrolyte functional groups.

Here, we describe preparation of supramolecular polyampholyte hydrogels exhibiting pH-dependent swelling behavior, swelling-to-collapse transition, and anti-polyelectrolyte property. The hydrogels were prepared by photopolymerization of the non-ionic monomer *N,N*-dimethylacrylamide (DMA) with the ionic monomers acrylic acid (AAc) and 4-vinylpyridine (4VP) under solvent-free condition (Scheme 1a). The choice of these monomers as building blocks of supramolecular hydrogels is due to the fact that both poly(DMA) and poly(4VP) are well known proton acceptor polymers able to form interpolymer complexes with several proton donor polymers such as poly(AAc) [26]. Moreover, it was shown that poly(AAc) and poly(4VP) form hydrogen-bonded complexes in aqueous solutions through the cooperative hydrogen-bonding interactions [27]. We used equimolar amounts of AAc and 4VP between 10 and 20 mol% in the gel preparation together with the hydrophobic monomer stearyl methacrylate (C18) at a concentration of 2 mol% to create hydrophobic associations [28,29] (Scheme 1b). As will be seen below, both the electrostatic interactions between AAc and 4VP segments carrying weak anionic and cationic groups, respectively, and the hydrophobic interactions between C18 segments produce intermolecular linkages acting as physical cross-link zones that are stable in water. Hydrogels are in swollen states at pH < 4 and pH > 6 while they undergo a collapse transition between these pH values. The results also show that polyampholyte hydrogels adopt a collapsed conformation over a range of pH including their isoelectric points. This finding is in agreement with the prediction of the classical Flory-Rehner swelling theory coupled to the Donnan equilibrium and indicates different pHs between the inside and outside of the gel phase. Rheological measurements reveal reversible nature of the cross-link zones in the hydrogels with finite lifetimes. The hydrogels containing 80–92% water exhibit Young's moduli between 18 and 58 kPa and sustain tensile strains up to 560%, while those prepared using a chemical cross-linker are brittle in tension. Cyclic mechanical tests show a large mechanical hysteresis and the existence of reversibly and irreversibly broken bonds under large strain.



**Scheme 1.** (a) Structure of the monomers used in the preparation of polyampholyte hydrogels. (b) Scheme showing intermolecular electrostatic interactions between ionized AAc and 4VP segments (1), and hydrophobic interactions between C18 segments of polyampholyte hydrogels (2).

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