



New stimuli-responsive polyampholyte: Effect of chemical structure and composition on solution properties and swelling mechanism



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ABSTRACT

New polyampholyte linear polymers and hydrogels based on *N*-acryloyl-*N'*-ethyl piperazine (AcrNEP) and maleic acid (MaA) were prepared by free-radical solution polymerization. The microstructure of copolymers was statistically estimated by the terminal copolymerization model. A maximum tendency (80%) of alternating sequence of monomers units occurred at about 85 mol % of AcrNEP in the reaction feed. The copolymers at definite monomer compositions (40 mol % of AcrNEP and 59.6 mol % of MaA) exhibited lower critical solution temperature (LCST) behavior in water. The LCST was dependent on monomer composition, pH of external solution, type and concentration of simple salts. The isoelectric points (IEP) of copolymers were found to be influenced by the overall composition of ionic monomer units. The influence of high maleic acid content (14 mol % and 59 mol %) and the type of chemical crosslinker on pH-responsive swelling behavior, water diffusion and dye sorption properties of the hydrogels were studied in detail. The gels exhibited interesting swelling behavior as function of pH (ionic strength = 0.01 M) due to a combination of factors such as pK_a of the monomers, charge density, and type of crosslinker. The IEP of the gels were also determined from swelling experiments. The swelling ratio of the gels increased at the IEP with increase in ionic strength of the solution due to anti-polyelectrolyte effect. However below the IEP, the swelling ratio decreased considerably. Dynamic swelling properties of the amphoteric gels in water without added salt were measured. The swelling behavior was found to depend on the ionization state of the monomers, and the swelling followed non-Fickian (anomalous) mechanism. The swelling process of the hydrogels in water followed second-order kinetics. The amount of bound and unbound water in swollen gels was quantified using differential scanning calorimetry. Dye adsorption capacity of the new hydrogels was investigated using a Congo red as a model dye and was in the range 8.37–11.45 mg g⁻¹. This corresponds to an absorption efficiency of range 68–93%.

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1. Introduction

“Stimuli”-responsive or smart polymers are water soluble polymers that respond to changes in external stimuli such as pH, temperature, electric field, ionic strength, salt concentrations, pressure, light and magnetic field [1–5]. Given this responsive behavior, these polymers are of great technological and scientific importance and are used in controlled drug delivery systems, cosmetics, chemical sensors, protein purification, and paints [5–9]. Specifically, the polymers that respond to changes in external temperature are categorized into two main types [2]. The first type

of thermo-responsive polymers are soluble in water at low temperatures but phase separate when the temperature is raised above a critical temperature. This critical temperature point is called the lower critical solution temperature (LCST) [2,11]. A critical balance of hydrophilic and hydrophobic groups of the polymer system is an important parameter for the manifestation of LCST behavior. The second type of thermo-responsive polymers are soluble above a critical temperature point, called the upper critical solution temperature (UCST) [10]. The LCST in thermo-responsive polymers occur due to an entropic driven effect, while the UCST is driven by an enthalpy effect [2,10].

Recent interest in responsive polymer system focuses on aqueous solutions, hydrogels, nanogels, and interfaces [11–15]. The aqueous solution behavior of responsive polymers is still the major subject of scientific investigations for correlating the behavior of

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crosslinked polymers in the form of hydrogels. Stimuli-responsive hydrogels are crosslinked insoluble polymer networks that can absorb large quantities of water or physiological fluids and respond to changes in external environment [5]. These materials possess excellent properties such as permeability to small molecules, consistency, high equilibrium water content, and low interfacial tension. These properties make these materials good candidates for applications in targeted drug delivery systems, cosmetics, chemical sensors, enzyme immobilizations etc. [16–20]. The stimuli-response of a gel is in the form of volume change which is governed many factors such as hydrophilic-hydrophobic balance, osmotic pressure, crosslink density, conformation of chemical group etc. [21–23].

Depending on the nature of monomers, various type of stimuli-responsive linear polymers and gels such as anionic, cationic, non-ionic, and ampholyte have been prepared [24–27]. Polyampholyte linear polymers and networks contain both basic and acidic monomer units which can be ionized under suitable pH conditions [28–31]. These materials are usually prepared by copolymerization of two ionic monomers containing oppositely charged functional groups (acidic and basic). Some examples of common acids are acrylic acid, methacrylic acid, itaconic acid, vinyl phosphoric acid and maleic acid [31–34]. The common bases widely used are vinyl amine, vinyl pyridine, vinyl pyrrolidone etc. [35–37]. The net charge in a polyampholyte polymer/hydrogel can be tuned either by varying the monomer feed compositions during polymerization reaction or by changing the pH of external solution. These polymer/gels exhibit different but interesting properties compared with cationic, anionic, or non-ionic polymer/hydrogels [38,39].

An important property exhibited by polyampholyte gels is the anti-polyelectrolyte effect which causes the gels to swell in aqueous solutions of high ionic strength at its isoelectric point [40–42]. This property leads to a number of important applications both in theoretical studies and in technological applications. Therefore, in recent years, the study of polyampholyte polymer/hydrogels has gained much attention in order to understand their properties and applications in agrochemicals, water treatment and biomaterials [43–47].

N-acryloyl-*N'*-ethyl piperazine (AcrNEP) is an ionizable basic monomer of the class poly (amido-amines), which upon free-radical polymerization gives a water-soluble polymer [27]. This pH-sensitive polymer does not exhibit any LCST phenomenon in water. Maleic acid is a diprotic acid containing two carboxylic acid groups which ionizes at pH 2.0 and pH 7.0. The first and second pK_a of maleic acid are 1.85 and 6.06 respectively [48]. This large difference between the pK_a of the carboxylic acids makes maleic acid an interesting monomer in the development of polyelectrolyte and polyampholyte linear polymers and gels [31,32,43,49,50].

Poly(amido-amine)s are a unique family of synthetic functional polymers containing amide and amine groups [51–54]. These polymers have been widely developed for use both as biomedical materials and polymer therapeutics. Polyampholyte linear polymers and gels of amido-amines based monomers containing heterocyclic ring and maleic acid has not been considered in spite of their excellent properties. The ionization behavior of maleic acid along with ionization of the tertiary amine of AcrNEP ($pK_a = 4.1$) in polyampholyte linear polymer/hydrogel is expected to display interesting solution properties and swelling behavior as function of solution pH. Understanding the solution and swelling properties of these materials is of great interest for applications in water-treatment through chelation, adsorption, and ion-exchange processes [31,43,49].

In continuation of our research interest in piperazine-based polymers of poly amido-amines architecture [27,55–59], in this article we report the stimuli-responsive aqueous solution

properties and swelling characteristics of new polyampholyte linear copolymers and hydrogels containing two ionizable monomers viz. AcrNEP and maleic acid. The gels reported in this work contain high mole fractions of maleic acid (14 mol % and 59 mol %). The high mole fraction was chosen in order to demonstrate the physical crosslinking effects of maleic acid. The influence of hydrophilic-hydrophobic balance on the LCST, the swelling behavior, states of water, and adsorption of Congo red dye from water were examined and are presented in detail. Understanding the physical properties of this new polyampholyte type linear polymers and gels is an important criterion in the development of targeted drug delivery systems and hydrogel-based systems for water purification applications.

2. Experimental section

2.1. Materials

Maleic acid (MaA) (Aldrich), *N*-ethyl piperazine (Aldrich), triethylamine (Aldrich), ethylene glycoldimethacrylate (EGDMA) (Fluka), thionyl chloride (TCl), poly(ethylene glycol) diacrylate (PEGDA, $M_n = 575$) (Aldrich), azobiscyanovaleric acid (ACVA) (Aldrich), sodium chloride (NaCl) (Baker), sodium sulfate (Na_2SO_4) (Baker) and Congo red (Aldrich) were used as received. 1,4-Dioxane (Merck) was treated with molecular sieves and distilled prior to use. Deionized water was used for all aqueous sample preparations. Acidic and basic pH solutions were prepared using 0.1 M HCl and 0.1 M NaOH respectively. The ionic strength of the solutions was adjusted using sodium chloride. The pH of solutions was measured using a Mettler pH meter.

2.2. Synthesis of *N*-acryloyl-*N'*-ethyl piperazine (AcrNEP)

Acryloyl chloride and the monomer AcrNEP were synthesized according to the procedure described elsewhere [27,60].

2.3. Synthesis of linear copolymers

Linear copolymers of AcrNEP and MaA of various compositions were prepared by free-radical solution polymerization. The synthesis of copolymer A1M9 is described as follows: The monomers, AcrNEP (0.326 g, 1.94 mmol), MaA (2.71 g, 23.34 mmol), and the initiator, CVA (0.015 g, 0.05 mmol) were dissolved in 40 ml of freshly distilled dioxane in a 100 ml round bottom flask fitted with a glass tap. The reaction mixture was bubbled with dry nitrogen gas for 15 min to remove any dissolved oxygen which is a free-radical inhibitor. After purging, the flask was sealed and polymerization reaction was conducted at 75 °C for 24 h with constant stirring. The flask was then air-cooled to room temperature and the reaction mixture was poured gently into a beaker containing 300 ml of diethyl ether. The precipitated polymer was washed in ether and purified by re-precipitation method. The purified polymer was lyophilized by freeze-drying using water as solvent. (Yield 60%, white powder). Linear copolymers of other compositions were similarly prepared, and the compositions of monomers are summarized in Table 1. The chemical structure of the monomers AcrNEP and MaA are shown in Fig. 1.

2.4. Synthesis of copolymer hydrogels

Chemically crosslinked copolymer hydrogels of AcrNEP and MaA with different monomer compositions were synthesized by thermal free-radical solution polymerization at 75 °C. The crosslinker content and the total monomer concentration in the gels were fixed at 3.0 mol % and 5.0 wt %, respectively. The preparation

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