# Preparation and Characterization of Polyampholytic Poly(acrylic acid acrylamide) Hydrogels and Investigation of Swelling Behavior in Different Media

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**Summary:** Stimuli-responsive polyampholyte hydrogels were synthesized by the copolymerization of acrylic acid (AAc) and acrylamide (AAm) by thermal methods. Polyampholytic hydrogels are crosslinked networks composed of positively and negatively charged repeating units that show entirely different properties from their origins. In this work, polyampholytic poly (acrylic acid acrylamide) hydrogels prepared in different molar ratio in feed composition by thermal methods. The structures of hydrogels were characterized by FTIR analysis. Thermal stabilities of the hydrogels were investigated using TGA analysis. The swelling behavior of hydrogels investigated by some parameters such as pH, salt concentration and temperature. We determined this swelling capacity in different temperatures (25, 50 and 70 °C) and different pH (2, 7 and 12). In addition, we investigated the effects of different salts such as LiCl, $CaCl_2$, $Na_2SO_4$ and NaCl with concentration of 0.1, 0.2 and 0.3 M on swelling properties.

**Keywords:** hydrogels; swelling; thermal properties; thermogravimetric analysis (TGA)

## Introduction

Hydrogels show reversible volume phase transitions depending on external stimuli factors such as temperature, solvent composition, ionic strength, pH, electric field, light, etc. These properties made them promising materials in different fields including biotechnology, pharmaceutical, agriculture and industrial applications.[1] The possible applications include metal extraction, wastewater treatment, soft contact lenses, controlled release of drugs, enzyme supports, wound dressing, water managing materials, diapers and agrochemical release. Hydrogels are cross-linked networks of polymers, semi or fully interpenetrating networks of polymers, interpolymer complexes, and core-shell microspheres.[2] In recent years, numeral studies focused on the synthesis and characterization of synthetic polyampholytes.[3] Polyampholytic hydrogels are defined as cross-linked macromolecular networks containing positively and negatively charged repeating units and show very unusual properties from those of the parent polyelectrolyte polymers, which contain the same charge. Significant attention was given to synthetic polyampholytes due to their widespread applications as selective sorbents, membranes, flocculants, drug carriers, etc. The synthetic polyampholytic gels have a resemblance to proteins prompted them to use in the modeling of biological processes. In ampholyte hydrogels, apart from the hydrogen bondings and hydrophobic interactions, the coulombic attraction between oppositely charged monomer units, play a crucial role to determine their phase transitions that leads to a different chain configuration within the network structures. Ogawa et al.[4] designed a biochemomechanical polyampholytic gel system consisting of NIPAM, acrylic acid (AAc), and 1-vinylimidazole (VIM) units

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that undergo swelling and shrinking changes due to the electrostatic interaction between the opposite charges in the network. Takeoka et al.[5] have described that polyampholytic gels undergo a discontinuous phase transition depending on the interactions between its repeating units in the gels.[6] We prepared polyampholytic poly (Acrylic acid-Acrylamide) hydrogels. Since the entire properties of gels depend on their swelling characteristics,[1] in this work, we studied in detail the swelling/diffusion profiles of polyampholytic hydrogels in different swelling media including various pH, temperatures and salts.

## Experimental Part

### Materials

The Acrylic acid (AAc), Acrylamide (AAm), N,N-methylene bisacrylamide (MBA), Azobisisobutyronitryronitrile (AIBN) were all purchased from Aldrich Chemical Co. All the chemicals and reagents were used as received. Distilled water was used for preparing the solutions. To this monomer/polymer reaction mixture, cross linker and initiator were added sequentially. As soon as the (initiator) was added to the polymerization system, the polymerization started immediately. However, in order to get a complete network formation in the hydrogels, the polymerization was continued for 4 h at 60 °C. The gel obtained was transferred into a distilled water bath in order to leach out the unreacted chemicals. This leaching process was continued for three days by changing the water every 5 h and the swollen hydrogel was cut into small discs. Finally, the gels were dried completely in a hot air oven at 60 °C.

### Synthesis of Polyampholytic Poly (AAc-AAm) Hydrogels

The polyampholytic poly (AAc-AAm) hydrogels with various ratios of AAm/AAc, like 1/1, 0.5/1, 0.25/1, 1/0.5 and 1/0.25 were synthesized by free-radical polymerization method in 60 °C and 4 h by A.I.B.N.

### Swelling Studies

The completely dried and accurately weighed polyampholytic poly (AAc-AAm) hydrogel was immersed in 50 mL of swelling medium at 25 °C until the swelling equilibrium was attained (approximately for one day). The weight of the swollen gel ($W_e$) was determined after removing the surface water gently with tissue paper. $W_d$ is the dry weight of the hydrogel.[7]

$$Swelling\% = \frac{W_e - W_d}{W_e} \times 100$$

### Characterization of Polyampholytic Poly (AAc-AAm) Hydrogels

FT-IR spectrum was recorded on Nicolt 520 FT-IR spectrometer. The structures of polyampholytic poly (AAc-AAm) hydrogels were characterized by FTIR. Thermogravimetric analysis (TGA) of the hydrogels was performed using a NETZCH Thermogravimetric analyzer. Samples were run from 30 to 600 °C with a heating rate 10 °C/min under nitrogen atmosphere.

## Results and Discussion

### Preparation of Polyampholytic Hydrogels

As previously reported,[7] the formation of polyampholytic poly (AAc-AAm) hydrogel proceeds according to the simultaneous free radical copolymerization mechanism. In detail, the polymerization reaction starts with the reaction of the initiator, which carries unpaired valence electrons that are responsible for producing radicals. These free radicals are responsible for initiating the polymerization, copolymerization, and simultaneous crosslinking process of poly (AAc-AAm) to form highly crosslinked network hydrogels. The formed networks contain covalent bonds as well as ionic bonds. The covalent bonds in the hydrogels are responsible for maintaining the three-dimensional structure of hydrogel permanently and the ionic bonds provide a much higher mechanical strength and pH sensitivity of the hydrogels.

Over the past two decades, it was noticed that the physical-chemical characteristics of

*Table 1.*
Preparation condition and swelling properties of the polyampholytic poly (AAc-AAm) hydrogels.

| Hydrogel code (the ratio of AAm/AAc) | (AAc) (mol/cm$^3$) | (AAm) (mol/cm$^3$) |
|---|---|---|
| 1:1 | 0.35 | 0.35 |
| 0.5:1 | 0.35 | 0.17 |
| 0.25:1 | 0.35 | 0.08 |
| 1:0.5 | 0.17 | 0.35 |
| 1:0.25 | 0.08 | 0.35 |

Reaction conditions: [AIBN] = $2 \times 10^{-3}$ mg; [MBA] = $1 \times 10^{-3}$ mg; Temperature = 25 °C; Distilled water = 1.5 mL.

hydrogels are influenced by specific environmental parameters such as pH, temperature, solvent, electric field, light intensity and wavelength, ionic strength and nature of ions in the swelling medium. Therefore, in this study we investigated the detailed swelling characteristics of the polyampholytic poly (AAc-AAm) hydrogels.

### FT-IR Analysis of Poly Ampholyticpoly (AAc-AAm) Hydrogels

For Fourier transform infrared (FT-IR) spectroscopy was used to confirm the structure of polyampholyte hydrogels. The Spectra analysis of polyampholytic poly (AAc-AAm) hydrogels are given in Table 2.

### Thermogravimetric Analysis of Polyampholytic Poly(AAc-AAm) Hydrogels

The thermogravimetric analysis (TGA) results of polyampholytic poly (AAc-AAm) hydrogels are given in figure 2. By comparing the ratios of 1–0.25, 1–1 and 0.25–1, it is concluded the thermal stability in the ratio 0.25–1 is higher than the others, since it has made a better hydrogen bonding and enjoys higher order. In the ratio 1–1, the order of hydrogen bonding has been disturbed then it has started an early degradation. In the ratio 1–0.25, it has the least thermal stability.

### Effect of Temperatures on Swelling Behavior of Polyampholytic Poly (AAc-AAm) Hydrogels

In the same way, the swelling capacity of polyampholytic poly (AAc-AAm) hydrogels in distilled water was investigated at different temperatures (Figure 4). We found that the equilibrium swelling ratio of polyampholytic poly (AAc-AAm) hydrogels increased with an increase of temperature from 25 °C to 50 °C and from 50 °C to 70 °C. The swelling ratios of the hydrogels increased with increasing temperature. The hydrogels exhibited a temperature responsive swelling behavior due to the association/dissociation of the hydrogen bonding of the -COO$^-$ groups in the AAc, and the $-NH_3^+$ groups in the AAm of the hydrogels. From these results, it is surmised that the average distance between these fixed ions is long. Because there were no observation of contraction by the electrostatic interaction between the amine group and carboxyl group which were ionized in poly (AAc-AAm) hydrogel, when the average distance between fixed ions is long, it is known that the influence of counter ion osmotic pressure due to the Donnan effect becomes remarkable.[2] From this study, it was obvious that the swelling behavior of gels was dependent on the temperature of the swelling medium and higher swellings occurred at higher temperatures (Figure 3).

### Effect of pH on Swelling Behavior of Polyampholytic Poly(AAc-AAm) Hydrogels

The prepared polyampholytic poly (AAc-AAm) hydrogels contain amine and carboxylate groups in their interpenetrated networks. Among these groups, the carboxylate group dissociation or swelling/interaction is highly dependent on the pH of the medium.[9] We investigated the effect of pH on the swelling behavior of the polyampholytic poly (AAc-AAm) hydrogels by using buffer solutions with pH values of 2, 7 and 12. In the case of the polyampholytic poly (AAc-AAm) hydrogel, the amine group always shows the cationic charge in region acidic (pH = 2) and the water content increased a little due to ionic repulsion. In addition, since Cl$^-$ ions that can freely move exist in the solution, and the Donnan osmotic pressure based on the Donnan effect between free

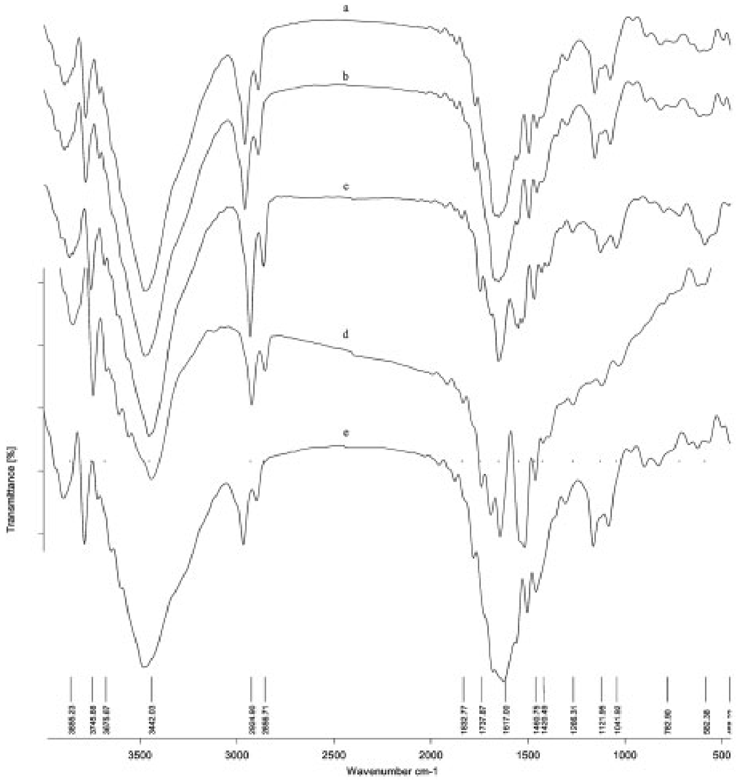

***Figure 1.***
FT-IR spectra of polyampholytic poly (AAc-AAm) hydrogels in various ratios of AAm/AAc**:** a:1–0.25, b: 1–0.5, c:1 -1, d: 0.5–1, e: 0.25–1.

ion ($Cl^-$) ion and fixed ion (cationic amine group) in AAm occurs, the water content of hydrogel increased. Donnan effect is greatly dependent on ionic strength of the external solution. In the case of polyampholytic poly (AAc-AAm) hydrogel, the carboxyl group of AAc does not dissociate into the anion at pH = 2, but the amine group of AAm shows the cationic charge at pH = 2. As a result, the hydrogel shows increase of water content due to repulsion by electrostatic interaction and swelling by the Donnan osmotic pressure as the hydrogel has the cationic charge. In pH = 7, since the carboxyl group of AAc and the amine group of AAm have the electric charge, the water content of the hydrogel increases due to expansion by electrostatic interaction.

In pH = 12, polyampholytic poly (AAc-AAm) hydrogel shows the anionic charge, because the amine group of AAm does not show the cationic charge mostly and the carboxyl group of AAc dissociate. Among

***Table 2.***
Spectra analysis of polyampholytic poly(AAc-AAm) hydrogels.

| ($cm^{-1}$) Wave number | Functional groups |
|---|---|
| 3442 | C-stretch H' O-stretch H |
| 2924 | N-H stretch |
| 1730 | stretch C = O |
| 1640 | bendN-H |
| 1462 | stretchC-N |
| 1350 | stretchC-O |
| 950 | out of plate bendO-H |
| 782 | out of plate bendN-H |

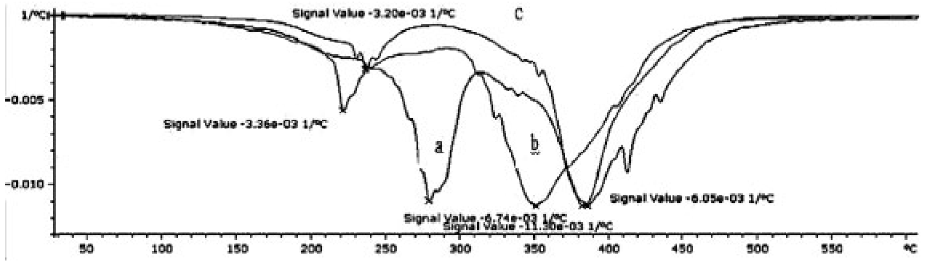

***Figure 2.***
TGA curves of polyampholytic poly (AAc-AAm) hydrogels in ratios of AAm/AAc; (a) 1:0.25, (b) 1:1, and (c) 0.25:1.

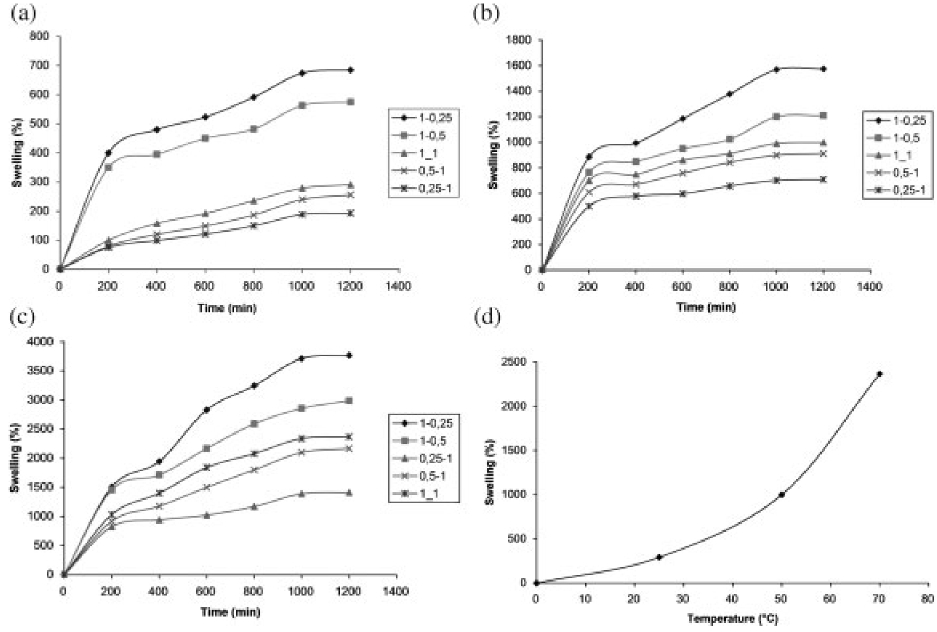

***Figure 3.***
The swelling capacity of polyampholytic poly (AAc-AAm) hydrogels in various ratios of AAm/AAc at different temperatures; (a) 25 °C, (b) 50 °C, and (c) 70 °C, (d) swelling behavior of polyampholytic poly (AAc-AAm) hydrogels with 1:1 ratio of AAm/AAc at different temperatures.

these Functional groups, the carboxylate group dissociation or swelling/interaction is highly dependent on the pH of the medium.[9] Therefore, the water content of poly (AAc -AAm) hydrogel increases remarkably based on repulsion by electrostatic interaction between the carboxy group and swelling by the Donnan osmotic pressure due to the Donnan effect between free ion ($Na^+$) and fixed ion (carboxy group of AAc). The results are shown in Figure 4.

## Effect of Salts on Swelling Behavior of Hydrogels

It is widely known that the swelling degree of uniformly charged polyelectrolyte decreases enormously upon addition of salts. In contrast, polyampholytic poly (AAc-AAm) hydrogels can exhibit a unique responsiveness towards brain environment.[10] Table 3 illustrates the effect of salts on the swelling properties of polyampholytic hydrogels. The swelling capa-

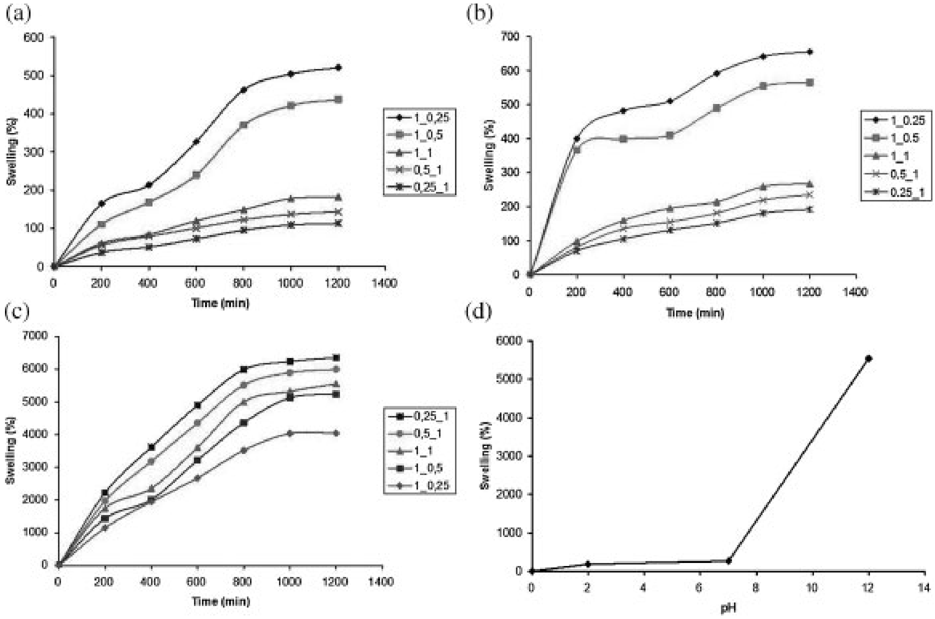

***Figure 4.***
The swelling capacity of polyampholytic poly (AAc-AAm) hydrogels in ratious of AAm/AAc at different pH; (a) 2, (b) 7, and (c) 12,(d) Swelling behavior of polyampholytic poly (AAc-AAm) hydrogels with 1:1 ratio of AAm/AAc at different pH.

city of the poly (AAc-AAm) hydrogels in the presence of salts was changed in this order: LiCl> NaCl> $CaCl_2$> $Na_2SO_4$. The swelling capacity of gels is influenced by the osmotic pressure variation apart from the radius of the ions. In addition, the effect of the salt concentration on the swelling capacity was examined. Figure 5 clearly demonstrates that the swelling of the hydrogels decreased with increasing the concentration of salts. This was attributed to the decrease in expansion of the gel networks, which was caused by the repulsive forces of the counter ions on the polymeric chain shielded by the ionic charge. Therefore, the difference of the osmotic pressure between the gel networks and the external solution decreased with an increase in the ionic strength of the saline concentration.

***Table 3.***
The swelling capacity of polyampholytic poly(AAc-AAm) hydrogels with various ratios of AAm/AAcin different salt solutions.

| Type of salt | Equilibrium swelling ratio | | | | |
|---|---|---|---|---|---|
| | ratios of AAc/AAm | | | | |
| | 1/1 | 1/0.5 | 1/0.25 | 0.5/1 | 0.25/1 |
| LiCl | 65.02 | 41.12 | 34.11 | 112.09 | 168.85 |
| NaCl | 58.24 | 35.41 | 27.23 | 102.25 | 152.91 |
| $CaCl_2$ | 51.65 | 31.01 | 23.01 | 91.01 | 125.30 |
| $Na_2So_4$ | 28.38 | 21.04 | 13.23 | 71.65 | 111.39 |

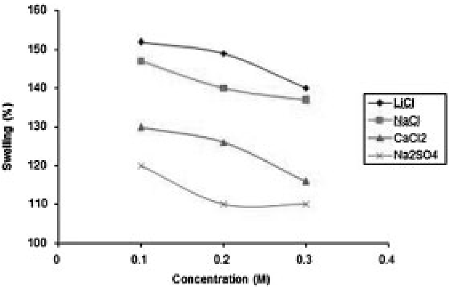

***Figure 5.***
Swelling behavior of polyampholytic poly (AAc-AAm) hydrogels with 1:1 ratio of AAc/AAm in solutions with different salts concentrations.

## Conclusion

In this work, a series of novel polyampholytic poly (AAc-AAm) hydrogels were successfully prepared and their swelling properties were investigated. These hydrogels were prepared in various ratios of AAc/AAm. Hydrogels with higher amounts of acrylamide show maximum swelling capacity. Moreover the higher swelling capacity in hydrogels were obtained at temperature of 70 °C, pH = 12 and in LiCl salt solution.

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