Thermoresponsive Crosslinked Ampholytic Terpolymers (CATs): Effect of Salt Concentration on Porosity, Thermal, Mechanical, Electrical Conduction, and Imprintable Properties

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Introduction

Ampholytes are compounds which can act either as acid or as base in dilute media and have at least two pKa values; at least one of which is acidic and at least one is basic. Polyampholyte hydrogels are prepared by polymerization of positively and negatively charged monomers and show characteristic properties of their homopolymers when these monomers are located in the same polymer chain. This is an advantage regarding use as selective sorbents/templates for drug molecules, biomolecules, charged species, toxic metal ions, dye molecules, surfactants, etc. [1-7]. Synthetic and natural hydrogels are commonly selected for preparing polyampholyte hydrogels [8-19]. Synthetic polymers with ionic side groups, such as poly(acrylic acid), polyethyleneimine, poly (methacrylic acid), poly (3-acrylamidopropyltrimethylammonium chloride), poly (dimethylaminoethyl methacrylate), poly (vinyl-2-aminoethoxyethyl ether), poly (acryloyloxyethyltrimethylammonium chloride) and poly (2-acrylamido-2-methylpropanesulfonic acid), and natural polymers such as gelatine, chitosan, gellan gum, hyaluronic acid, hydroxyethyl cellulose and dextran are widely used for preparing polyampholyte hydrogels [10-20]. Polyampholytes also called polyzwitterions contain both anionic, cationic, and uncharged monomer groups whereas polyelectrolytes include anionic or cationic groups. So, polyampholytes can be regarded as terpolymers because of the presence three different repeated units on the polymer backbone [21]. Besides, anionic and cationic groups in polyampholyte structure may form recognition holes for species to be entrapped. From this aspect, polyampholytes are identified as molecularly imprinted polymers (MIP) [22-23]. Polyelectrolytes possess extended conformations in dilute, saltfree, aqueous

Abstract

Intra- or inter-chain dipole–dipole interactions between opposite charges cause collapse of the structure in polyampholyte hydrogels formed by using ionic monomers with different charges. Furthermore, these interactions are unavoidable as in the case of clamped polymer chains. In this work; synthesis of crosslinked ampholyte terpolymers (CATs) with components of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), (3-acrylamidopropyl)-trimethyl ammonium chloride (APTMACl), and 2-hydroxyethyl methacrylate (HEMA) was realized. The aim was to observe how NaCl electrolyte added into the medium during synthesis changed the physical properties of the CATs. CATs were synthesized with solution polymerization and were named as CAT-0, CAT-0.5, CAT-1.0, and CAT-1.5, which refers the maximum salt concentration used during the synthesis. The characterization of the CATs was done with IR spectroscopy, DSC analysis, SEM-EDX analyses, and mechanical tests, conductive and swelling studies. Pore sizes are 87-129 µm, 101-126 µm, 47-73 µm, and 36-61 µm for CAT-0, CAT-0.5, CAT-1.0, and CAT-1.5 samples, respectively. The CAT-0, CAT-0.5, and CAT-1.0 hydrogels break with forces of 3.85 N, 4.60 N, and 4.60 N, while the CAT-1.5 hydrogel fractured after a force of magnitude 6.95 N was applied. CATs swelled in NaCl solutions with concentration range between 0.5 M and 3.0 M, solutions with pH 1.1 and pH 7.4, and deionized water, and electrical conductivity of the CATs was calculated. The CATs swollen in acidic medium show the highest conductivity values of 4.04x10^{-4} ± 0.44x10^{-5} S cm^{-1}. T_g values were determined as 300 °C and 325 °C for CAT-0 and CAT-1.0 hydrogels, respectively. In light of results found, CAT hydrogels are semi-conductive polyampholyte hydrogels with enhanced mechanical properties and able to respond to surrounding environmental changes like ionic strength, temperature, and pH. The CATs could be used as support materials for mainly drug or biomolecule release systems, as biosensors and for biotechnological applications and as imprintable gel/dialysis membrane for removal of excess electrolytes such as Na^+ and Cl^- due to their features mentioned above.

Keywords: Polyampholyte; Thermoresponsive Hydrogel; Conductive Gel; Imprintable Gel; Drug Release; Dialysis
solution media as a result of repulsions of like charges and according to this, hydrodynamic volumes of polyelectrolytes and solution viscosities are increased [24]. On the other hand, the addition of low molecular weight electrolyte such as NaCl, KCl salts or changes in the solution pH screens the repulsive electrostatic forces, and the polyelectrolyte coils shrink. This conformational change, known as “polyelectrolyte effect”, was defined by Fuoss [25-28]. It is known that polyelectrolyte hydrogels demonstrate both polyelectrolyte and antipolyelectrolyte behavior depending on the salt concentration and pH of the solution in contact [29]. The most characteristic feature of polyelectrolytes is the possibility of intramolecular electrostatic interactions of fixed charges such as carboxylate and ammonium groups which leads to pseudo-neutral behavior and globular structures at the isoelectric pH [30]. In other words, these interactions lead to both collapse and aggregation of the polymer chains [31-34]. So, these groups act as ionic crosslinks and cause insolubility for noncrosslinked polyelectrolytes. The terpolymer sequence is the principal parameter which can be applied during polyelectrolyte synthesis and can be controlled by the intramolecular electrostatic interactions of fixed charges. For this, neutral monomers such as acrylamide or 2-hyroxethyl methacrylate monomers are generally inserted between charged groups (Scheme 1).

More relaxation of chains may be ensured by changing the amount of such neutral monomers; in other words, electrostatic interactions between the charged groups could prevail over pH, ionic strength, and temperature of the medium. Specific species (surfactants) are the other relevant variables for chain relaxation after synthesis.

The influence of the electrolyte added to the synthesis medium on polyelectrolyte properties of the crosslinked ampholyte terpolymers (CATs) is the main interest of this article. With this aim, different amounts of NaCl were added to the polymerization medium to prevent electrostatic interactions between oppositely charged groups lying along the main chains. 2-acrylamido-2-methylpropane sulfonic acid (AMPS), (3-acrylamidopropyl)-trimethyl ammoniumchloride (APTMACl), and 2-hydroxyethyl methacrylate (HEMA) were selected as ionic and neutral monomers, respectively. In this way, an attempt was made to renew collapsed polyelectrolytes by interaction of –SO\(_3\) groups in AMPS with Na\(^+\) ions and of –NH\(\equiv\) groups in APTMACl with Cl- ions.

The characterization of the CATs prepared in cylindrical shapes was verified with IR spectroscopy, DSC analyses, mechanical tests, SEM-EDX analyses, swelling studies by weighing, and electrical conduction studies.

### Synthesis of the CATs

Four CAT hydrogels (CAT-0, CAT-0.5, CAT-1.0, CAT-1.5) were synthesized by using AMPS, APTMACl, and HEMA monomers. PEGDAG (poly (ethyleneglycol diacrylate), Mn=575 g mol\(^{-1}\)) was chosen a flexible crosslinker (Table 1). CATs with different NaCl composition were prepared as follows: monomers (AMPS, 0.882 g in 2 mL of deionized water (DW), APTMACl, 1.1 mL, HEMA, 2 mL) and 1.3 mL of PEGDAG solution (1% v/v in alcohol) were vortexed. The accelerator TEMED (N,N,N,N’-tetramethylenediamine) was added.

<table>
<thead>
<tr>
<th>Hydrogel</th>
<th>(n_0)/n (_T)</th>
<th>(n_{\text{HEMA}})/n (_T)</th>
<th>(n_{\text{PEGDAG}})/n (_T)</th>
<th>(n_{\text{NaCl}})/n (_T)</th>
<th>(n_{\text{TEMED}})/n (_T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAT-0</td>
<td>25</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>CAT-0.5</td>
<td>25</td>
<td>50</td>
<td>1</td>
<td>0.5</td>
<td>2.30</td>
</tr>
<tr>
<td>CAT-1.0</td>
<td>25</td>
<td>50</td>
<td>1</td>
<td>1.0</td>
<td>2.30</td>
</tr>
<tr>
<td>CAT-1.5</td>
<td>25</td>
<td>50</td>
<td>1</td>
<td>1.5</td>
<td>2.30</td>
</tr>
</tbody>
</table>

\(n_0\): AMPS+APTMACl+HEMA
\(n_T\): AMPS or APTMACl
TEMED: 400 μL

Table 1: Percent composition by mole of the CATs
tetramethylethylenediamine, 400 µL) was added and mixed before degassing for 20 min with N2. Then, 0.16 g of KPS (potassium persulfate) was added to this solution and vortexed. Then, 0, 0.25, 0.5 and 0.75 g of NaCl were used to prepare CAT-0, CAT-0.5, CAT-1.0, and CAT-1.5, respectively. The amount of NaCl could not be increased due to insolubility of the salt. After salt was added and mixed, solution was transferred to plastic straws and allowed to react for at least 24 h at 25 °C. Finally, the long cylindrical hydrogel samples were cut into small pieces (4–5 mm in length) and placed in deionized water to remove unreacted species. DW was replaced every day for 7 days. Wet gels were dried in air and a vacuum, and stored.

**FT-IR Analysis**

FT-IR spectra of all CATs were obtained using a Perkin Elmer Spectrum 100 to observe the structural differences between the CAT-0 and CAT-1.5 samples. Spectra were taken in the range of 650 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

**SEM-EDX Analysis**

SEM images and EDX graphs were obtained using a LEO-MODEL 440 equipped with an Energy Dispersive System X-Max detector. Surfaces and cross-sections of the CAT-0, CAT-0.5, CAT-1.0, and CAT-1.5 hydrogels were coated with a 30 nm layer of AuPd (80%-20%) alloy.

**Mechanical Analysis**

The compressive tests of the hydrogels were assessed on a universal testing machine (SHIMADZU AG-XD 50kN) at room temperature. The cylindrical wet hydrogels (3 mm diameter and 4 mm thickness, swollen in deionized water for 24 h) were set on the lower plate and compressed by the upper plate. During the test, the compression rate was set as 0.5 mm/min and each test was repeated three times and the mean value was reported.

**Thermal Analysis**

The DSC Perkin Elmer Diamond instrument was used for the thermal characterization of the CAT-0 and CAT-1.0 hydrogels. Thermograms were obtained at the rate of 10 °C/min and in the range of 25-550 °C.

**Swelling Studies**

The clean, dried CAT hydrogels were submerged in deionized water or acidic-neutral solutions at 37 °C for kinetic swelling studies. The weights of the wet gels were measured at various times previously determined. pH-sensitive swelling studies of the CATs were done using solutions with pH values of 1.0 to 13.0. Ionic strength-sensitive swelling studies were completed in solutions of pH 1.1, pH 7.4, and DW with ionic strength, I = 0.1-0.25-0.5-1.0-2.0-3.0 M mol dm⁻³ (adjusted by NaCl) at 37 °C. Effect of temperature on swelling behaviors of the CATs was examined by changing the temperature of media ranging from 25 to 85 °C in DW for 24 h.

**Conductivity Studies**

Electrical resistance of the CATs swollen in DW, pH 1.0, pH 7.0, and salt solutions was measured with a multimeter (BM-869s) by using copper strips. Then, self-conductivity values of the wet CATs were calculated.

**Results and Discussion**

**FT-IR Analysis**

To investigate the structural analysis, the spectra of the CAT-0 and CAT-1.5 were taken and are comparatively presented in Figure 1a. The wide band in the range 3700-2800 cm⁻¹ comes from O-H stretching vibrations in the CATs spectra due to hydrogen bonds which occur between the monomers. The peaks at 1452 cm⁻¹ and 1478 cm⁻¹ signal –NH₄⁺ groups of APTMACl. The characteristic –SO₃⁻ band of AMPS was present at 1154 cm⁻¹. Further, peaks at 1718 cm⁻¹, 1648 cm⁻¹, and 1547 cm⁻¹ were assigned to amide I (C=O strength) and amide II (N–H strength), arising from AMPS and APTMACl. Peaks at 800 to 1100 cm⁻¹ are due to –C–N bonds. Small peaks at about 1387 cm⁻¹ may be attributed to –CH₃ vibrations. As shown in Figure 1a, there is no difference in the spectra of CAT-0 and CAT-1.5 samples. The same spectra were obtained for CAT-0.5 and CAT-1.0.
SEM-EDX Analysis

To investigate the morphology changes originating from different concentrations of salt, SEM micrographs of the CATs are shown in Figure 2. SEM micrographs of the samples were taken both from the top and side to observe porosity in the hydrogels in more detail. As can be seen from the SEM micrographs taken from different regions, porosity and pore sizes of the hydrogels changed as the amount of NaCl used in synthesis increased. The order of pore sizes are 87-129 µm, 101-126 µm, 47-73 µm, and 36-61 µm for CAT-0, CAT-0.5, CAT-1.0, and CAT-1.5 samples, respectively. On the other hand, it was concluded that both pore size and porosity decreased by increasing the amount of salt added during synthesis. The polymerization reactions of hydrophilic monomers are exothermic reactions, while bulk polymerization which proceeds very rapidly could result in different structures [35]. In this study, ionic components added to the synthesis medium played an important role in rearrangement of polymer chains and led to more homogeneous and less porous structure. These evaluations could be explained by the formation scheme of the CATs. Decreasing the porosity causes more compact structure which agrees well with mechanical test results. Additionally, all CATs have smooth and uniform surface morphology.

In order to confirm the presence of Na⁺ ions in the CATs, EDX patterns are also inserted into Figure 2. The EDX spectrum shows the presence of carbon, oxygen, nitrogen, and sulfur that correspond to elements present in the polyampholyte gel composition. C, O, N, and S peaks also demonstrate the presence of AMPS, APTMACi, and HEMA. Meanwhile, it was realized from these results that there are no sodium ions in the synthesized CAT-0.5, CAT-1.0, and CAT-1.5 samples. All of the Na⁺ and Cl⁻ ions were removed from the hydrogels during washing studies with deionized water over one week.
Mechanical Analysis

To investigate the effect of salt concentration on performance of the CAT hydrogels, mechanical tests were evaluated at room temperature and compression-displacement graphs of the hydrogels are presented in Figure 3.
As seen from Figure 3, all CAT hydrogels preserved their physical integrity up to loading with a certain force and again they disintegrated slowly and gradually after a certain force value was applied. The CAT-0, CAT-0.5, and CAT-1.0 hydrogels break with forces of 3.85 N, 4.60 N, and 4.60 N, while the CAT-1.5 hydrogel fractured after a force of magnitude 6.95 N was applied. In other words, CAT-1.5 hydrogels are mechanically stronger than the other samples. When the porosity of the hydrogels was increased, mechanical strength was weakened [35-36]. This result is consistent with the SEM observations. In more porous gels, the ability to absorb forces is reduced when any force is applied as the gel fraction of the total mass reduces and as a result the gel disintegrates.

**Thermal Characterization**

To investigate the effect of the concentration of salt on glass transition temperatures ($T_g$) of the CAT hydrogels, DSC thermograms of the CAT-0 and CAT-1.0 hydrogels were taken and are presented in Figure 4. DSC curves were recorded in the range of 0 (or 10)-550 °C and the glass transition temperatures of the hydrogels were determined as 300 °C and 325 °C for CAT-0 and CAT-1.0 hydrogels, respectively. Transition from a porous to less porous structure of the hydrogel caused a rise in $T_g$ values.
Swelling Studies of the CATs

The percent swelling degrees of the CATs (S_t%) were calculated and S_t-t curves of the CATs are illustrated in Figure 5. It can be said that the equilibrium swelling time is about 20h in solution from the swelling curves of the CATs.

Figure 5: Swelling curves of the CATs in acidic and neutral medium
\( \circ \); CAT-0, \( 
\quad \square \); CAT-0.5, \( 
\quad \triangle \); CAT-1.0, \( 
\quad \blacktriangle \); CAT-1.5.

The percent equilibrium swelling degrees of the CAT hydrogels are close to each other in both media. Se%, which represents maximum equilibrium swelling degree, of all CATs are about 400% in both media; in other words, CATs absorb 4 g solution per g dry gel.

As can be seen from the curves, anionic and cationic groups in the hydrogels contributed to swelling of the hydrogels to the same degree. Changes in the environment of ionic gels could be caused to some different behaviors of the gels, i.e. swelling, deswelling, bending, orientation, and degradation. So, the S_e%-pH graphs of the CATs were constructed and are shown in Figure 6.

Figure 6: The swelling profiles of the CAT hydrogels as a function of pH
\( \Delta \); CAT-0, \( 
\quad \bigcirc \); CAT-0.5, \( 
\quad \blackbox \); CAT-1.0, \( 
\quad \blacktriangle \); CAT-1.5.

It was seen that the CATs have pH-sensitive swelling behavior due to the dissociation of sulfonic groups (-SO_3-) of PAMPS where charge varies with pH. The hydrogels exhibited pH-sensitive swelling behavior with maximum swelling at pH 12. The pK_α of PAMPS is 2.0-2.3 and it is estimated that swelling degrees will increase. The compact structure of the CATs could prevail after pH 11 due to the increase of –OH- ions in the medium. However, Se% values of all CAT hydrogels are close to others in the pH range 1 to 11. It was determined that these values became a little more differentiated at pH 11 and 12. The reason for the lack of increase is that PAMPS and PAPTMACl hydrogels are in a severely collapsed conformation in the pH range of 1-12 [37-38]. Keeping the mole ratios of both ionic monomers high (n_m/n_T%= 25) encourages the formation of this compact structure. All hydrogels disintegrated at pH 13 and so, swelling experiments were ended.

Polyampholyte hydrogels could show swelling-deswelling behaviors when the ionic strength of the medium is changed. Ions present in the medium such as Na^+, Cl^-, Ca^{2+}, SO_4^{2-}, and K^+ change the osmotic pressure inside the hydrogel by interacting with ionic groups of the hydrogel. This causes swelling degrees of the hydrogels to change. Meanwhile, drug molecules, DNA or RNA biomolecules
entrapped within the hydrogel are easily released out of the hydrogel. With this aim, equilibrium studies were completed in salt solutions (NaCl) which have concentrations between 0.1 mol dm\(^{-3}\) and 3.0 mol dm\(^{-3}\) and were prepared with solutions of pH 1.1 and pH 7.4 as solvent. S\(\%\)-I graphs were constructed and are shown in Figure 7.

**Figure 7:** Graphs of ionic strength response of the polyampholyte hydrogels at 37 °C.
\(\Delta\); CAT-0, \(\odot\); CAT-0.5, \(\square\); CAT-1.0, \(\blacklozenge\); CAT-1.5.

It was seen that equilibrium swelling values are changed by raising the ionic strength; in other words, synthesized CAT hydrogels have polyampholyte character. The addition of electrolyte resulted in the disruption of electrostatic interactions by shielding oppositely charged monomer units allowing the CATs to swell (anti-polyelectrolyte effect) [39-41]. This shielding gains significance more and more after this range with increased concentration of the salt solution and the number of water molecules entering the gel decreases and gel deswells. If there is a need to express it thermodynamically, osmotic pressure inside the gel and the number of ions within the gel increase as the electrolyte concentration is increased. Osmotic pressure inside and outside the hydrogel must be equalized for a swollen gel to be balanced thermodynamically; in other words, the variation in free enthalpy should be zero during swelling. Then, S\(\%\) value of the hydrogel decreases after a certain concentration of salt solution.

Another remarkable point on the S\(\%\)-I graphs is that the CAT-0 hydrogels with higher porosity swell less than CAT-0.5, CAT-1.0, and CAT-1.5 hydrogels with lower porosity. Swelling of a gel increases when the porosity in the gel is increased, but here, the opposite situation is the case for two media. This can be explained by the molecular imprinting in the character of the polyampholytes [42-43]. Na\(^+\) and Cl\(^-\) ions added to the reaction medium during synthesis behaved as templates inside the CAT-0.5, CAT-1.0, and CAT-1.5 hydrogels. Consequently, prepared CAT-0.5, CAT-1.0, and CAT-1.5 polyampholytes (host) are also molecularly imprinted polymers (MIPs) for NaCl electrolyte (guest).

Another factor which affects swelling degrees of polyampholyte hydrogels is the temperature of the medium. So, S\(\%\)-t graphs were plotted for a range of 25-85 °C and are shown in Figure 8.

**Figure 8:** Influence of temperature on swelling-deswelling of the CATs
\(\Delta\); CAT-0, \(\odot\); CAT-0.5, \(\square\); CAT-1.0, \(\blacklozenge\); CAT-1.5.

The swelling degrees of the CATs are influenced by temperature in deionized water as proven from the profiles in Figure 8. All polyampholyte hydrogels are able to attain the highest S\(\%\) degrees at 35 °C temperature, which is very close to body temperature. Electrostatic interactions between opposite groups in polyampholytes could be overwhelmed at this temperature. As the temperature
increases, the slightly swollen gel undergoes a volume change after 35 °C, resulting in the shrunken state. This is probably due to the enhancement of hydrophobic interactions in polyampholytes. In other word, CATs synthesized in this study are also temperature-sensitive polyampholytes. This is also an advantage for medical studies, which could be applied to the body such as controlled drug release. These gels could release drug molecules at maximum swelling temperature, i.e. body temperature [44-47].

The increase in $S\%$ values up to 0.5 M concentration of salt solution will contribute positively to their use in these applications because the physiological salt concentration in the body is within this range. The temperature- and ionic strength-sensitive swelling behaviors displayed by CAT hydrogels will be an advantage for swelling-controlled release of drugs or biomolecules.

When hydrogels are used as support matrix for controlled release studies it is important to determine whether the hydrogels are electrically conductive or not. If they have conductive properties, they should be estimated because electric stimulation may ease the escape of drug molecules which are trapped physically or chemically within the hydrogel [20,48-51]. So, electrical conductivity experiments were also done for CAT polyampholytes. The self-conductivity of the CATs was investigated with the aid of a multimeter. With this aim, Cu conductive strips were attached to the dry and swollen gels (0.4 x 0.2 cm in size) in DW, pH 1.0, pH 7.0, 0.5 M NaCl, 1.0 M NaCl, and 3.0 M NaCl solutions and the resistance of the gels were measured with a multimeter. $\sigma$ values of the CATs were calculated according to equation:

$$\sigma = \frac{l}{AR}$$

$\sigma$ is self-conductivity (S cm$^{-1}$), $l$ is the thickness of the gel sample; $A$ (cm$^2$) is the area of contact, and $R$ (S$^{-1}$) is the resistance of the gel. The effect of swelling medium on conductivity of the CATs is illustrated in Figure 9a. It is understood from column graphs in Figure 9a that electrical conductivities of swollen CATs in acidic, basic, and neutral media are about $10^{-4}$ S cm$^{-1}$; in other words, CATs prepared in this study are semi-conductive polyampholytes, while dry CATs are not conductive. Conductivity values and the standard deviations of the wet CATs swollen in different media are presented in Table 2. The highest conductivity was measured for acidic medium and this value is between $5.55 \times 10^{-4}$ ± $2.98 \times 10^{-5}$ S cm$^{-1}$ and $4.04 \times 10^{-4}$ ± $0.44 \times 10^{-5}$ S cm$^{-1}$. With the aim of trialing the electrical conductivity of the CATs swollen in acidic medium, the setup shown in Figure 9b, was prepared. As seen in the photograph, a CAT-1.5 sample prepared by cutting to cylinder geometry allows electrical current to pass. The same response was obtained for all CATs.

<table>
<thead>
<tr>
<th>Medium</th>
<th>CAT-0</th>
<th>CAT-0.5</th>
<th>CAT-1.0</th>
<th>CAT-1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW</td>
<td>$4.20 \times 10^{-6}$ ± $5.21 \times 10^{-7}$</td>
<td>$2.18 \times 10^{-6}$ ± $1.95 \times 10^{-7}$</td>
<td>$3.10 \times 10^{-6}$ ± $2.21 \times 10^{-7}$</td>
<td>$1.80 \times 10^{-5}$ ± $1.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.5 M NaCl</td>
<td>$7.40 \times 10^{-6}$ ± $3.53 \times 10^{-7}$</td>
<td>$5.61 \times 10^{-6}$ ± $2.84 \times 10^{-7}$</td>
<td>$2.59 \times 10^{-7}$ ± $3.61 \times 10^{-8}$</td>
<td>$1.28 \times 10^{-7}$ ± $1.41 \times 10^{-8}$</td>
</tr>
<tr>
<td>1.0 M NaCl</td>
<td>$2.82 \times 10^{-6}$ ± $1.39 \times 10^{-7}$</td>
<td>$7.17 \times 10^{-7}$ ± $2.06 \times 10^{-7}$</td>
<td>$1.75 \times 10^{-6}$ ± $6.02 \times 10^{-8}$</td>
<td>$1.31 \times 10^{-6}$ ± $1.67 \times 10^{-8}$</td>
</tr>
<tr>
<td>3.0 M NaCl</td>
<td>$2.33 \times 10^{-6}$ ± $2.44 \times 10^{-7}$</td>
<td>$1.35 \times 10^{-6}$ ± $6.53 \times 10^{-7}$</td>
<td>$1.61 \times 10^{-6}$ ± $1.74 \times 10^{-7}$</td>
<td>$1.05 \times 10^{-6}$ ± $0.55 \times 10^{-7}$</td>
</tr>
<tr>
<td>pH 7.4</td>
<td>$2.37 \times 10^{-6}$ ± $3.45 \times 10^{-7}$</td>
<td>$2.48 \times 10^{-6}$ ± $1.07 \times 10^{-7}$</td>
<td>$4.60 \times 10^{-6}$ ± $1.39 \times 10^{-7}$</td>
<td>$1.59 \times 10^{-6}$ ± $0.82 \times 10^{-7}$</td>
</tr>
<tr>
<td>pH 1.1</td>
<td>$5.55 \times 10^{-6}$ ± $2.98 \times 10^{-7}$</td>
<td>$4.04 \times 10^{-6}$ ± $0.44 \times 10^{-7}$</td>
<td>$4.18 \times 10^{-7}$ ± $1.01 \times 10^{-8}$</td>
<td>$4.43 \times 10^{-7}$ ± $0.09 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Table 2: Conductivity values of CATs for different media

However, it is not a surprise that all CATs have the highest $\sigma$ values for acidic and salt solutions (3.0 M) because electrical conductivity is increased with H$, Na^+$, and Cl$^-$ ions in medium. The higher $\sigma$ values of CAT-0 sample for both media compared to those of other CAT samples are related to porosity of CAT-0 samples. In light of these findings, the type of electrical conductivity of the CATs is ionic conductivity by ions which are located in pores of the CAT polyampholytes. Conductivity properties of the CATs allow the applications of these polyampholytes to expand further.
Conclusion

In this study, the aim was to investigate whether intra- or inter-chain dipole-dipole interactions between opposite charges are overwhelmed or not by adding both neutral monomers and electrolytes during synthesis. The results determined in the study are summarized as follows:

Increasing salt concentration had the effect of decreasing the size of pores and porosity of the CAT hydrogels. The results of SEM-EDX analyses show that the porosity of the CATs decreases in the following order: CAT-0>CAT-0.5>CAT-1.0>CAT-1.5. Complete removal of Na⁺ and Cl⁻ ions added to the medium from the CAT structure during the gel washing processes was revealed by EDX analysis. CAT-1.5 hydrogels disintegrated under a force of 6.95 N while CAT-0 hydrogels disintegrated under a loading magnitude of 3.85 N. Thermal stability is higher for the CAT-1.0 hydrogels with less porosity compared to CAT-0 hydrogels. CAT-0.5, CAT-1.0, and CAT-1.5 are also molecularly imprinted in character which enables removal of excess NaCl electrolytes in the medium. CATs exhibited the highest swelling degree in salt solution (I=0-0.5 M) and at temperatures (35-37 °C) which are compatible with physiological body fluids. S, values of all CATs are about 4 in physiological body fluids; in other words, CATs absorb 4 g solution per g dry gel. CATs have pH-, temperature-, and ionic strength-sensitive swelling behaviors, and they also have electrical conduction properties. In conclusion, prepared CATs are hydrogels with polyampholyte and MIP character and may be evaluated as semi-conductive hydrogels which could be used for medical applications such as controlled release and dialysis systems.

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References