

# SÍNTESIS Y CARACTERIZACIÓN DE HIDROGELES A PARTIR DE N,N-DIMETILACRILAMIDA Y TELEQUÉLICOS DE 2-OXAZOLINAS

Juan Carlos Rueda<sup>\*a</sup>, Javier Alfredo Cano<sup>a</sup>

## RESUMEN

Se sintetizaron dos series de hidrogeles mediante la polimerización por radicales libres, en medio acuoso, de N,N-dimetilacrilamida (DMAA) y telequéllicos de 2-oxazolinás (MK-10 y MK-32), usando persulfato de potasio (KPS) y N,N,N',N'-tetrametiletilendiamina (TEMED) como sistema de iniciación. Previamente se sintetizaron los telequéllicos de 2-oxazolinás mediante polimerización catiónica por apertura de anillo de 2-metil- (en el caso de MK-10) (ó 2-etil- (en el caso de MK-32))-2-oxazolina (EtOxa) y 2-metoxicarboniletil-2-oxazolina (EsterOxa). Los telequéllicos fueron funcionalizados con grupos vinilos y éster. Se determinó por <sup>1</sup>H RMN que los telequéllicos MK-10 y MK-32 tuvieron grados de polimerización de 9,5 y 20 respectivamente. Se investigó la influencia de la proporción inicial de los monómeros y de la estructura de los telequéllicos en las propiedades de los hidrogeles. Los hidrogeles fueron caracterizados por espectroscopía infrarroja (FTIR), absorción de agua, rendimiento de la síntesis, y análisis termogravimétrico. Se determinó que los hidrogeles sintetizados con el telequéllico MK-10 tuvieron mayor capacidad de absorción de agua que los sintetizados con el telequéllico MK-32. Los grupos éster de los hidrogeles fueron hidrolizados para formar grupos carboxilatos de sodio. Los hidrogeles hidrolizados tuvieron mejor absorción de agua respecto a los hidrogeles no hidrolizados y fueron sensibles al cambio de pH.

**Palabras clave:** Hidrogel, N, N-dimetilacrilamida, telequéllicos, 2-oxazolinás.

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<sup>a</sup> Sección Física, Pontificia Universidad Católica del Perú, Av. Universitaria 1801, Lima, Perú,

\* jrueda@pucep.edu.pe

# SYNTHESIS AND CHARACTERIZATION OF HYDROGELS BASED ON N,N-DIMETHYLACRYLAMIDE AND 2-OXAZOLINE TELECHELICS

## ABSTRACT

Two series of hydrogels were synthesized by free-radical polymerization of N,N-dimethylacrylamide (DMAA) and 2-oxazoline telechelics (MK-10 and MK-32), using potassium persulfate (KPS) and N,N,N',N'-tetramethylethylenediamine (TEMED) as initiator systems. The 2-oxazoline telechelics were previously synthesized by cationic ring-opening polymerization of 2-methyl- (for MK-10) or 2-ethyl- (for MK-32)-2-oxazoline (EtOxa) and 2-methoxycarbonyl-ethyl-2-oxazoline (EsterOxa). The telechelics were functionalized with vinyl and ester groups. It was determined by  $^1\text{H}$  NMR that the telechelics MK-10 and MK-32 had degrees of polymerization of 9.5 and 20 respectively. The influence of the initial monomer ratio and the telechelic structure on the hydrogel properties was investigated. The hydrogels were characterized by Fourier transform infrared spectroscopy (FTIR), water absorption, synthesis yield, and thermogravimetric analysis. It was determined that the hydrogels synthesized with telechelic MK-10 had a higher water absorption capacity than those synthesized with telechelic MK-32. The ester groups of the hydrogels were hydrolyzed to form sodium carboxylate groups. The hydrolyzed hydrogels had better water absorption compared to the non-hydrolyzed hydrogels and were sensitive to pH changes.

**Keywords:** Hydrogel, N,N-dimethylacrylamide, telechelics, 2-oxazolines.

## INTRODUCTION

2-Oxazolines are heterocyclic compounds that polymerize via cationic ring-opening polymerization<sup>1</sup>. The polymerization of these monomers is considered "living," meaning that chain termination or transfer reactions do not occur<sup>2</sup>, thus enabling the production of polymers with predefined degrees of polymerization and functionality<sup>1-3</sup>.

Polymers derived from 2-oxazolines allow the synthesis of different polymeric structures, such as block and graft copolymers, macromonomers, and telechelics<sup>3,4</sup>.

Telechelics are polymers that possess functional groups at the ends of their chains<sup>3,5</sup>.

They can be synthesized, for example, by incorporating these functional groups using the terminator method<sup>3</sup>. This method involves employing a polymerization terminator containing the desired functional group to be incorporated at the end of the polymer chains. Telechelics with vinyl functional groups at their chain ends can function as crosslinking agents and can produce hydrogels<sup>3</sup>.

Hydrogels are cross-linked polymers that have the ability to absorb water due to interactions between water molecules and the hydrophilic functional groups present in their structure<sup>6-9</sup>.

This research presents the synthesis and characterization of hydrogels from the free-radical polymerization of DMAA and telechelic 2-oxazolines.

## EXPERIMENTAL PART

The substances and reagents were used as received or were purified according to the methods described in the literature<sup>5-7</sup>. 2-Methyl-2-oxazoline (98%, Aldrich), *p*-chloromethylstyrene (90%, Merck), and TEMED (98%, Aldrich) were distilled before use. 2-Methoxycarbonylethyl-2-oxazoline (EsterOxa) and 4-vinylbenzylpiperazine were synthesized in previous research<sup>5,6</sup>. DMAA (99%, Aldrich), KPS (99%, Merck), and sodium iodide (99%, Merck) were used as received. Nuclear magnetic resonance (<sup>1</sup>H-NMR) and Fourier transform infrared (FTIR) analyses of the substances used or synthesized were performed using the methods described in the scientific literature<sup>5,6</sup>. Bruker Ascend 500 MHz nuclear magnetic resonance (NMR) spectrometer, 300 MHz for <sup>1</sup>H, deuterated chloroform solvent. Perkin Elmer Frontier Fourier Infrared Spectrometer (FTIR), ATR method, measurement range: 4000 to 400 cm<sup>-1</sup>. Netzch STA 449F3 thermogravimetric analyzer (air, 10°C/minute).

### Synthesis of telechelic MK-32

Telechelic MK-32 was synthesized by ring-opening polymerization of 2-ethyl-2-oxazoline (EtOxa, 2.60 g, 26.3 mmol) and 2-methoxycarbonylethyl-2-oxazoline (EsterOxa, 4.13 g, 26.3 mmol) initiated by 1,4-*trans*-dibromobutene (2.34 mmol) in 12.5 mL of acetonitrile at 78°C for 5.5 hours and terminated with 4-vinylbenzylpiperazine (14.8 mmol) dissolved in 6 mL of acetonitrile, as described in a previous publication<sup>5</sup>.

<sup>1</sup>H-RMN (CDCl<sub>3</sub>): δ: 1.10 (-CH<sub>3</sub>); 3.0 (-CO-CH<sub>2</sub>-CH<sub>3</sub>); 2.60 (-CH<sub>2</sub>CH<sub>2</sub>-COO-); 3.50 (N-CH<sub>2</sub>CH<sub>2</sub>); 3.60 (-O-CH<sub>3</sub>); 3.95 (=CH-CH<sub>2</sub>-); 5.25 y 5.75 (=CH<sub>2</sub>); 5.255 (=CH-CH<sub>2</sub>); 6.7 (Ar-CH=); 7.25-7.4 (H<sub>Ar</sub>).

### Synthesis of Telechelic MK-10

Telechelic MK-10 was synthesized by ring-opening polymerization of the monomers 2-methyl-2-oxazoline (MeOxa) and EsterOxa. In a 100 mL reaction flask, 1.10 g (7.33 mmol) of sodium iodide was mixed with 2.7 mL (19.8 mmol) of 2-EsterOxa and 2.10 mL (24.92 mmol) of MeOxa in 12 mL of acetonitrile under a dry nitrogen atmosphere with constant stirring. Polymerization was initiated by adding 0.50 mL (3.55 mmol) of *p*-chloromethylstyrene (CMS) and heating the reaction mixture to 78°C for 7 hours. After this time, the mixture was cooled to room temperature. Polymerization was terminated with 4.0 g (19.77 mmol) of 4-vinylbenzylpiperazine (VBP), and to deprotonate the telechelic end, the mixture was stirred with 2 g. of potassium carbonate at 20°C for 12 hours. The MK-10 telechelic was purified by precipitation using the chloroform/diethyl ether system.

<sup>1</sup>H-RMN (CDCl<sub>3</sub>): δ: 2.10 (-CH<sub>3</sub>); 2.70-2.95 (-CH<sub>2</sub>CH<sub>2</sub>-COO-); 3.50 (N-CH<sub>2</sub>CH<sub>2</sub>); 3.60 (-O-CH<sub>3</sub>); 4.60 (Ar-CH<sub>2</sub>); 5.30 y 5.80 (CH<sub>2</sub>=); 6.70 (=CH-Ar); 7.10-7.30 (H<sub>Ar</sub>).

### Hydrogel Synthesis

Two series of hydrogels (HGs) were synthesized by free-radical polymerization. In the first series (HGJ-A to HGJ-D hydrogels), DMAA and telechelic MK-32 were used as monomers, and in the second series (HGJ-E to HGJ-H), DMAA and the telechelic MK-10 were used as monomers. Typical procedure (e.g., HGJ-B hydrogel): 0.53 g (5.35 mmol) of DMAA, 0.30 g (0.1 mmol) of MK-32, and 0.0325 g (0.28 mmol) of TEMED were weighed into a beaker and dissolved in 3 mL of deionized water. Dry nitrogen was

bubbled through the mixture for 10 minutes. In parallel, 0.0375 g (0.14 mmol) of KPS was dissolved in 1 mL of deionized water in another beaker. Both mixtures were cooled to 5°C for 10 minutes. The solutions were then quickly mixed, poured into a glass mold, and refrigerated (5°C) for 24 hours. The hydrogel was then washed four times with deionized water at 4-hour intervals to remove any remaining reagents. The hydrogel was then oven-dried at 45°C until a constant weight was achieved. The HGJ-B hydrogel was characterized by FTIR ( $\text{cm}^{-1}$ ): 2918 (C-H, methylene  $\text{CH}_2$ ), 1721 (C=O, ester), 1615 (C=O, amide), 1400 (aromatic carbon  $\text{arC-C}$ ), 1256 (C-N, amide). The other hydrogels were synthesized and characterized similarly.

### Hydrolysis of the hydrogels

Procedure (e.g., HGJ-B): 0.7372 g of dry hydrogel was weighed into a beaker, and 40 mL of 0.1 N aqueous NaOH solution was added. The mixture was allowed to stand for 3 days at room temperature. The hydrolyzed hydrogel was washed with 200 mL of deionized water for 4-hour periods until a neutral pH was obtained. The hydrolyzed hydrogel was named HGJ-BH.

### Water Absorption Test (Q)

A fraction of hydrogel swollen in water at equilibrium at 25°C (Ph) was weighed. The hydrogel was then oven-dried at 40°C until a constant weight was reached (Ps). The degree of water absorption of the hydrogel was calculated using the following equation:  $Q = (\text{Ph} - \text{Ps}) / \text{Ps}$

Where: Q = degree of water absorption of the hydrogel (grams of water per gram of dry hydrogel), Ph = mass of hydrogel swollen in water at equilibrium, and Ps = mass of the dry hydrogel.

### pH Sensitivity Test

A fraction of hydrolyzed hydrogel swollen in deionized water (pH=5.7) at equilibrium was weighed and oven-dried at 45°C until a constant weight. The dried hydrogel was immersed in a buffer solution of a specific pH and allowed to stand for 24 hours. After this time, the weight of the swollen hydrogel at equilibrium was obtained at this new pH. The water absorption of the hydrogel at the different pH levels was compared, and the difference in absorption was interpreted as the hydrogel's sensitivity to pH.

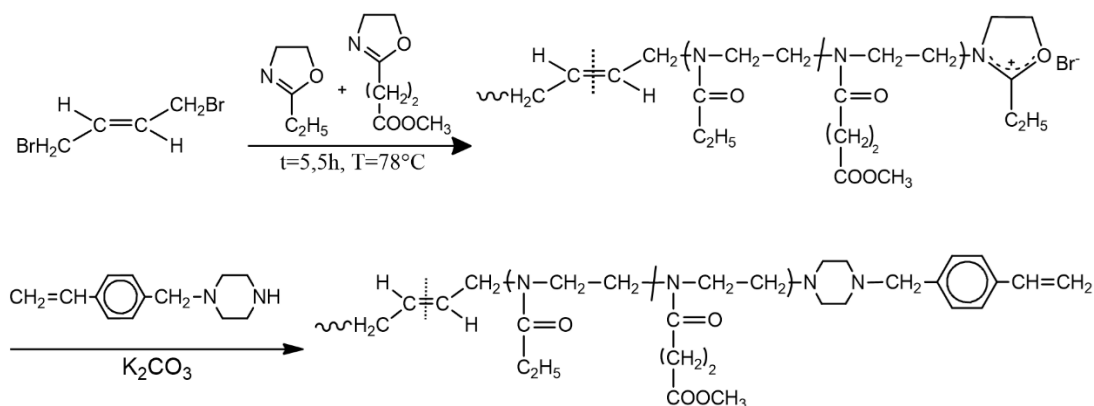
The procedure was performed with different pH values using buffer solutions of pH=2, 4, 8, and 10.

## RESULTS AND DISCUSSION

### Synthesis and characterization of the telechelic polymers MK-32 and MK-10

The telechelic polymers MK-32 and MK-10 were synthesized at 78°C in acetonitrile via the cationic ring-opening polymerization of 2-methoxycarbonyl-ethyl-2-oxazoline (EsterOxa) and 2-ethyl-2-oxazoline (EtOxa) for MK-32, and of EsterOxa and 2-methyl-2-oxazoline (MeOxa) for MK-10. The 2-oxazoline polymerizations are of the "living" type, without chain-transfer or termination reactions, and therefore no interferences were observed. The synthesis of MK-32 was carried out according to a previous publication<sup>5</sup>.

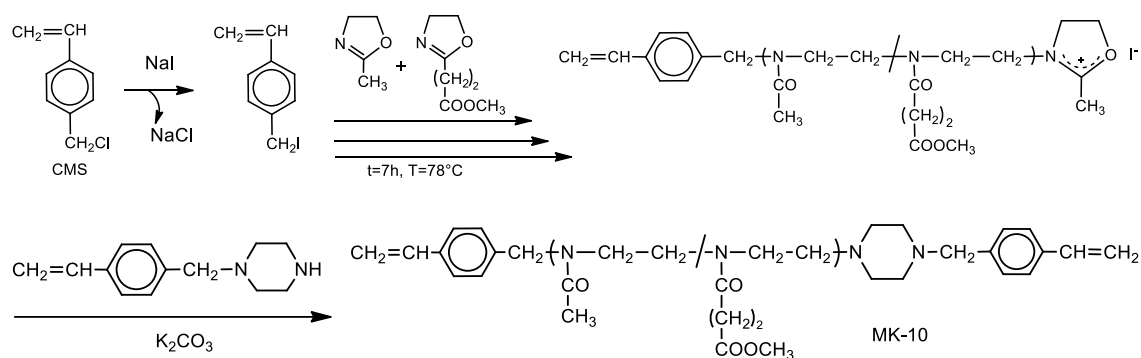
In the case of MK-32, the initiator was 1,4-*trans*-dibromobutene and the terminating agent was 4-vinylbenzylpiperazine (4-VBP). The proposed mechanism is shown in Scheme 1. The DBB initiator, which has double functionality, then allows polymerization to proceed to the right and to the left, and finally the 4-VBP, upon completion of polymerization, introduces the vinyl groups at both ends of the polymer.



**Scheme 1.** Synthesis of the MK-32 telechelic.

MK-32 was a statistical polymer, characterized by  $^1\text{H-NMR}$ : a degree of polymerization of 23 units was obtained, from which a molecular weight of 3564 was calculated. The molar percentages of EtOxa and EsterOxa were 44% and 56%, respectively. This fact is corroborated by literature data which indicates that EsterOxa has greater reactivity than EtOxa<sup>7</sup>. MK-32 was a telechelic polymer, possessing polymerizable vinyl groups at both chain ends.

In the case of MK-10, *p*-chloromethylstyrene (CMS) and sodium iodide were used as the initiating system, and 4-vinylbenzylpiperazine (4-VBP) was used as the terminating agent, as described in the experimental section. The proposed mechanism is shown in Scheme 2. Starting with CMS and NaI, *p*-iodomethylstyrene is generated *in situ*. This initiates the polymerization of MeOxa and EsterOxa (thus introducing the first vinyl group into the polymer chain), producing an oxazoline propagating cation. At the end of the polymerization, this cation reacts with the amine group of 4-VBP, terminating the reaction and introducing the second vinyl group into the polymer chain.



**Scheme 2.** Synthesis of the MK-10 telechelic

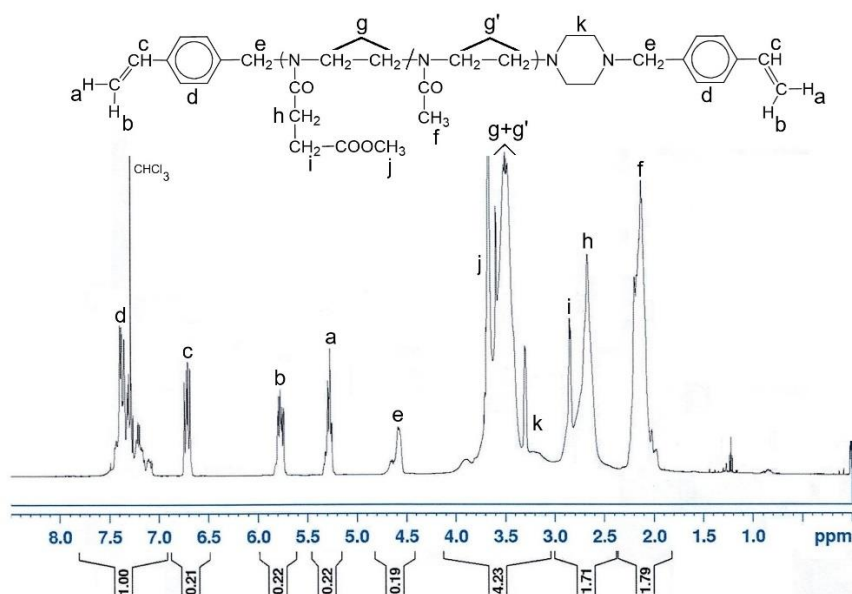


**Figure 1.**  $^1\text{H}$ -NMR spectrum of telechelic MK-10 in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

Characterization of MK-10 by  $^1\text{H}$ -NMR (Figure 1) demonstrated the presence, in the telechelic structure, of the monomers, initiator, and terminator used and allowed the determination of the molar percentage of MeOxa and EsterOxa by comparing the integral of the “f” signal of the MeOxa methyl group with the integral of the “i+h” signal of the EsterOxa (Figure 1). The molar proportion of MeOxa and EsterOxa was 58% and 42%, respectively, values very close to the theoretical values. The degree of polymerization was determined by comparing the sum of the integrals of the “f” and “i+h” signals with the average of the integrals of the “a”, “b”, and “c” signals of the initiator in the  $^1\text{H}$ -NMR spectrum (Figure 1). A degree of polymerization of 9.5 units was obtained. So, the molecular weight of MK-10 was calculated to be 1414.

In both cases (MK-32 and MK-10), the monomers were added simultaneously at the beginning of the polymerization, resulting then in statistical telechelic polymers.

### Synthesis and characterization of the hydrogels (HGJ)

Hydrogels were synthesized by free-radical polymerization of monomers N,N-dimethylacrylamide (DMAA) and the telechelics (MK-32 and MK-10) of 2-oxazoline (crosslinking agents), at  $5^\circ\text{C}$  and using the redox initiation system potassium persulfate (KPS) and N,N,N',N'-tetramethylethylenediamine (TEMED)<sup>10</sup> (Table 1, Scheme 3).

The redox system (KPS/TEMED) generates the free radicals that polymerize DMAA and the telechelics. Due to their double functionality (two vinyl groups per macromolecule), the telechelics act as crosslinking agents in this polymerization, enabling the formation of hydrogels.

A low temperature ( $5^\circ\text{C}$ ) was used to attenuate the reaction rate, which was very rapid at room temperature and did not allow for a homogeneous mixture of the reactants. The hydrogels were obtained in 20 minutes, but the system was allowed to react for 24 hours at  $5^\circ\text{C}$  to maximize the polymerization of the monomers. In the synthesis, the molar ratio of the monomers (MK/DMAA) was varied.

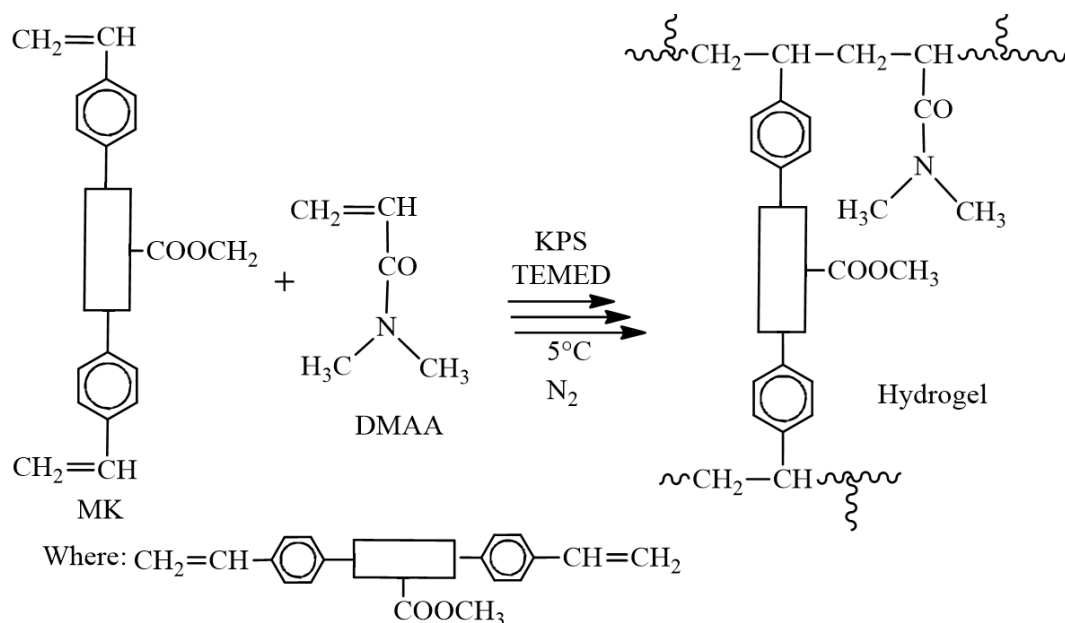
**Table 1.** Synthesis and characterization of hydrogels.

| Hydrogel <sup>a)</sup> | DMAA <sup>b)</sup><br>(mmol) | MK <sup>c)</sup><br>(mmol) | KPS <sup>d)</sup><br>(mmol) | R <sub>1</sub> <sup>e)</sup> | R <sub>2</sub> <sup>f)</sup> | %Yield <sup>g)</sup> | Q (g H <sub>2</sub> O/g HGs) <sup>h)</sup> |            |
|------------------------|------------------------------|----------------------------|-----------------------------|------------------------------|------------------------------|----------------------|--------------------------------------------|------------|
|                        |                              |                            |                             |                              |                              |                      | Original                                   | Hydrolyzed |
| HGJ-A                  | 5.18                         | 0.168                      | 0.14                        | 32.4                         | 2.68                         | 68                   | 4.2                                        | 5.1        |
| HGJ-B                  | 5.30                         | 0.083                      | 0.14                        | 15.6                         | 2.57                         | 90                   | 8.6                                        | 15.3       |
| HGJ-C                  | 5.20                         | 0.042                      | 0.14                        | 8.0                          | 2.70                         | 85                   | 27.4                                       | 64.2       |
| HGJ-D                  | 5.25                         | 0.017                      | 0.14                        | 3.2                          | 2.69                         | 80                   | 63.5                                       | 143.8      |
| HGJ-E                  | 5.39                         | 0.190                      | 0.14                        | 34.4                         | 2.48                         | 90                   | 12.0                                       | 22.5       |
| HGJ-F                  | 5.41                         | 0.090                      | 0.14                        | 15.9                         | 2.48                         | 83                   | 25.6                                       | 54.2       |
| HGJ-G                  | 5.33                         | 0.040                      | 0.14                        | 8.0                          | 2.67                         | 73                   | 61.2                                       | 165.2      |
| HGJ-H                  | 5.35                         | 0.020                      | 0.14                        | 4.1                          | 2.53                         | 86                   | 113.9                                      | 211.5      |

Where: a) Synthesized hydrogels. In all cases, the hydrogels were synthesized at 5°C, and in a reaction time of 24 hours, the number of moles of TEMED was twice that of KPS, and 4 mL of distilled water was used as the solvent; b) N,N-Dimethylacrylamide (DMAA); c) Polymer telechelic (MK): for hydrogels HGJ-A to HGJ-D, telechelic MK-32 (molecular weight 2985) was used, and for hydrogels HGJ-E to HGJ-H, telechelic MK-10 (molecular weight 1414) was used; d) Potassium persulfate (KPS); e) Initial molar ratio MK/DMAA multiplied by 1000; f) Molar percentage of initiator with respect to the monomers (100 (KPS) / (DMAA+MK)); g) Polymerization yield (100 (weight of hydrogel)/(sum of monomers weights)); h) Degree of water absorption of original hydrogels and after being hydrolyzed (in grams of water per gram of dry hydrogel).

The polymerization yields were relatively high, ranging from 68% to 90% (Table 1), indicating that the monomers reacted and were incorporated into the hydrogel.

Since the telechelics are macromolecules, they should have lower diffusivity in the reaction medium than DMAA, which is a simple molecule and therefore it has more mobility and react more with the propagating macroradicals. Consequently, the telechelics will have lower reactivity than DMAA, and DMAA will be incorporated primarily in the initial stages of polymerization, followed by the telechelics.

**Scheme 3.** Synthesis of hydrogel HGJ.

The degree of water absorption ( $Q$ ) of the hydrogels was determined. The results obtained are shown in Table 1 and Figure 2 (DMAA/MK molar ratio graph). It can be observed that, in each series, as the amount of crosslinker (MK) decreases, i.e., as the initial DMAA/MK molar ratio increases, then water absorption increases. This is because decreasing the proportion of crosslinker increases the pore size of the hydrogels, thus increasing their water absorption capacity. Hydrogels HGJ-A to HGJ-D (first series) have a crosslinker (MK-32) with 20 repeating units; in contrast, hydrogels HGJ-E to HGJ-H (second series) have a crosslinker (MK-10) with 9.5 repeating units. That is, hydrogels with MK-32 should theoretically have a larger pore size and greater water absorption than hydrogels with MK-10. However, experimental results show the opposite (Table 1). This could be due to the chemical structure of the telechelic MK-32, which has a double bond in the center of the macromolecule, which, due to steric hindrance, does not undergo modifications during free-radical polymerization<sup>3</sup>. These olefinic groups are hydrophobic; they can cluster together to form a hydrophobic microdomain and could generate repulsive forces with water, resulting finally in smaller hydrogel pores and less hydrogel water absorption. Another factor that would explain why the second series of hydrogels absorb more water than the first series is that the second series contains 2-methyl-2-oxazoline (MeOxa) monomers in its structure, which are more hydrophilic than the EtOxa monomers of the first series.

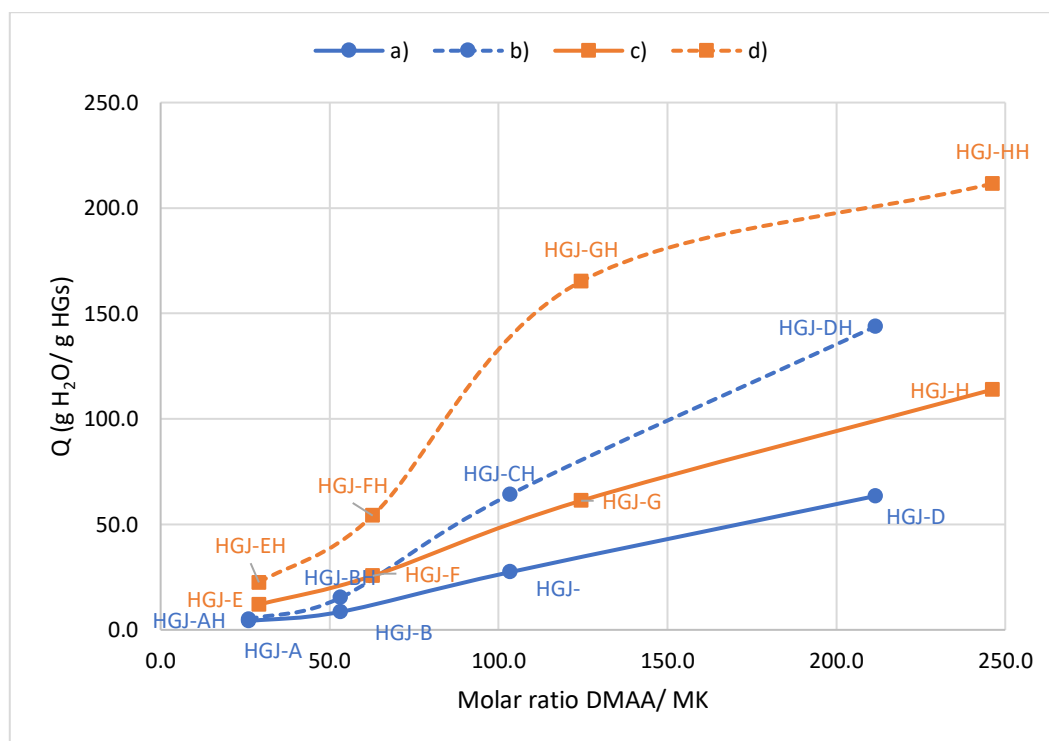


**Figure 2.** Degree of water absorption of the hydrogels synthesized with telechelic MK-32, (a) original and (b) hydrolyzed, and hydrogels synthesized with telechelic MK-10, (c) original and (d) hydrolyzed.

Basic hydrolysis of all hydrogels was performed, generating two new series of hydrogels containing, in equilibrium, sodium carboxylate ( $-\text{COO}^-\text{Na}^+$ ) and carboxylic acid ( $-\text{COOH}$ ) functional groups. The water absorption values of the hydrolyzed hydrogels are higher than those of their non-hydrolyzed counterparts (Figure 12). This can be explained

by the presence of carboxylate (ionic) and carboxylic acid (non-ionic) groups in the hydrolyzed hydrogels, which have a stronger interaction with water molecules, forming ion-dipole interactions and hydrogen bonds, respectively, compared to the amide and ester groups (both non-ionic) present in the original hydrogels, which only form hydrogen bonds with water molecules<sup>6</sup>.

### FTIR infrared spectroscopy of the hydrogels

The hydrogels were characterized by FTIR spectroscopy to identify the functional groups present (Figure 3)<sup>7</sup>.

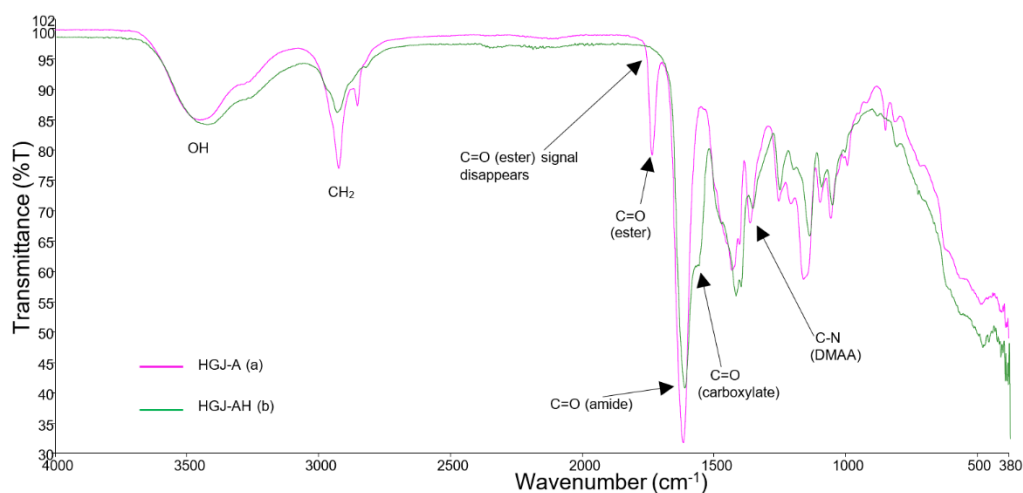


**Figure 3.** FTIR spectrum of the (a) HGJ-A hydrogel and (b) HGJ-AH hydrogel.

As example, in Figure 3a, the following signals were identified for the HGJ-A hydrogel:  $3449\text{ cm}^{-1}$  for OH (probably moisture absorbed by the hydrogel);  $2924\text{ cm}^{-1}$  for the methylene  $\text{CH}_2$  groups;  $2853\text{ cm}^{-1}$  for the  $-\text{C}-\text{H}$  of the methyl ester;  $1734\text{ cm}^{-1}$  for the carbonyl ( $\text{C}=\text{O}$ ) group of the ester group;  $1615\text{ cm}^{-1}$  for the carbonyl group of the amide group;  $1431\text{ cm}^{-1}$  for the aromatic carbon stretching  $\text{ArC}-\text{C}$  of the aromatic rings; and  $1253\text{ cm}^{-1}$  for the  $\text{C}-\text{N}$  of the substituted amide group. In the FTIR spectrum of the HGJ-AH hydrogel (HGJ-A hydrolyzed) (Figure 3b), the disappearance of the carbonyl signal associated with the ester group is observed. This indicates that the hydrolysis of the HGJ-A hydrogel was complete. This finding is repeated for the other hydrogels. The reason only the ester groups hydrolyzed and not the amide groups is because weak hydrolysis conditions were used ( $25^\circ\text{C}$ ,  $0.1\text{ N NaOH}$ , short hydrolysis time), and amide groups require more stronger conditions to hydrolyze than esters. For example,  $100^\circ\text{C}$ , a longer reaction time, and a high concentration of  $\text{NaOH}$  ( $1\text{ N}$ ). If amide groups had been hydrolyzed, then the structure of the hydrogel would have been destroyed. In the hydrolysis process, the ester groups were transformed into carboxylic acid and sodium carboxylate groups. The FTIR signal of the carbonyl group of the carboxylic acid groups is located in a region near  $1700\text{ cm}^{-1}$  and overlaps with the amide carbonyl signal, and the carboxylate carbonyl signal is observed as a "shoulder" of the amide carbonyl signal<sup>11</sup> at approximately  $1550\text{ cm}^{-1}$ .

## Water Absorption Kinetics of Hydrogels

The water absorption rate of the HGJ-C and HGJ-E hydrogels and their hydrolyzed versions was studied. Figure 4 shows the water absorption ( $Q$ ) of the hydrogels vs time in hours. It can be observed that, during the first two hours of the process, the absorption rate is high, then gradually decreases. Furthermore, it can be observed that, starting at 6 hours, water absorption reaches practically its maximum. Figure 4 shows that the HGJ-C and HGJ-CH hydrogels absorb more water than HGJ-E and HGJ-EH, respectively. This is because they are approximately three times less cross-linked than the latter ( $1000 \times \text{MK/DMAA} = 8.0$  vs. 34.4; Table 1).

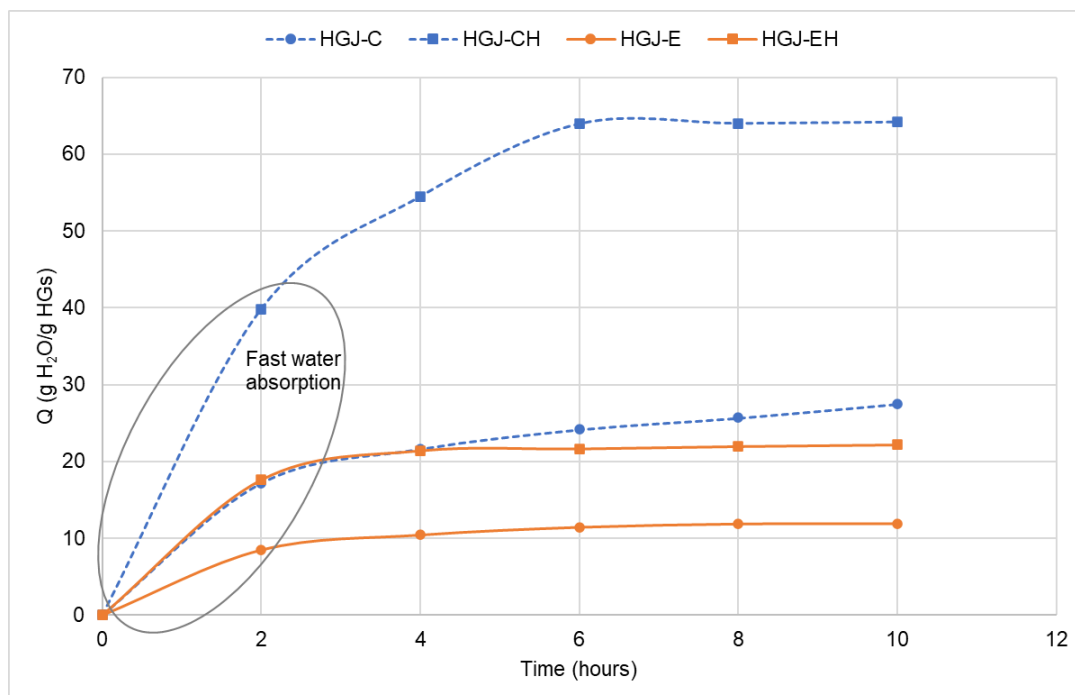


**Figure 4.** Water absorption kinetics of the hydrogels HGJ-C, HGJ-CH, HGJ-E and HGJ-EH.

## pH Sensitivity of Hydrogels

The hydrolyzed hydrogels HGJ-AH and HGJ-EH were characterized by their sensitivity to pH changes. It was demonstrated that the hydrolyzed hydrogels were sensitive to the pH of the aqueous medium. This sensitivity may be due to the presence of carboxylate and carboxylic acid functional groups, which are derived from the crosslinking agent (telechelic). Starting at pH 5.7, as the pH increased to acidic pH (pH 2 and 4), a contraction of the hydrogels was observed. From pH 5.7 to pH 8, an increase in volume was observed, followed by further contraction at pH 10 (Figure 5).

In the hydrogel, it is possible to determine the relationship between the concentration of carboxylic acid groups and that of carboxylate groups through the pKa value (an indicator of the dissociation strength of a weak acid) and pH 6. If  $\text{pH} = \text{pKa}$ , there is an equal percentage of carboxylic acid and carboxylate groups.

For this type of hydrogel, containing carboxylic acid and carboxylate groups derived from EsterOxa, the pKa reported by previous research was 5.6. Three situations could occur:

- If  $\text{pH} < \text{pKa}$  ( $\text{pH} < 5.6$ , e.g.,  $\text{pH} = 2$  and  $\text{pH} = 4$ ), there will be a majority of carboxylic acid groups. Hydrogen bonds will form between the carboxylic acids and the amides,

and also between the carboxylic acids themselves, therefore, hydrogels have a contraction, resulting in smaller pores in the hydrogels and, and there is a reduced water absorption of hydrogels.

- If  $\text{pH} > \text{pKa}$  ( $\text{pH} > 5.6$ , e.g.,  $\text{pH} = 8$ ), there will be a greater number of carboxylate groups. An electrostatic repulsion would occur between the negatively charged carboxylate groups, resulting in their expansion leading to the formation of larger pores in the hydrogels, and greater water absorption. At  $\text{pH}=10$ , instead of continuing to expand, the hydrogel contracts (Figure 5). This phenomenon could be due to the total ionic charge within the hydrogel at relatively high pH values, as reported in the literature<sup>12</sup>.
- At  $\text{pH} = \text{pKa}$  ( $\text{pH} = 5.6$ ).  $\text{pH} 5.7$  is very close to  $\text{pH} 5.6$  ( $\text{pKa}$ ). The concentration of acid groups would be practically equal to the concentration of sodium carboxylate groups, representing an intermediate state between the previous two.

### Thermogravimetric analysis of the hydrogels

The thermal stability of hydrogels HGJ-BH and HGJ-EH was evaluated by thermogravimetric analysis (TGA) and it was shown that the hydrogels were thermally stable up to approximately  $350^{\circ}\text{C}$ , a value that is usual for polymers.

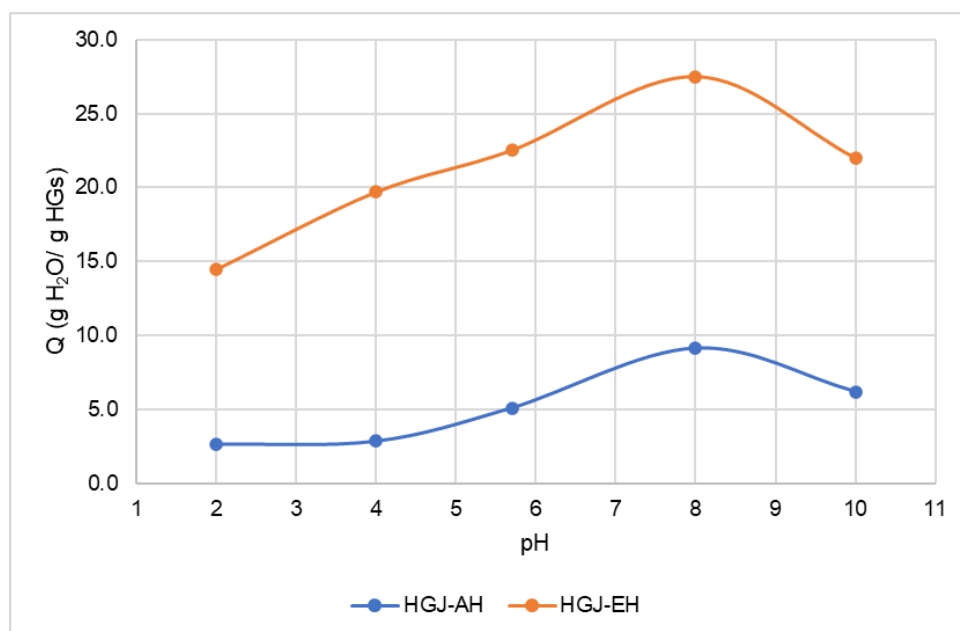


**Figure 5.** Degree of water absorption of the hydrogels (a) HGJ-AH and (b) HGJ-EH, at different pH values.

## CONCLUSIONS

Two series of hydrogels were synthesized by free-radical polymerization of N,N-dimethylacrylamide and 2-oxazoline telechelics using the KPS/Temed redox initiator system in aqueous solution at  $5^{\circ}\text{C}$ . The initial molar ratio of the monomers and the structure of the telechelics were varied. The telechelics MK-32 and MK-10 acted as crosslinking agents because they contained two vinyl groups in each macromolecule. The hydrogels were characterized by FTIR, confirming the presence of the monomer

functional groups in the hydrogels. The water absorption capacity of the hydrogels was determined, and it was concluded that lower amounts of telechelic resulted in greater water absorption. In addition, the hydrogels made with the telechelic MK-32 had a lower water absorption capacity than the hydrogels synthesized with the telechelic MK-10. Hydrogels containing carboxylate groups were obtained by hydrolyzing the ester groups, of the telechelics, contained within them. The hydrolyzed hydrogels exhibited a greater water absorption capacity than their non-hydrolyzed counterparts. This increased water absorption is due to the stronger interactions between the carboxylate groups of the hydrolyzed hydrogels and water molecules compared to the interactions of water with the amide and ester groups of the non-hydrolyzed hydrogels. The pH sensitivity of the hydrolyzed hydrogels was determined, demonstrating that decreasing the pH of the aqueous medium reduces water absorption capacity and causes the hydrogels to contract. However, increasing the pH of the aqueous medium causes the hydrogels to expand, resulting in increased water absorption capacity, reaching a maximum at pH 8.

## ACKNOWLEDGMENTS

To the Master's Program in Chemistry at the Graduate School, the Chemistry Department and the Research Promotion Department (DFI) of the Pontifical Catholic University of Peru.

## REFERENCES

1. Verbraeken B, Monnery BD, Lava K, Hoogenboom R. The chemistry of poly(2-oxazoline)s. *Eur Polym J.* 2017; 88: 451–69. <http://dx.doi.org/10.1016/j.eurpolymj.2016.11.016>
2. Hoogenboom R. The future of poly(2-oxazoline)s. *Eur Polym J.* 2022; 179: 111521. <http://dx.doi.org/10.1016/j.eurpolymj.2022.111521>
3. Pizzi D, Humphries J, Morrow JP, Fletcher NL, Bell CA, Thurecht KJ, et al. Poly(2-oxazoline) macromonomers as building blocks for functional and biocompatible polymer architectures. *Eur Polym J.* 2019; 121: 109258. <http://dx.doi.org/10.1016/j.eurpolymj.2019.109258>.
4. Jana S., and Uchman M. (2020). Poly(2-oxazoline)-based stimulus-responsive (co)polymers: An overview of their design, solution properties, surface-chemistry and applications, *Progress in Polymer Science*, 106: 101252.
5. Gudiel Honores H, Rueda JC. Síntesis y caracterización de polímeros telequelícos de 2-oxazolinás. *Rev Soc Quím Perú.* 2024; 90 (2): 106-119. <http://dx.doi.org/10.37761/rsqp.v90i2.473>
6. Rueda J, Santillán F, Komber H, Voit B. Synthesis and characterization of stiff, self-crosslinked thermoresponsive DMAA hydrogels. *Polymers (Basel).* 2020; 12 (6): 1401. <http://dx.doi.org/10.3390/polym12061401>
7. Zschoche S, Rueda JC, Binner M, Komber H, Janke A, Arndt K-F, et al. Reversibly switchable pH- and thermoresponsive core-shell nanogels based on poly(NiPAAm)-graft- poly(2-carboxyethyl-2-oxazoline)s. *Macromol Chem Phys.* 2012; 213 (2): 215–26. <http://dx.doi.org/10.1002/macp.201100388>.

8. Dargaville, T. R., Park, J. R., & Hoogenboom, R. (2018). Poly (2-oxazoline) Hydrogels: State-of-the-Art and Emerging Applications. *Macromolecular Bioscience*, 18(6), 1800070.
9. Rengifo J. Zschoche S., Voit B., Rueda J. C., Synthesis and characterization of new interpenetrated hydrogels from N-isopropylacrylamide, 2-oxazoline macromonomer and acrylamide, *European Polymer Journal*, 2022; 177: 111456.
10. Feng, X. D., Guo, X. Q., & Qiu, K. Y. (1988). Study of the initiation mechanism of the vinyl polymerization with the system persulfate/ N, N, N', N'-tetramethylethylenediamine. *Die Makromolekulare Chemie: Macromolecular Chemistry and Physics*, 189(1), 77-83.
11. Günzler H, Gremlich H-U. *IR Spectroscopy: An Introduction*. Weinheim, Alemania: Wiley-VCH Verlag; 2002.
12. Rueda JC, Campos E, Komber H, Zschoche S, Haussler L, Voit B., Synthesis and characterization of new pH- and thermo-responsive hydrogels based on N-isopropylacrylamide and 2-oxazolines. *Designed Monomers and Polymers*. 2014; 17(3): 208-216. <http://dx.doi.org/10.1080/15685551.2013.840471>.