

# Synthesis and Characterization of poly (N-glycidyl-2-oxazolidone) Using a Green and Efficient Catalyst

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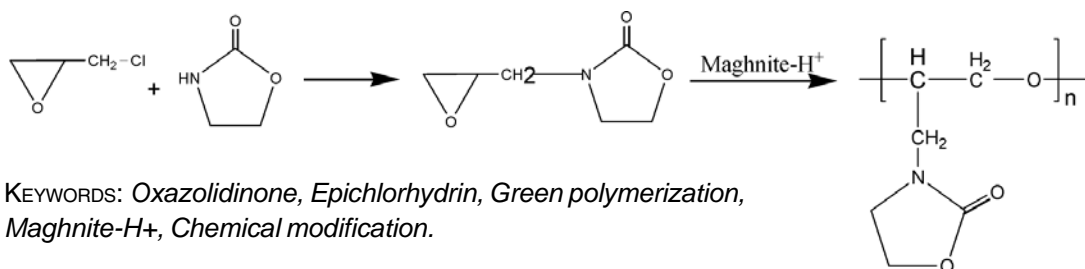
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## ABSTRACT

In the present paper, we report the synthesis of a new amino polymer made of oxazolidinone using an efficient ecocatalyst called Maghnite-H<sup>+</sup>. The synthesis process contains two steps: the first consists to the preparation of an amino oxiran 3-(oxiran-ylmethyl) oxazolidin-2-one (OMO) by a substitution reaction of epichlorhydrin by 2-oxazolidinone, the second step concerns a green polymerization of the resultant oxiran by a ring opening reaction catalysed by Maghnite-H<sup>+</sup>.

The polymer have been successfully prepared and characterized by various techniques, such as <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, which were used to elucidate the structural characteristics of the resulting polymers. The effects of the amount of Maghnite-H<sup>+</sup> and temperature on the conversion and number average molecular weight of polymers were studied. The polymerization conversion and number average molecular weight, increased as the proportions of catalyst were increased.



## 1. INTRODUCTION

Heterocycles represent an important class of compounds found in a wide variety of natural bioactive compounds, as well as in synthetic products with demonstrated utility such as pharmaceuticals, fungicides and other industrial products<sup>[1-8]</sup>... The oxazolidin-2-ones have a very important class of heterocyclic compounds. This is one of the classes of synthetic antibacterial agents over the past 30 years<sup>[9, 10]</sup>. Currently, scientific research has been devoted to the synthesis of polyoxazolidinone by different methods and using various catalysts<sup>[11-13]</sup>. On the other hand, epoxides are useful polyvalent intermediates which are widely used in organic synthesis because of their high reactivity to a wide variety of nucleophilic species and which are used in the manufacture of wide ranges of important commercial compounds<sup>[14, 15]</sup>. The combination of oxazolidinone ring with an epoxide may, in our view, constitute an access route to potential new poly-heterocyclic compounds.

In the literature 3-(oxiran-2-ylméthyl) oxazolidin-2-one (N-Glycidyl-2-oxazolidone) was polymerized at 70°C by Lewis acids, boron trifluoride etherate and aluminum chloride to give polymers with low molecular weight and the yield not exceeding 33%<sup>[16]</sup>. The catalysts used have several drawbacks: they are toxic and require rigorous conditions such as purification of the solvents used, the presence of nitrogen or argon atmosphere, etc.<sup>[17, 18]</sup>.

In recent times, Belbachir and col. have developed an activated clay catalysts for cationic polymerization of various monomers called Maghnite-H<sup>+</sup><sup>[19]</sup>.

Maghnite-H<sup>+</sup> has been shown to exhibit a higher efficiency in the cationic polymerization and copolymerization reaction<sup>[20-34]</sup>. Maghnite H<sup>+</sup> is a very interesting catalyst for several reasons: it is non-toxic environmentally friendly material, it is abundant, easily recoverable by simple filtration and it is reusable.

In this work, and following our search for the preparation of amino polymers using an ecological catalyst which is Maghnite-H<sup>+</sup><sup>[35]</sup>, we propose a new method of preparation of polyoxazolidinone, it is the synthesis and the polymerization of 3-(oxiran-2-ylméthyl) oxazolidin-2-one (OMO) using Maghnite-H<sup>+</sup> as catalyst.

## 2. EXPERIMENTAL

### 2.1. Materials

1,2-Epoxy-3-chloro propane (Epichlorohydrine, ECH) (Prolabo), 2-oxazolidinone (Alfa Aesar), sodium hydroxide (Biochem), Magnesium sulfate (Biochem), Raw-maghnite: Algerian montmorillonite clay was procured from "BENTAL" (Algerian Society of Bentonite), chloroform.

### 2.2. Instruments

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker AC200, Avance 300 instruments, in CDCl<sub>3</sub>. chemical shifts were reported in parts per million (ppm) relative to (Me)<sub>4</sub>Si as external standard. Infrared spectra were recorded on a diamond alpha Bruker FTIR spectrometer. Polymer average molecular weights (Mn and Mw) and dispersity (Đ = Mw/Mn) were determined by Size Exclusion Chromatography (SEC). Polymers were dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered (0.45 μm) and analyzed at 25°C using a Varian PL-GPC50 device equipped with two mixed packed columns (PL gel mixed type C). The mobile phase was CH<sub>2</sub>Cl<sub>2</sub> and PMMA standards (from 875 to 680000 g mol<sup>-1</sup>) were used for calibration.

### 2.3. Preparation of Maghnite-H<sup>+</sup>

The Maghnite-H<sup>+</sup> was prepared according to the process similar to that described by Belbachir et al [16]. 30 g of raw-maghnite was crushed for 20 min using a prolabo ceramic balls grinder. The maghnite was placed in an Erlenmeyer flask together with 100 mL of distilled water then stirred using a magnetic stirrer for 2 h at room temperature, a solution of sulfuric acid 0.25M was added to The mixture and stirring, over 2 days at room temperature until saturation was achieved, the mineral was then washed with distilled water up to pH 7. after filtration, the activated Maghnite is dried in the stove for 24 hours at 105°C.

### 2.4. Preparation of 3-(oxiran-ylmethyl)oxazolidin-2-one

To 8.7 g of 2-oxazolidinone dissolved in 100 ml of chloroform, 9.25 g of epichlorohydrin was added. The mixture was boiled for 4 h, the precipitate (the salt) was filtered off, then 100 ml of sodium hydroxide solution (4 %) was added. After 1 h, the reaction was stopped. The liquid product was extracted in 100 ml of chloroform, the product was dried with MgSO<sub>4</sub>, then the solvent was evaporated and the yield of the reaction was 4.35 g (30.40 %) (Scheme 1).

### 2.5. Preparation of the Polymer

The reaction consisted of mixing 1 g of OMO and an amount of Maghnite-H<sup>+</sup>. Before use, the catalyst was

dried at 120°C over night, and then cooled to ambient temperature under vacuum. The mixture (OMO/ Magh-H<sup>+</sup>) was agitated with a magnetic stirrer in sealed tubes. The tubes were kept in a constant temperature bath. When the reaction time was over, the mixture was cooled. The crude product was washed by chloroform, precipitated in methanol, dried, weighed and analyzed (Scheme 2).

## 3. RESULTS AND DISCUSSIONS

### 3.1. Characterization of the Maghnite-H<sup>+</sup>

The bulk structure of the catalysts was analyzed by XRD. X-ray diffraction. The diffractograms (Fig. 1) shows that the calculated basal spacing (d001) from XRD patterns, applying Bragg equation ( $2d \sin \theta = n\lambda$ ) is 12.5 Å for Raw-Mag and 14.5 Å for Mag-H<sup>+</sup>. This increase in basal spacing is explained by the substitution of single water between the sheet of Raw-Mag by two interlamellar water layer in Mag-H<sup>+</sup>.

The chemical composition of the catalysts (Table 1) shows that SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are main components of the catalyst with a low amount of Fe<sub>2</sub>O<sub>3</sub>, MgO and others.

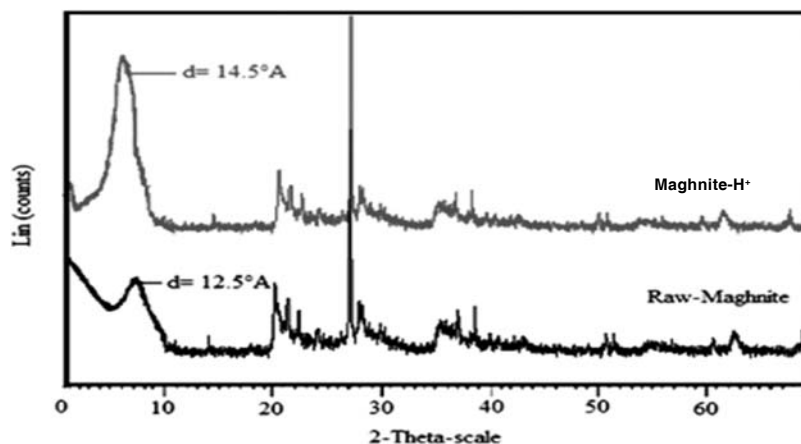


Figure 1. X Ray diffractogram of Raw-Maghnite (black) and Maghnite-H<sup>+</sup> 0.25 M (gray)

TABLE 1. Elementary composition of Maghnite

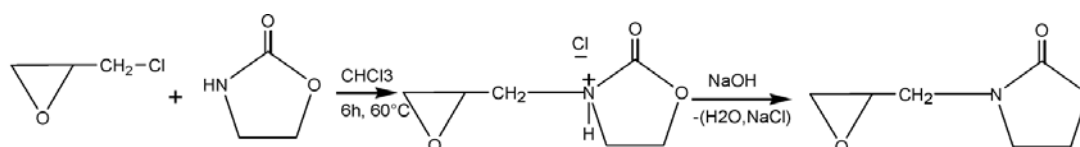
Sample	Composition in wt%									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	SO <sub>3</sub>	FL*
Raw-Mag	69.39	14.67	1.16	1.07	0.30	0.50	0.79	0.16	0.91	11
Mag-H <sup>p</sup>	71.70	14.03	0.71	0.80	0.28	0.21	0.77	0.15	0.34	11

\*FL flame loss

### 3.2. Synthesis of OMO

3-(oxiran-ylmethyl) oxazolidin-2-one has obtained by replacement of the chlorine group

of epichlorhydrin by the oxazolidinone ring (Scheme 1). This is confirmed by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR.



Scheme 1. Schematic representation of the synthesis of monomer (OMO)

The IR measurements of the product (Fig. 2) show the characteristic vibrations of: (CH<sub>2</sub>-C) at 2920-2998 cm<sup>-1</sup>, (-C=O) at 1734 cm<sup>-1</sup>, (C-O) of the epoxide of epichlorhydrin at

850- 910 cm<sup>-1</sup>. In addition to the bands characteristic of OMO, the strong band characteristic of the valence vibration of (C-Cl) at 650-800 cm<sup>-1</sup> disappears.

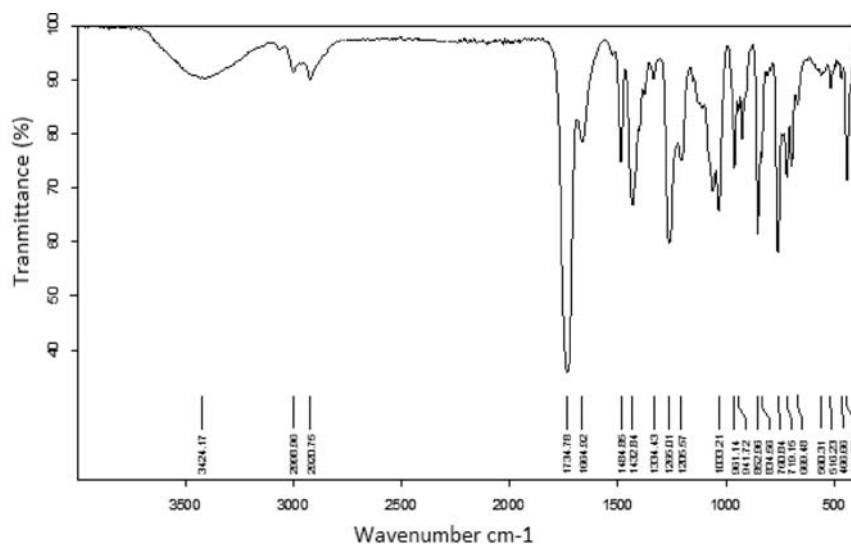


Figure 2. FT-IR spectra of OMO

The  $^1\text{H-NMR}$  spectrum of OMO is shown in (Fig. 3). The peak at 2.50-3.34 ppm is assigned to the protons of the epoxide ring and the characteristic protons of the oxazolidinone ring appeared at 3.63-4.22 ppm.

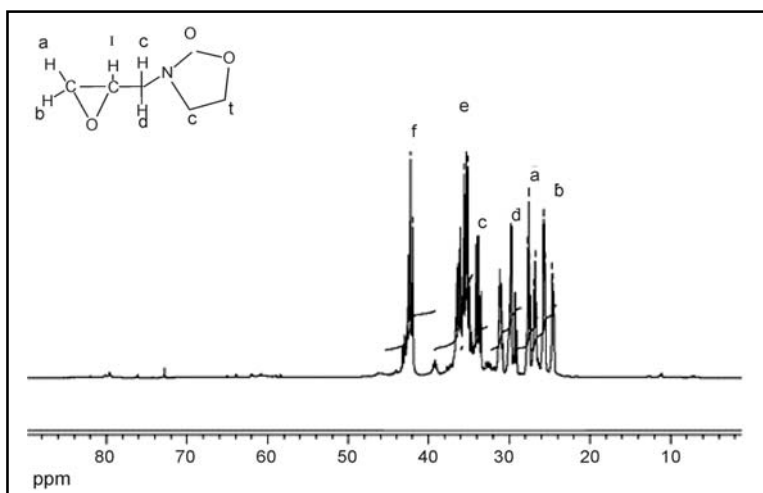


Figure 3.  $^1\text{H}$  NMR spectra of OMO / $\text{CDCl}_3$

$^{13}\text{C-NMR}$  spectrum of OMO is shown in Fig. 4, the carbonyl characteristic of the oxazolidinone ring appeared at 158.59 ppm, for the carbons of the epoxide showed the peaks at 45.42; 50.01 ppm and the peak at 40.59; 51.26 ppm corresponding to the carbon bonded to the nitrogen.

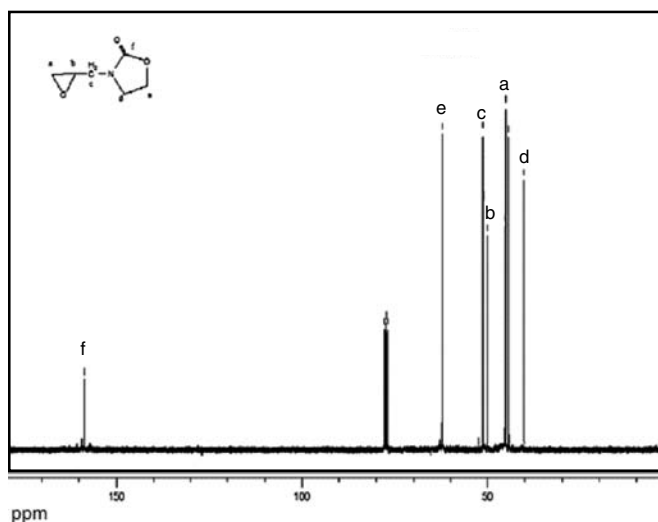


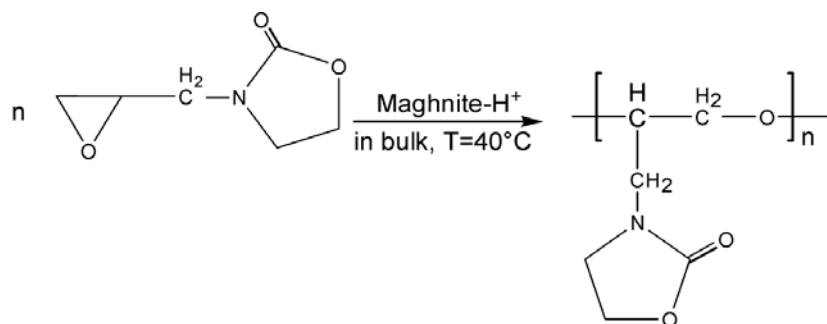
Figure 4.  $^{13}\text{C}$  NMR spectra of OMO/  $\text{CDCl}_3$

### 3.3. Ring Opening Bulk Polymerization of OMO

The present study is also concerned with the polymerization and examines the catalytic activity of Algerian proton exchanged montmorillonite clay for polymerization of the

resultant oxiran by a ring opening reaction. The structure and the composition of the catalyst were reported in previous works<sup>[19, 36, 37]</sup>.

The cationic ring opening bulk polymerization of OMO was examined in the presence of Maghnite-H<sup>+</sup> at 40 °C (Scheme 2).



Scheme 2. Schematic representation of the synthesis of poly (OMO)

The IR measurements of the product are in a good agreement with the poly OMO structure (Fig. 5). The characteristic vibration of C–O band is observed respectively at 1127 cm<sup>-1</sup>. A weak absorbance around 3500 cm<sup>-1</sup> assigned

to the hydroxyl group was observed. This indicated that polyoxiran possessed hydroxyl groups at the end of the chain, which seemed to be introduced by terminating and initiating processes.

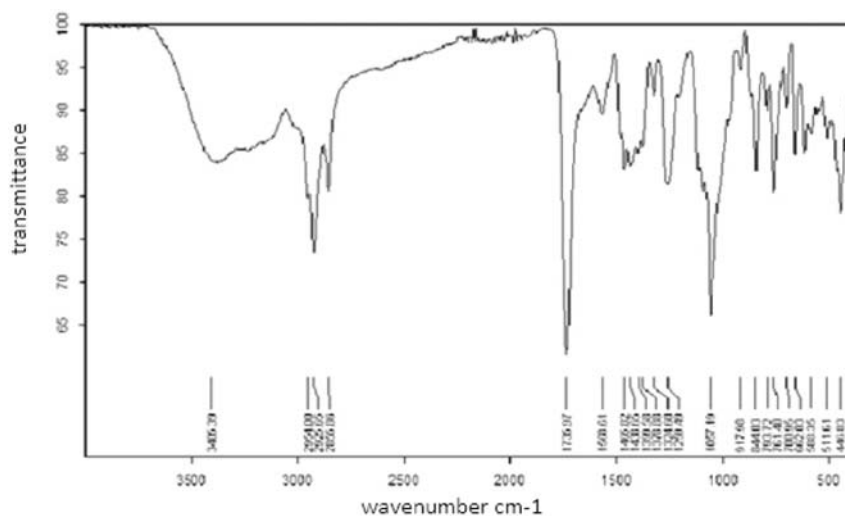


Figure 5. FT-IR spectra of poly OMO

$^1\text{H}$  and  $^{13}\text{C}$ NMR measurements (Figs. 6 and 7) confirm the structure of poly OMO that resulted from the reaction of polymerization. As shown in  $^1\text{H}$  NMR spectrum of the product, the signals appearing at 3,527 and 3,858 ppm indicate the

formation of ether, the signals at 1, 9 and 2, 15 ppm correspond to OH [37, 38] (Fig. 6).

$^{13}\text{C}$  NMR analysis (Fig. 7) also clearly showed the resonances corresponding to poly OMO carbons,  $\delta = 64,94$  ppm and  $\delta = 70,13$  ppm .

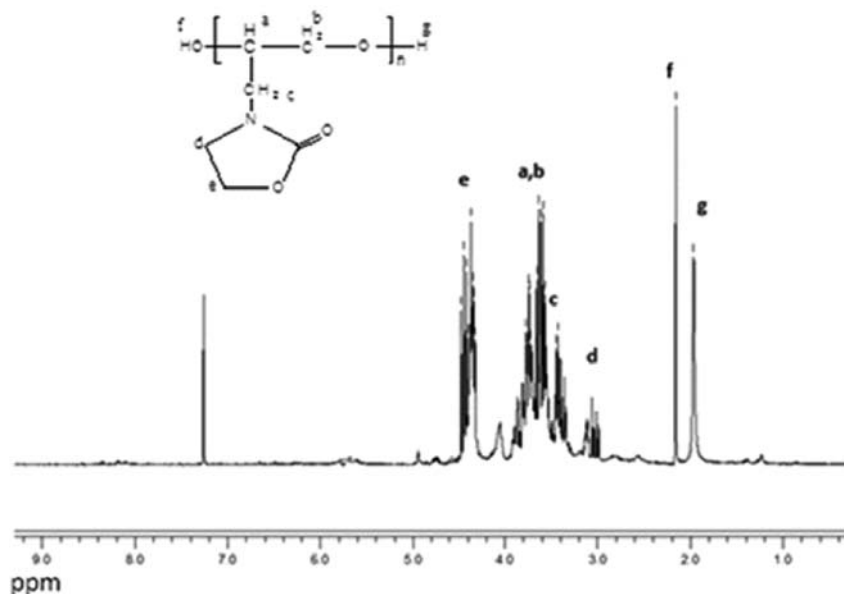


Figure 6.  $^1\text{H}$  NMR spectra of poly OMO/ $\text{CDCl}_3$

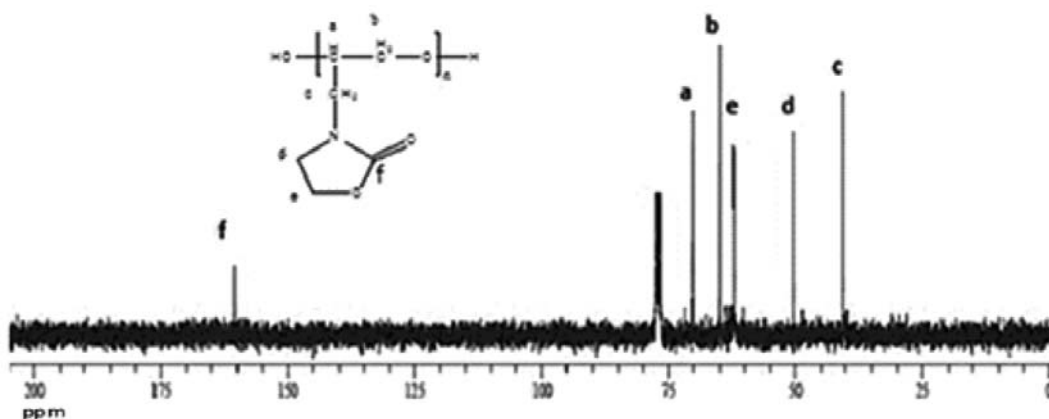


Figure 7.  $^{13}\text{C}$  NMR spectra of poly OMO/ $\text{CDCl}_3$

### 3.4. Study of the Catalytic Activity of Mag-H<sup>+</sup> on the Polymerization

The temperature effect on the polymerization of OMO with Mag-H<sup>+</sup> as catalyst is followed, in order to choose the adequate temperature for the reaction.

The experiments are carried out for 6 hours with 10% of Mag-H<sup>+</sup>.

The result, shown in table 2, indicates the decrease in molecular weight at 60°C, probably because of the increase in the rate of chain transfer reaction of the growing polymer cation (inter and intramolecular)<sup>[39, 40]</sup>.

TABLE 2. Effect of temperature on the polymerization of OMO by mag-H<sup>+</sup>

Experiment	Temp. (°C)	Yield %	M <sub>v</sub>	M <sub>n</sub>	M <sub>w</sub>
1	40	66	1034	1030	1035
2	60	68	931	922	933

In figure 8, we examined the catalytic activity of Mag-H<sup>+</sup> in the polymerization of OMO measured by the yield. Different weights of the catalyst were employed (0.02, .005, 0.10, 0.15, 0.20 g). Poly (OMO) was obtained with higher conversion from 0.15g (15%), then, it became constant. It is probably related to the protonation equilibrium between the monomer and polymer<sup>[35, 37]</sup>.

Figure 9 shows the result of the evolution study of the average molecular weight of poly OMO using different amount of the catalyst. It is noticed that M<sub>n</sub> reached its highest value with 10% of catalyst, then, it decreased. This is probably justified by the formation of several polymers of small masses. This result is similar with that obtained in the polymerization by ring opening reaction using Mag-H<sup>+</sup> clay as catalyst<sup>[35, 41-46]</sup>.

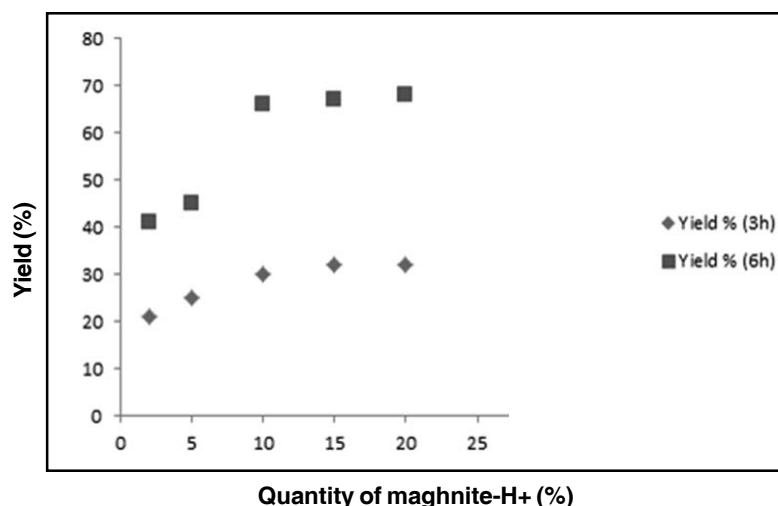


Figure 8. Conversion versus the quantity of mag-H<sup>+</sup> curve for the polymerization of OMO at 40°C



It is observed that increasing the catalyst percentage leads to a steady increase in conversion and a decrease in the average molecular weight. This result shows the cationic nature of the mechanism involved.

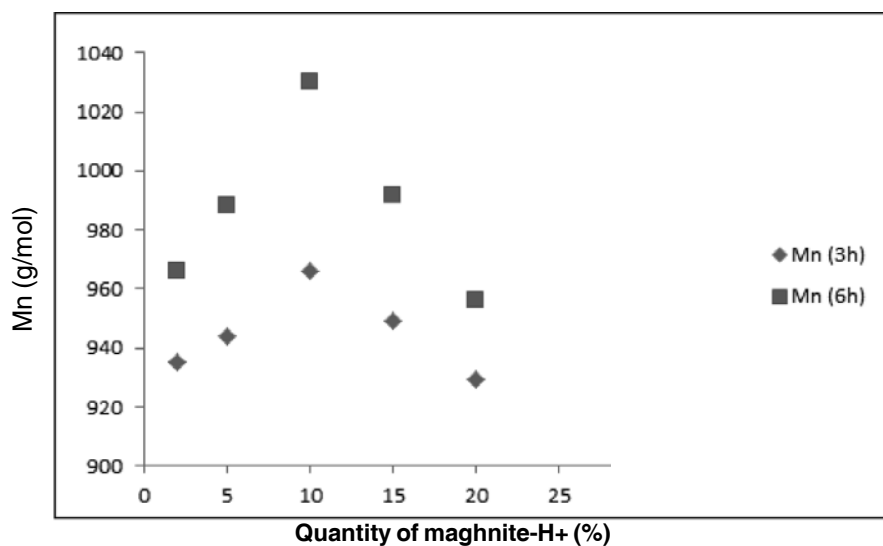


Figure 9. Molecular weight versus the quantity of Mag-H+ curve for the polymerization of OMO at 40 °C

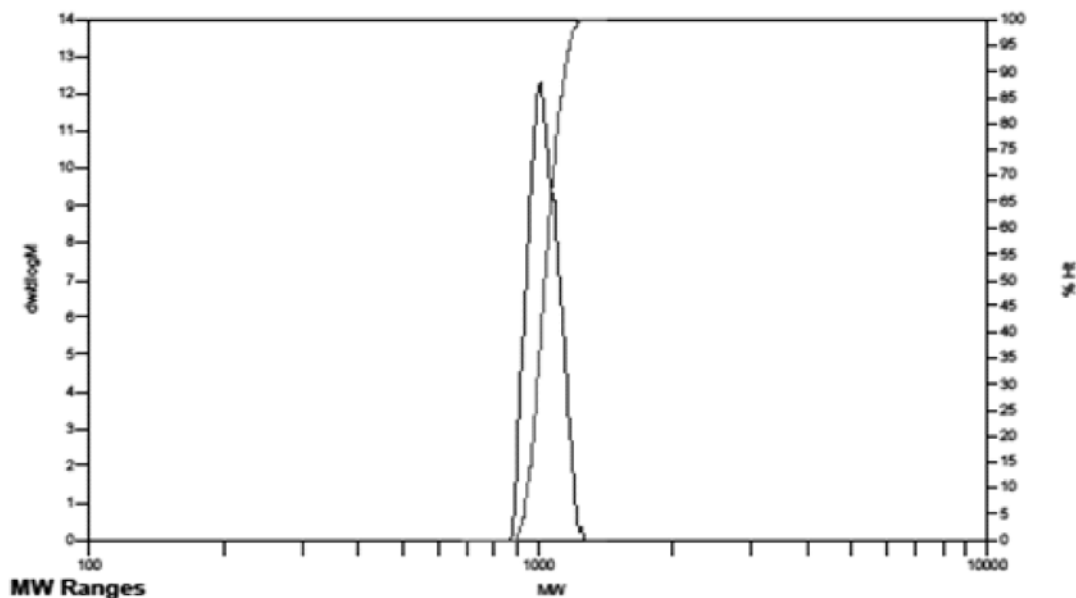


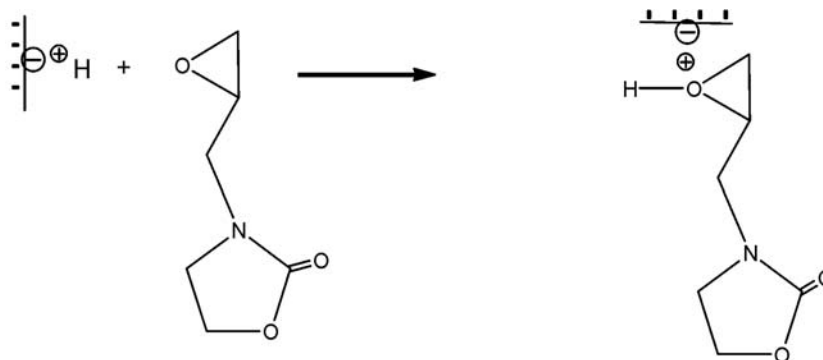
Figure 10. GPC curve of poly (OMO) prepared at 40 °C (10 % Maghnite 0.25M, t = 6h)

### 3.5. Mechanism of Polymerization

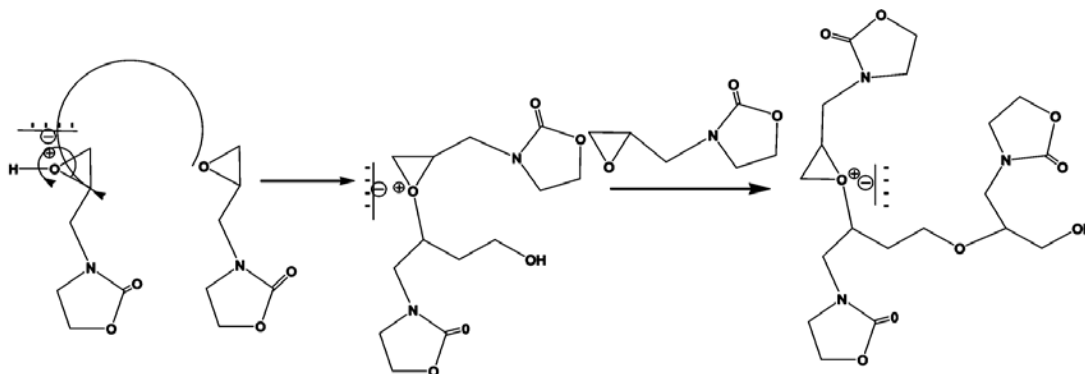
The structure of the polymer, proven by proton and carbon NMR, makes it possible to deduce that the sheets of clay and the protons interposed between them form the initiator system. We propose that the initiation step consists of a protonation of the monomer from which the proton attacks the oxiran oxygen (Scheme 3).

The propagation is carried out by the successive insertion of the monomers between the active center (the propagating chain) and its counterion (Scheme 4).

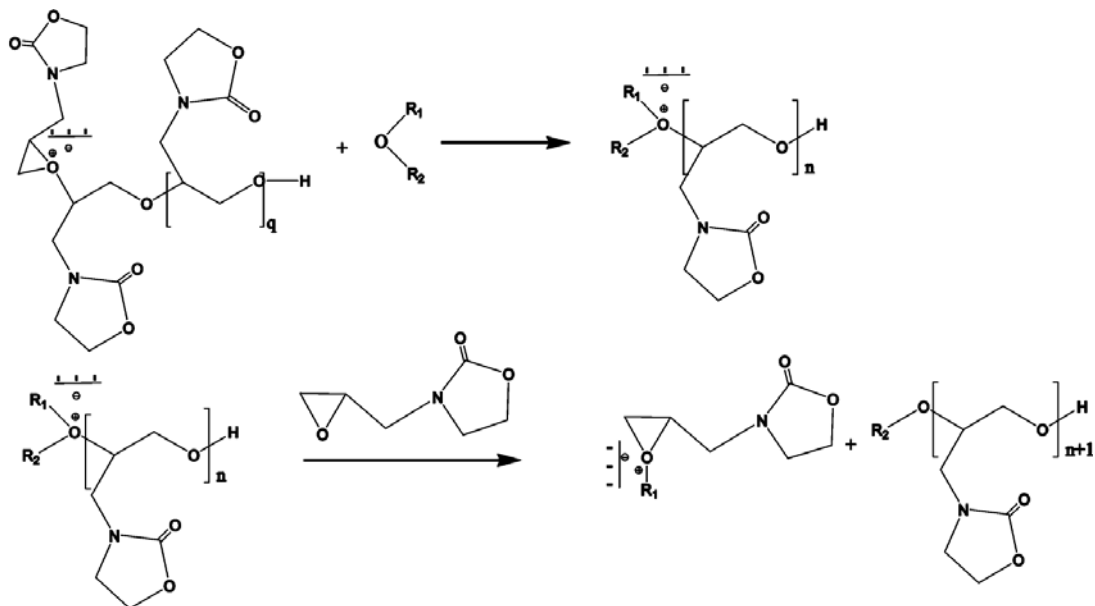
Termination by proton transfer to an initiator produces cyclization onto Poly (OMO) chains (Scheme 5, 6).



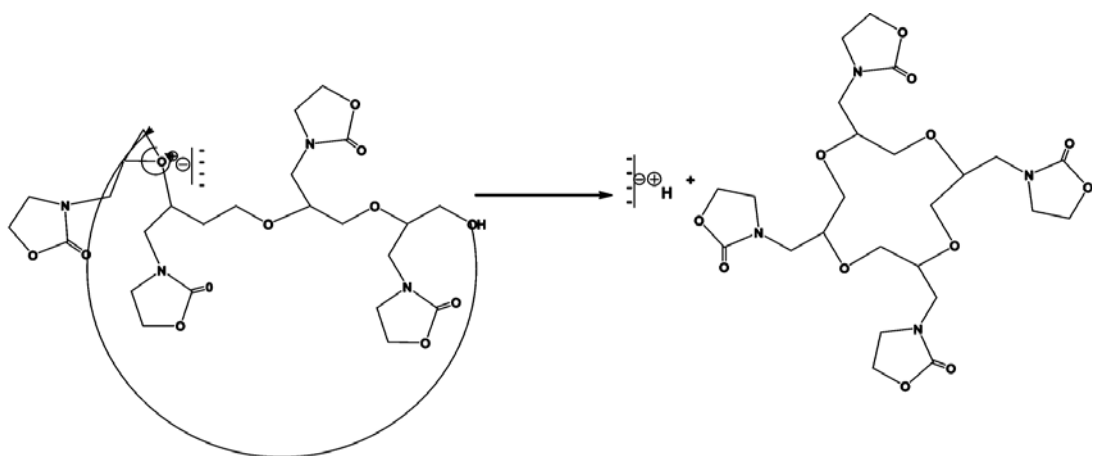
Scheme 3. Initiation step



Scheme 4. Propagation step



Scheme 5. Termination step



Scheme 6. Cyclization

#### 4. CONCLUSION

In conclusion, we have successfully developed an easy and efficient strategy of the synthesis of poly(*N*-Glycidyl-2-oxazolidone) by cationic

process, using an catalyst acid exchanged montmorillonite clay as heterogeneous phase called Maghnite-H<sup>+</sup>, an effective initiator for polymerization of vinylic and heterocyclic monomers. The polymerization proceeds

smoothly, and a simple filtration is sufficient to recover the catalyst. The catalyst could be removed from the mixture of the products by simple filtration for the possibility of another use without a loss of catalytic activity. The catalytic activity as measured by the conversion rate and the molecular weight of formed polymers depend on the catalyst proportion in the reaction medium and the reaction temperature. The polymerization was considered to be initiated by the proton addition from Maghnite-H<sup>+</sup> to monomer and the propagation proceeds with Maghnite as counter-ion.

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