

## Synthesis of bio-based poly limonene oxide with green catalyst

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### ABSTRACT

In the present work, the polymerization of limonene oxide (LO) catalyzed by Maghnite H<sup>+</sup> (Mag- H<sup>+</sup>) is investigated. Mag-H<sup>+</sup> is Algerian montmorillonite sheet silicate clay exchanged with protons. The poly limonene oxide (PLO) is obtained by cationic ring opening polymerization in bulk and with solvent. The effect of the reaction time, the temperature and the amount of catalyst are studied and discussed in order to find the optimal reactions conditions. The polymerization in solution at 0 °C with 5% by weight of catalyst leads to the best yield 61.34% for a reaction time of 1h. The structure of the obtained products is characterized by XRD, <sup>1</sup>H-NMR, <sup>13</sup>C-RMN, ATR-FTIR, DSC and TGA.

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## 1. Introduction

The preparation of bio-based polymers by using renewable monomers; which respects the principles of green chemistry; is currently an important alternative solution to petroleum derived polymers.<sup>1</sup> Several products derived from natural resources; which are produced from renewable agricultural and biomass feedstock; have become commercially available. Among these products, is LO. Limonene oxide C<sub>10</sub>H<sub>16</sub>O; which is derived from monoterpene natural cyclic limonene; is produced by more than 300 plants.<sup>2</sup> Limonene oils are obtained industrially as a by-product of the citric fruit juice processing and are then oxidized to form mono and di-functional epoxides.<sup>3,4</sup> The low cost of LO makes them attractive organic renewable monomers for the synthesis of the PLO.<sup>5</sup> The ring opening polymerization of LO was first reported in 1985 by Aikins and al work.<sup>6</sup> They found that the cationic polymerization induced radiation gives high conversion of LO into the PLO, which can reach a high yield of 80%. In Han Jin Park et al work, the photoinitiated cationic ring-opening polymerization of LO is studied using diaryliodonium salt and triarylsulfonium salt as a photoinitiators. However, this type

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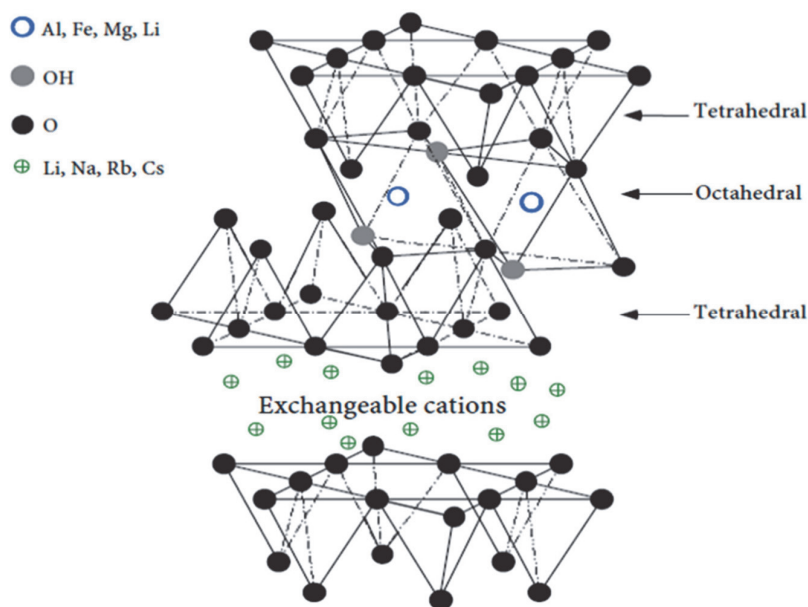
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of reaction leads to side reactions with nonpolymeric products.<sup>1</sup> Hisatoyo Morinaga and al, studied the polymerization of LO based on radical reaction, through the double bonds with branched polyethyleneimine. This leads to a network polymer leading to a high thermal resistance in high yields.<sup>2</sup> LO represents an excellent choice for copolymerization reactions with other monomers. One of the most known reaction is with the carbon dioxide using zinc-based catalysts to obtain polylimonene carbonate, which many functional materials can be derived.<sup>7-10</sup>

Among the principles of green chemistry is the use of renewable material feedstock and the environmentally benign substances, including solvents and catalysts. The existing literature related to the research work based on the homopolymerization of LO through the epoxide function is in fact very modest, one of the reasons for which this paperwork is proposed. The objective of this present paper is to extend the scope of other promising new domain of polymer synthesis by using another catalyst system, which has been shown to exhibit a higher efficiency. The novelty in this paper is the synthesis of PLO by a simple method respecting the principles of green chemistry using a green catalyst called Maghnite-H<sup>+</sup>. The polymerization of LO is prepared in bulk and in the presence of dichloromethane as solvent. The best yield is obtained in the reaction with solvent. The structure obtained of the PLO is confirmed by the FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR analysis. The thermal properties of the prepared polymers are given by TGA and DSC analysis. The effects of the different synthesis parameters, such as the amount of Mag-H<sup>+</sup>, the temperature and the polymerization time, are also investigated.

### 1.1. Green catalyst Maghnite

The Maghnite is an Algerian layered montmorillonite, which has a high ratio of aluminium and silicium.<sup>11</sup> Maghnite sheets are made up of octahedral layers, which lie between two octahedral layers, and between the octahedral layers are exchangeable cations and water molecules as shown in **Fig. 1**, depicting the structure of Maghnite confirmed by XRD analysis and ATR-FTIR. In its acid activated form, the Maghnite is used as a catalyst for cationic polymerization of vinylic and heterocyclic monomers. The activation of Maghnite; which has a typical composition as reported in **Table 1**;<sup>11</sup> can cause some changes in its elementary composition. It can be observed in this table that the acid treatment leads to a decrease in Al<sub>2</sub>O<sub>3</sub> concentration and silica enrichment. By examining the literature, it is found that the studies of the catalytic properties used in cationic polymerization are investigated in several international papers.<sup>12-19</sup>



**Fig. 1.** Maghnite structure<sup>11</sup>

**Table 1.** Chemical composition of raw Maghnite and Maghnite H<sup>+</sup>.<sup>11</sup>

Species	Raw Maghnite	Maghnite H <sup>+</sup> (%)
SiO <sub>2</sub>	69.3	71.7
Al <sub>2</sub> O <sub>3</sub>	1.16	0.71
Fe <sub>2</sub> O <sub>3</sub>	0.30	0.28
MgO	0.50	0.21
CaO	1.07	0.80
Na <sub>2</sub> O	0.79	0.77
K <sub>2</sub> O	0.16	0.15
YiO <sub>2</sub>	0.91	0.34

## 2. Results and Discussion

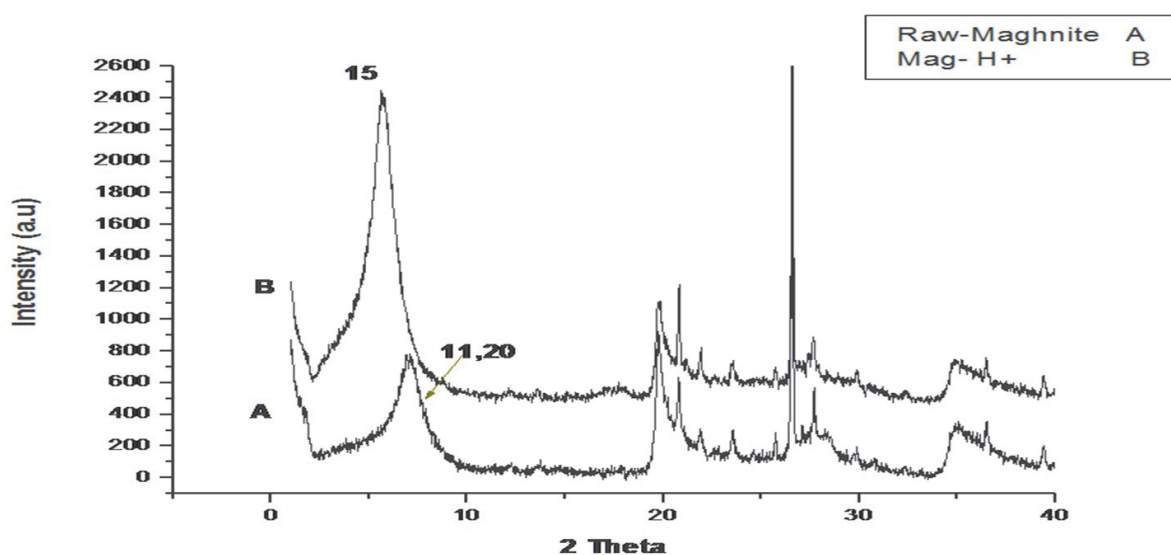
### 2.1. Results of catalyst

#### 2.1.1 XRD Analysis

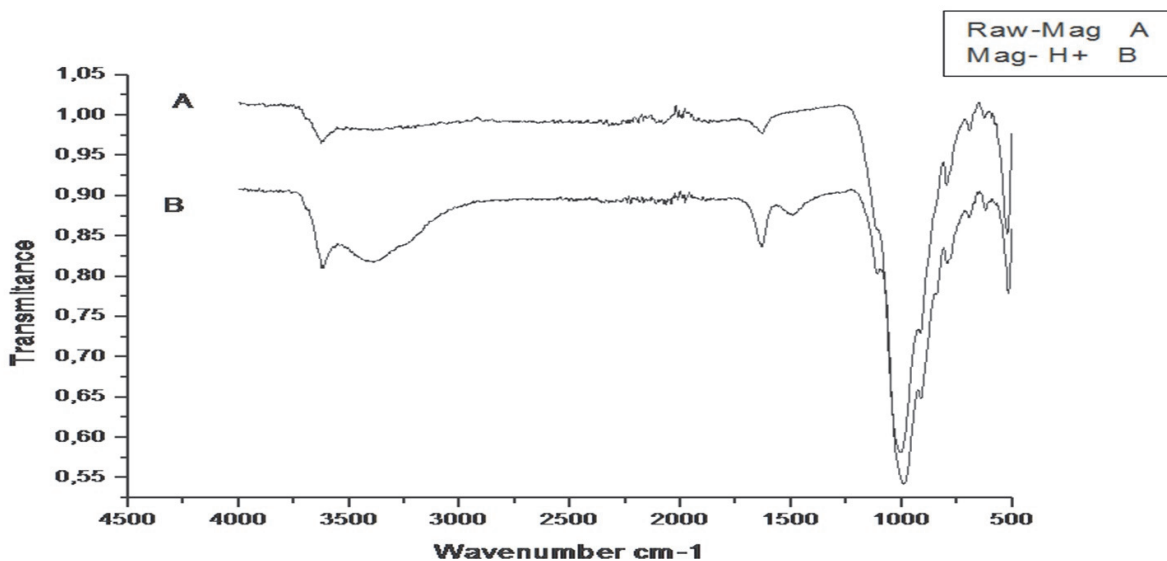
The Montmorillonites have both bronsted and Lewis acid sites and when exchanged with cations having high charges density, as protons, they produce highly active catalysts for acid catalysed reactions.<sup>20</sup> The diffractogram of raw Maghnite and Mag-H<sup>+</sup> showed a shifting of a peak (d001) from  $2\theta=7.5^\circ$  to  $2\theta=5^\circ$ , which corresponds to an interlayer spacing change from  $11.20\text{\AA}$  to  $15\text{\AA}$  in **Figure 2**. This increase in basal spacing is explained by the substitution of single water between the sheets of raw Maghnite by two interlamellar water layers in Mag-H<sup>+</sup>.<sup>21</sup>

#### 2.1.2 Infrared Spectroscopy (IR)

Infrared analysis of Mag-H<sup>+</sup> compared to raw Maghnite in **Fig. 3** shows the appearance of a large band at  $3400\text{--}3600\text{cm}^{-1}$  which indicates the hydrated structure of Mag-H<sup>+</sup>. The infrared analysis spectrum of raw Maghnite and Maghnite-H<sup>+</sup> indicates that the band observed at  $3400\text{--}3600\text{ cm}^{-1}$  corresponds to OH groups bonded to octahedral aluminum. The intense band at  $1004\text{ cm}^{-1}$  corresponds to the valence vibration of Si-O in the tetrahedral layer. A low intensity band at  $780\text{ cm}^{-1}$  is attributed to tetravalent silicon due to the presence of amorphous silica. The comparison of the intensities of this band in the spectra of the treated and untreated Maghnite makes it possible to deduce that there is an alteration of the structure. This is reflected by the increase of this intensity during the acid treatment.<sup>22</sup>



**Fig. 2.** X Ray diffractogram of Raw-Maghnite (A) and Maghnite-H<sup>+</sup> 0.25 M (B)

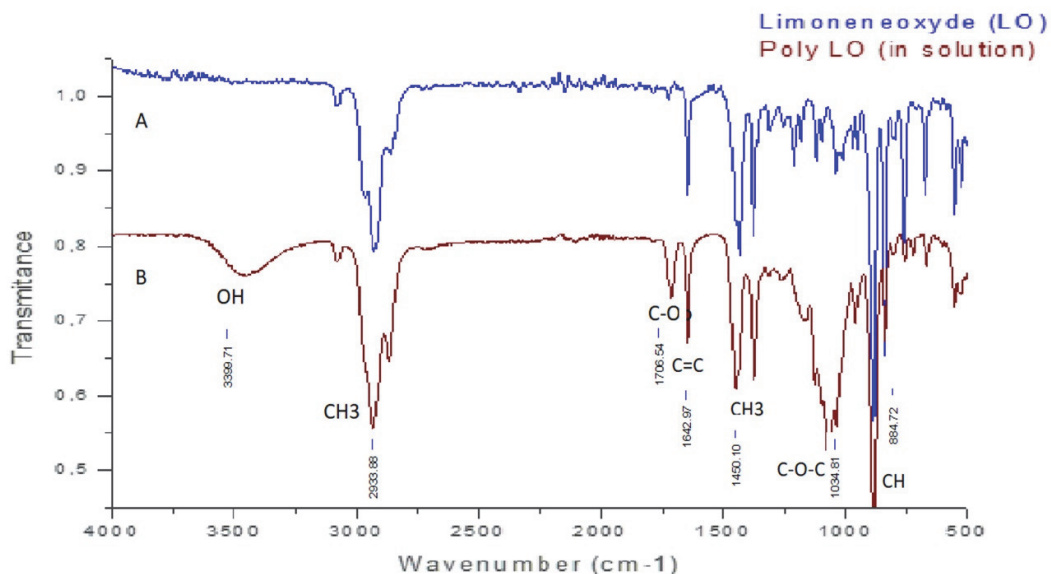


**Fig. 3.** FTIR spectrum of Raw-Maghnite (A) Maghnite-H<sup>+</sup> 0.25 M (B)

## 2.2. Results of PLO

### 2.2.1 Infrared Spectroscopy (IR)

The IR spectra in **Fig. 4** depicts the superposition of the monomer LO (A) and the PLO (B) obtained in solution using dichloromethane as solvent. LO and PLO have shared characteristic bands at 1450 cm<sup>-1</sup>, 2933 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> corresponding to the bond of CH<sub>3</sub> and C=C respectively. For PLO, new bands appear in the spectrum at 1700 cm<sup>-1</sup>, 1034 cm<sup>-1</sup> and 3399 cm<sup>-1</sup> that can be attributed to C-O, C-O-C and OH bonding respectively. These results confirm the opening of the epoxide ring and the formation of the PLO with hydroxyl ends. If these results are compared with the results of alpha pinene oxide; which is part of the monoterpenes; it can be seen that the same results are provided, namely the bonds (OH, CH ethylenic, CH of group CH<sub>3</sub>, (R)<sub>3</sub>CH, C = C, CO).<sup>23</sup>

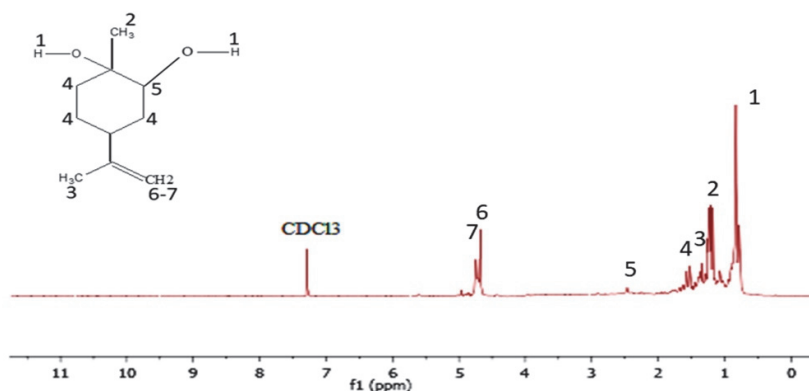


**Fig. 4.** FTIR spectra of limonene oxide, poly limonene oxide

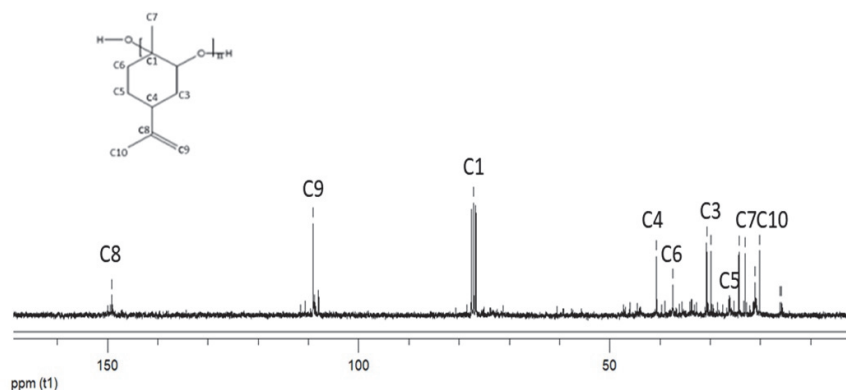
### 2.2.2 NMR Analysis

The chemical displacement of the protons  $^1\text{H-NMR}$  of the PLO is shown in **Fig. 5**. There are appearances of peaks at 1.68-1.73 ppm and 4.62-4.66 ppm attributed to the methyl protons and vinylidene protons respectively of the pendant isopropenyl ( $\text{CH}_3\text{-C}=\text{CH}_2$ ) groups. A peak at 1.31 ppm in the polymer spectrum also appears and is assigned to the methyl protons at  $\text{C}_1$  carbon ( $\text{CH}_3\text{-C}_1$ ) of cyclohexane rings. The conservation of the vinylidene double bond peak in the spectrum of PLO can confirm that the polymerization does not occur through the double bond but by ring opening of the epoxide function.

The PLO  $^{13}\text{C-NMR}$  spectrum shown in **Fig. 6** represents the characteristic peaks of the PLO. If the polymerization takes place through the epoxide group as expected in the  $^1\text{H-NMR}$  and IR spectra, the repeating unit will be as indicated **Scheme 1** with the retention of the isopropenyl group in  $\text{C}_4$ . In our case, the  $^{13}\text{C-NMR}$  peaks of  $\text{C}_8$ ,  $\text{C}_9$  and  $\text{C}_{10}$  of the isopropenyl group have chemical shifts located at 149.12 ppm, 109.10 ppm and 20.19 ppm respectively. These results reinforce the conclusion drawn previously from the studies of  $^1\text{H-NMR}$  and IR of the PLO. The same results are obtained by Aikins and al.<sup>6</sup>



**Fig. 5.**  $^1\text{H-NMR}$  spectrum of PLO prepared in solution at  $0^\circ\text{C}$  for 1h



**Fig. 6.**  $^{13}\text{C-NMR}$  spectrum of PLO prepared in solution at  $0^\circ\text{C}$  for 1h

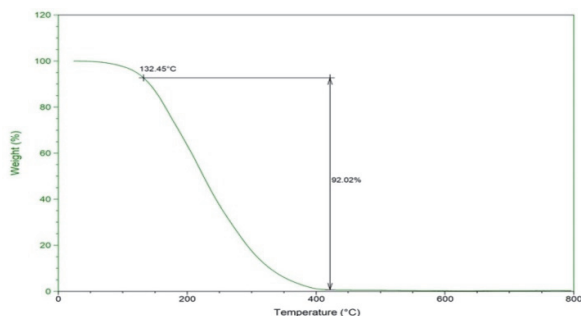
### 2.2.3 TGA Analysis

The thermal stability of the obtained PLO is illustrated in **Fig. 7**. The TGA curve obtained is the representation of the relative mass loss as a function of the heating temperature. It can be observed that the PLO is thermally stable with a degradation start temperature greater than  $130^\circ\text{C}$ . After this

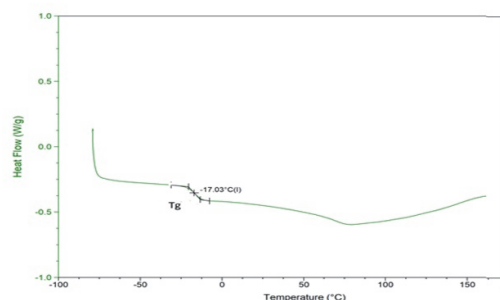
temperature, it begins to degrade in one major step due to the decomposition of its polymeric chains. The degradation rate of the PLO is increased with increasing temperature and it reaches the maximum at 400 °C. This degradation in a single major step also indicates that the product obtained does not keep any trace of solvent or LO starting product knowing that the boiling point of LO is 113 °C and that the evaporation temperature of the solvent dichloromethane is of 40 °C. These two temperatures are different from those shown on the curve, hence confirming the formation of a new PLO product more stable than LO.<sup>13</sup>

#### 2.2.4 DSC Analysis

**Fig. 8** shows the result of the differential scanning calorimetry (DSC) measurement carried for the sample obtained in dichloromethane at 0 °C using 5% of Mag-H<sup>+</sup> for 1h. The glass transition temperature (T<sub>g</sub>) of the PLO is observed at the range temperature of -17.03 °C. The DSC study of the PLO sample made it possible to demonstrate its flexible nature at low temperature.



**Fig. 7.** TGA curves of PLO prepared in solution at 0 °C for 1h



**Fig. 8.** DSC curves of PLO prepared in solution at 0 °C for 1h

### 2.3. Kinetic study

#### 2.3.1 Effect of reaction time

**Fig. 9** shows the variation in the polymerization yield as a function of the reaction time, which is defined as: (amount of polymer/initial amount of monomer) x100%. In the first step during 60 min of the reaction, the polymerization is accelerated and the yield is reached at a maximum of 60%, and then it decreases to 43% until 90min. In the last step, the evolution of the reaction remains almost constant with a yield of around 40%. The decrease in the yield over time can be explained by chain transfer reactions or by depolymerization reactions.

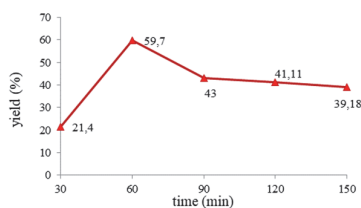
#### 2.3.2 Effect of Mag-H<sup>+</sup> content

According to **Fig. 10**, it has been observed that the variation of the yield as a function of the Mag-H<sup>+</sup> amount proceeds through two states: an increase then a decrease of the yield. When the catalyst amount is between the interval 1% and 5%, the highest yield observed is around 60%. The use of a higher amount of Mag-H<sup>+</sup> beyond 5% causes a lowering of the yield because the catalyst may cause secondary reactions other than the LO polymerization. Otherwise, Aikins found almost the same evolution in the yield of the LO polymerization as a function of the irradiation dose, where a maximum yield of 80% at 1.355 Mrad is obtained.<sup>6</sup>

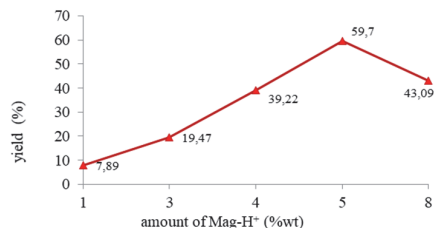
#### 2.3.3 Effect of reaction temperature

**Fig. 11** shows the yield variation as a function of the temperature varying from -10 °C to +25 °C. The influence of temperature on the yield of LO polymerization is studied in solution with 5% Mag-H<sup>+</sup> for 1h. The yield reaches its maximum of 61% at 0 °C. This temperature is considered as the ceiling

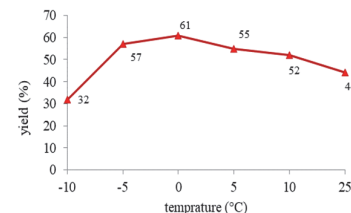
temperature ( $T_c$ ) of cationic polymerization by opening the LO cycle beyond which the yield begins to decrease by up to 44% at 25 °C. It should be noted that at -10 °C, the yield is low 32%, which can be explained by the very viscous state of the monomer at very low temperatures. This condition can hinder the LO polymerization process. On the other hand, Aikins<sup>6</sup> found that during the polymerization of LO by process irradiation at (-78 °C and -196 °C), that the yield is very low, between 2% and 12%. This has been explained by the glassy state of the monomer at these temperatures, thus preventing polymerization.



**Fig. 9.** Effect of reaction time on the yield of PLO



**Fig. 10.** Effect of catalyst percentage on the yield of PLO



**Fig. 11.** Effect of temperature on yield of PLO

### 3. Conclusions

In this paper, the polymerization of limonene oxide based on the use of a natural catalyst called Maghnite is described. By using an activated Maghnite with sulfuric acid, a good catalyst for cationic polymerization is obtained. It has the advantage of being ecological, economical, regenerable by simple filtration. The results of this work demonstrate that a simple method of polymerization with this green catalyst is successfully synthesized in mild conditions. The optimal conditions of the PLO synthesis to obtain the best yield around 61% are 5% of mag-H<sup>+</sup> during 1h using dichloromethane as solvent at 0 °C. It is noted that a synthesis of the PLO is also carried out in bulk with 5% of Mag-H<sup>+</sup> during 1h at ambient temperature, giving a yield of 50%. The structure of the obtained bio-based polymer is perfectly confirmed by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR. It is shown that the polymerization occurs by opening the epoxy function of the LO without touching the double bond. The thermal properties are given by DSC and TGA analysis. The PLO presents a glass transition temperature  $T_g$  of -17.03 °C and a degradation temperature start of 130 °C. The study of the influence of the synthesis parameters such as the amount of catalyst, the reaction time and the temperature have shown that the yield decreases when the amount of catalyst exceeds 5% and the reaction time exceeds 1h. As for the temperature, the yield is important at 0 °C.

## 4. Experimental

### 4.1. Materials and Methods

LO, methanol and dichloromethane are purchased from sigma-aldrich and are used as received. Raw Maghnite Algerian montmorillonite clay comes from a quarry located in Maghnia; north-west of Algeria; and it is supplied by ENOF; the Algerian factory specialized in the production of non-ferric products and useful substances.

### 4.2. General procedure

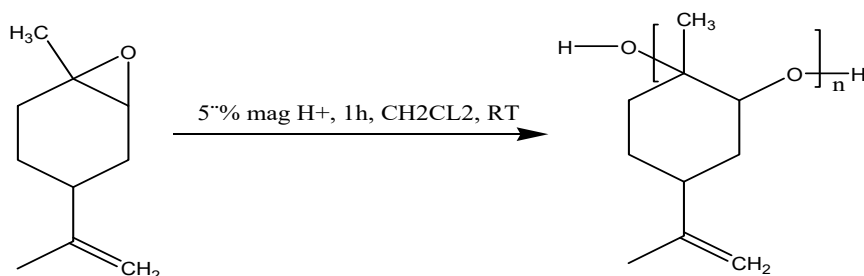
#### 4.2.1. Preparation of Maghnite H<sup>+</sup>

The preparation of the Mag-H<sup>+</sup> is carried out using a method similar to that described by Belbachir and al.<sup>11</sup> A mass of 30g of raw Maghnite is dispersed in 500ml of distilled water. The mixture is stirred using a magnetic stirrer for 2h at room temperature, then 14ml of a solution of sulfuric acid is added and made up to 1000ml. The stirring is continued for 48h and then the mineral is filtered off and washed

several times with distilled water up to pH 7. After filtration, Mag-H<sup>+</sup> is dried in an oven for 24h at 105 °C and is then crushed.

#### 4.2.2. Synthesis of Poly limonene oxide

Cationic ring opening polymerization of limonene oxide in the presence of Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>) as a catalyst is carried out in bulk and in dichloromethane solvent under different conditions to study the effects of different synthesis parameters. In bulk, 1g of LO and 0.05g of Mag-H<sup>+</sup> are mixed and kept under stirring for 1h. In solution, three series of PLO are prepared by dissolving 1g of LO in 10ml of dichloromethane. For each series, the quantity of the catalyst is varied as well as the temperature and the reaction time respectively as shown in **Table 2**. At the end of each reaction, the Mag-H<sup>+</sup> is recovered by filtration and then the sample dissolved in dichloromethane is precipitated in cold methanol. The precipitated polymer is separated by the evaporation of solvents. The obtained polymer is a yellow viscous liquid as in **Scheme 1**.



**Scheme 1.** Polymerization reaction of LO

**Table 2.** Experimental conditions of the PLO in solution

Mag-H <sup>+</sup> (wt %)	Time (min)	T (°C)	Yield(%)
1	60	20	7.89
3	60	20	19.47
4	60	20	39.7
5	60	20	59.7
8	60	20	43.09
5	30	20	21.4
5	90	20	43
5	120	20	41.11
5	150	20	39.18
5	60	-10	32
5	60	-5	57
5	60	0	61
5	60	5	55
5	60	10	52
5	60	25	44

#### 4.3 Physical and Spectral Data

The X-ray diffraction (XRD) patterns of the samples are carried out at room temperature on a Bruker D8 Advance X-ray diffractometer (40kV, 30mA) with a graphite monochromator using CuK $\alpha$  radiation ( $\lambda = 0.154$  nm) at a rate of  $5^\circ \text{ min}^{-1}$  in the range of  $2\theta = 2^\circ \text{C} - 80^\circ \text{C}$ . The Infrared (IR) analysis of the polymers obtained is conducted using a Bruker Alpha FT-IR spectrometer equipped with an attenuated total reflection (ATR) Diamond accessory. The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) measurements are carried on a 300MHz Bruker NMR spectrometer; It is to note that the CDCL<sub>3</sub> tetramethylsilane (TMS) is used as the internal standard in these cases. The thermogravimetry (TGA)



analysis is conducted by TGA 500 V 20.10 Build 36, for the PLO starting with the temperature of 0 °C up to 800 °C. The mass of the sample to be analyzed is 9.9780mg. The polymer thermal stability is evaluated using the calorimetric analysis (DSC) Q200 V 24.4 Build 116. The heating rate is 10 °C/min from (- 100 °C) under N<sub>2</sub> and the sample weighed about 5mg.

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