



Research Article

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## Polymerization of alpha pinene oxide catalyzed by maghnite $H^+$

Bekhemas Kheira, Hachemaoui Aicha and Yahiaoui Ahmed

Laboratory of Organic Chemistry, Macromolecular and materials, Faculty of Science and Technology, Route Mamounia, Mascara-Algeria

### ABSTRACT

*The main goal of this work is to study the cationic polymerization of terpenes, particularly alpha pinene oxide with heterogeneous catalyst maghnite  $H^+$ . In order to find the optimal reaction conditions and improve the productivity of poly ( $\alpha$ -pinene oxide) we studied the influence of the amount of catalyst, time, temperature and solvent on the yield. The resulting polymers were characterized by different analysis methods:  $^1H$  NMR and infrared spectroscopy (IR) confirmed the structures of the synthesized products.*

**Keywords:** Alpha pinene oxide; heterogeneous catalysis; poly (alpha pinene oxide); terpenes. Cationic polymerization.

### INTRODUCTION

Terpenes are one of the vastest families of organic compounds, produced by various plants, particularly conifers, but also by some insects, marine micro-organisms and fungi. Most terpenes are derived from isoprene (2-methyl-1, 4-butadiene, see Figure 2-1), which can be linked together “head to tail” to form linear chains and rings. Many terpenes have been used as components in natural agricultural pesticides, as green solvent [1], and in flavours and fragrances [2].

The first reported polymerization of terpenes was in 1798, when Bishop Watson added a drop of sulphuric acid to terpene and produced a sticky resin [3]. In 1950, William Roberts studied the cationic polymerization of limonene,  $\alpha$ -pinene and  $\beta$ -pinene with Friedel-Crafts type catalysts (such as  $AlBr_3$ ,  $SnCl_4$  and  $ZnCl_2$ ), using toluene as a solvent. [4]

Several other terpenic components have been submitted to cationic polymerization. These include terpene oxides. The cationic polymerization of  $\alpha$ -pinene oxide, using  $BF_3$  or  $PF_5$  as initiators proceeded through the initial protonation of the oxirane oxygen atom followed by the isomerization of the oxonium ion to give the tertiary exocarbenium ion responsible for the chain growth, [3].

The purpose of this paper is to study the cationic polymerisation of POAPIN using a montmorillonite clay which has undergone a proton exchange process (mag- $H^+$ ), a new, non-toxic cationic catalyst for heterocyclic monomers [5]

### EXPERIMENTAL SECTION

#### 2.1. Apparatus

IR spectra of the monomer and the polymers as thin films or KBr pellets were recorded with a ATI Matson FTIR N°9501165 spectrometer.  $^1H$  and  $^{13}C$  nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in  $CDCl_3$ . Tetramethylsilane (TMS) was used as the internal standard in these cases.

## 2.2. Materials

Pinène oxide (2,3-epoxypinane ) (Merck)), was dried over calcium hydride and distilled under reduced pressure before use. Dichloromethane, Chloroform, Carbon tetrachloride,

Acetonitrile and toluene were purified following standard techniques and used after distillation over their respective drying agents. Methanol was used as received.

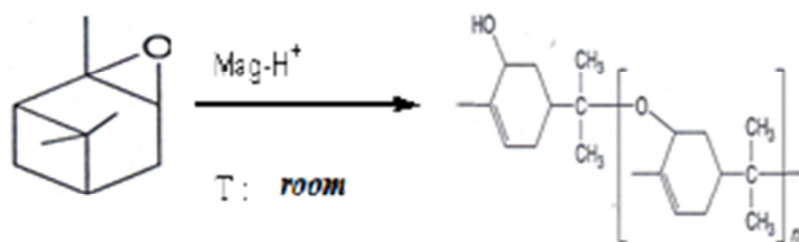
The clay, which has been used as catalyst, is supplied by a local company known as ENOF Maghnia (Western of Algeria). Its chemical composition is given in Table 1. The greatest proton saturation of the <2 mm fractions of clay were obtained by first saturating with Na<sup>+</sup> ions using 1M NaCl solution, then the protonated forms of montmorillonite (Mag-H<sup>+</sup>) were prepared by shaking the clay in a solution of sulfuric acid 0.25M until saturation was achieved (normally after 2 days at room temperature). The cation-exchanged clay was then recovered by filtration, and again suspended in deionized water. This process was repeated until no sulfate ions were indicated present in the filtrate using BaCl<sub>2</sub>. The Mag-H<sup>+</sup> was then isolated by filtration, dried at 105 °C and then finely ground. The cation exchange capacity (CEC) and surface area of the clay was found to be 84 mEq (100 g)<sup>-1</sup> of dried clay and 786 m<sup>2</sup>.g<sup>-1</sup> respectively.

## 2.2 Catalyst preparation

Montmorillonite clay, or 'raw-maghnite' was obtained from ENOF Maghnia (Western of Algeria). The preparation of the "Maghnite-H<sup>+</sup>" was carried out by using a method similar to that described by Belbachir and al [6] by shaking the clay in a solution of sulfuric acid until saturation was achieved (normally after 2 d at room temperature). The cation exchanged clay was then recovered by filtration, and again suspended in deionized water. This process was repeated until no sulfate ions were indicated present in the filtrate using BaCl<sub>2</sub> the mag-H<sup>+</sup> was then isolated by filtration, dried at 105 °C and then finely ground.

## 2.3. Polymer preparation

In a flask containing a mass of alpha-pinene oxide, we pay an amount of Mag-H<sup>+</sup> previously well dried for 30 minutes in the oven at 105C °, allowed all the stirring for 24 hours at room temperature (scheme 1).



Scheme 1: Polymerization of Pinène oxide by Maghnite-H<sup>+</sup>

At the end of the reaction, the mixture is filtered, and at the same time washed with a solvent to recover the catalyst. To remove the solvent from the mixture an apparatus which is a rotary evaporator is used.

## RESULTS AND DISCUSSION

The poly (alpha pinene oxide) was prepared from alpha-pinene oxide using Maghnite H<sup>+</sup> as catalyst. The experimental conditions and results are reported in Table.1

Experiences	OAPIN(g)	Mag-H <sup>+</sup> (% by weight)	Solvent	Yield
POAPIN1	1	3	/	71
POAPIN2	1	3	chloroforme	61
POAPIN3	1	3	dichloromethane	63

The polymer obtained was a viscous yellow liquid.

### 3.1. Characterization of Products

#### FT-IR spectroscopy:

The main IR bands with their attributions of the polymer prepared poly (alpha pinene oxide) are show in Figure 1.

The POAPIN is essentially characterized by the main bands situated at (3400 cm<sup>-1</sup>, 3036 cm<sup>-1</sup>, 2990 cm<sup>-1</sup>, 1446 cm<sup>-1</sup>, 1680 cm<sup>-1</sup>, 1027 cm<sup>-1</sup>) corresponds to the stretching vibration of bonds (O-H, C-H ethylenic, C-H de groupe CH<sub>3</sub>, (R)<sub>3</sub> C-H, C = C, C-O), respectively.

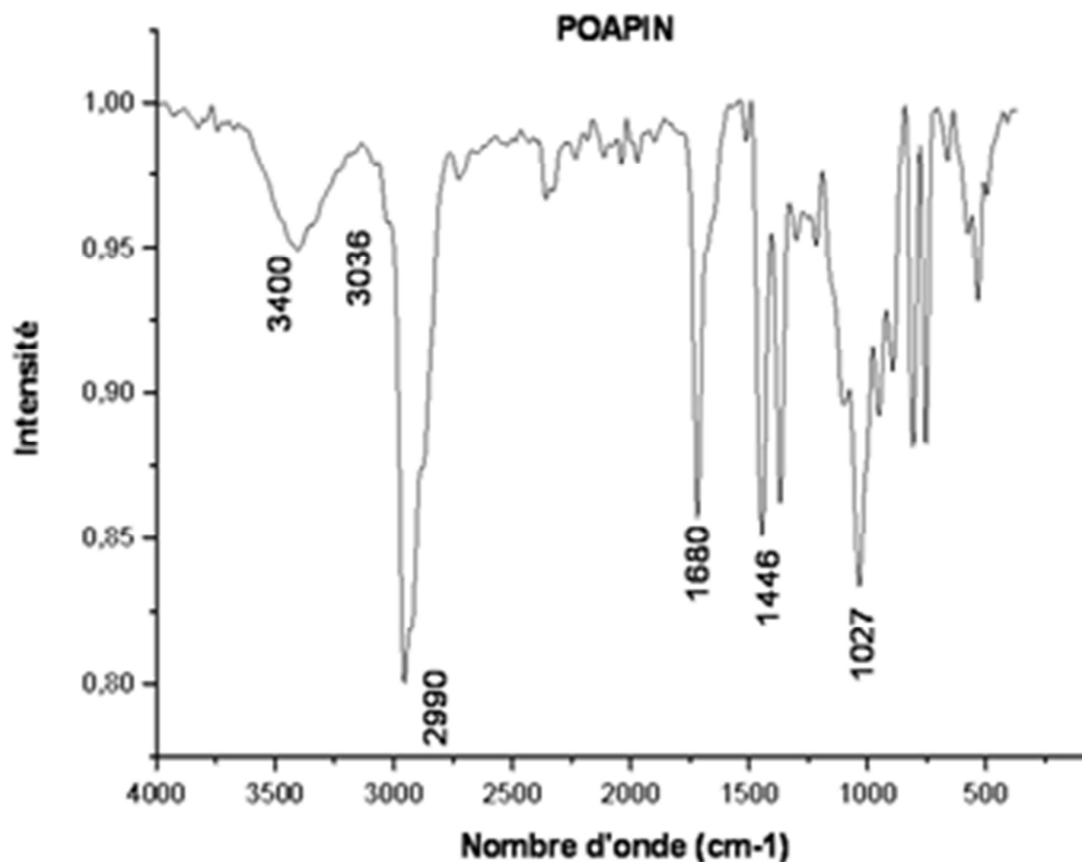


Figure. 1. FT-IR spectrum of POAPIN

#### H-NMR Study:

The poly (oxide of  $\alpha$ -pinene) prepared was analyzed by <sup>1</sup>H NMR (300 MHz). The <sup>1</sup>H-NMR spectra of POAPIN were obtained to further investigate and confirm the proposed structure.

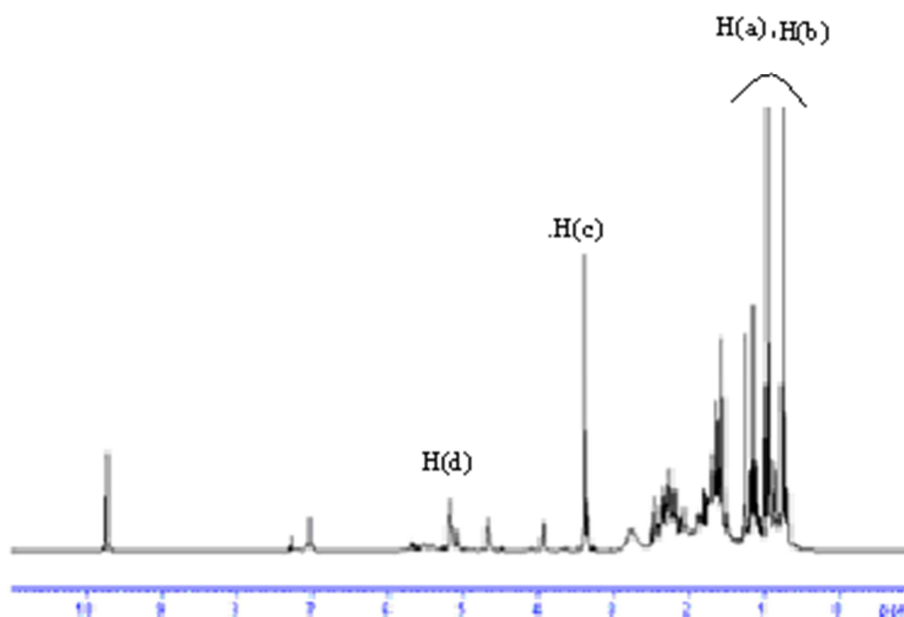


Figure. 2: <sup>1</sup>H-NMR spectrum (300 MHz) de POAPIN

Figure 2 gives the spectrum NMR proton H of the POAPIN obtained during polymerization, clearly shows:

- A signal between 0.9 and 1.5 ppm as interfered several peaks corresponding to the protons of the methyl group and methylene. H (a) H (b)
- The methine groups, which are bound to an electronegative oxygen atom, overlap to form a multiplet between 3.2 - 3.3 ppm. H (c)
- The  $^1\text{H}$  NMR spectrum of the polymer shows signals of proton of double bond ethylenic at 5 ppm corresponds to the proton  $=\text{CH}$ ; the proton couples with the adjacent  $\text{CH}_2$  protons to give a doublet splits

#### Effect of the amount of Mag-H+

Figure.3 show the effect of the amount of Mag-H+ on the polymerization of OAPIN

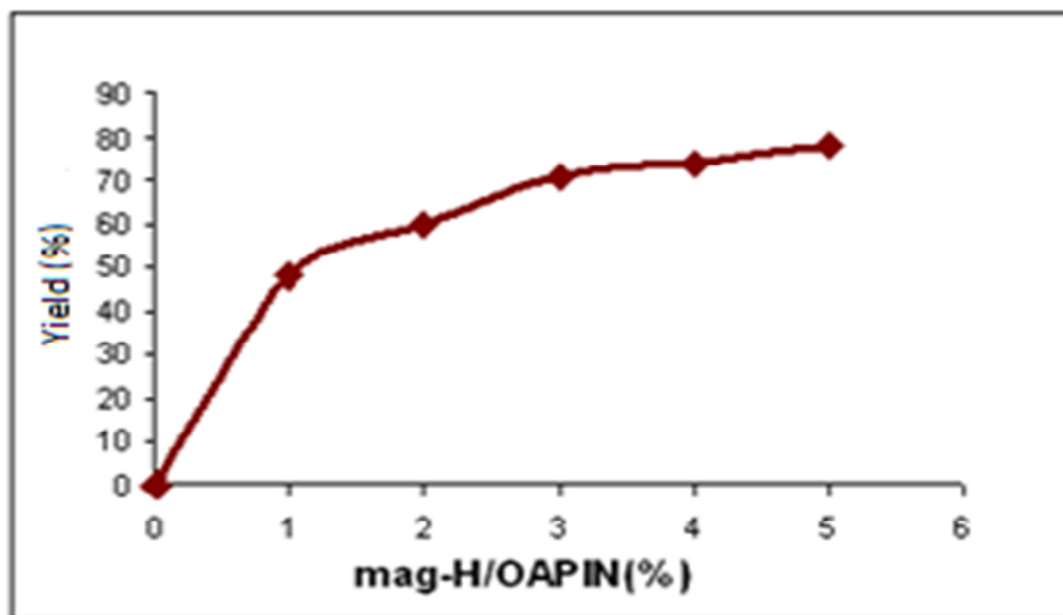


Figure 3. Effect of the amount of Mag-H+ on the yield of OAPIN polymerisation

From Figure 3 it is noted that, if we increase the amount of catalyst to monomer concentration constant this effectively increases the yield of polymer. Similar results are obtained by Yahiaoui *and al.* [7–10] in the polymerization of epichlorhydrin, propylene oxide and cyclohexene oxide by Mag-H+ and the polymerization of styrene by montmorillonite, respectively

This phenomenon is probably the result of the number of 'initiating active sites' responsible of inducing polymerization, this number is prorating to the catalyst amount used in reaction. This result is consistent with the work of NJOPWOUO and al. [11].

#### Effect of time

Figure 4 shows the yield of polymer versus time for polymerization of OAPIN using Mag-H+ as catalyst

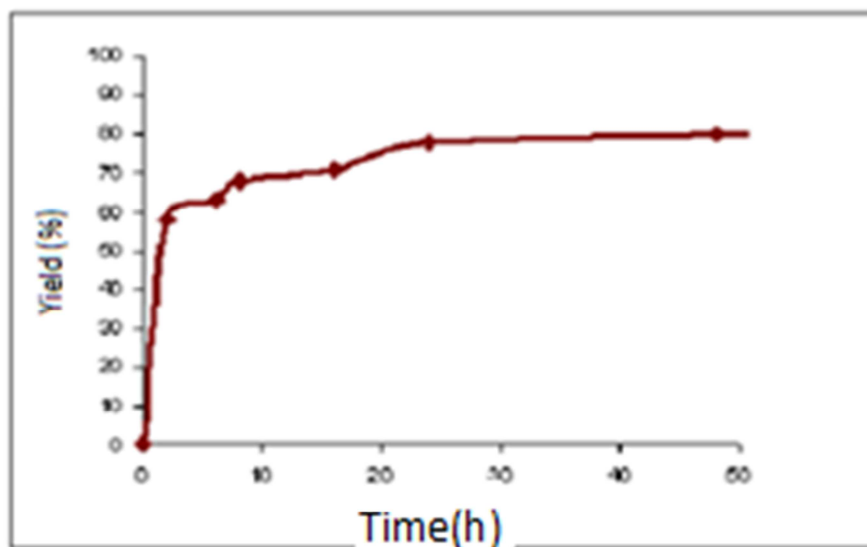


Figure 4. Change polymerization yield with time

As the figure 4 shows, polymerization takes place rapidly and smoothly, reaching a conversion of 58% after 2h, then it becomes slower. This allows conclude to a effective catalytic activity of  $\text{Mag-H}^+$  on the polymerization of OAPIN then it gradually slows down to 24 .The polymerization yield became constant at that time; this is probably the result of an increase in the medium viscosity. The curve of Figure 4 has the same shape as that obtained by Franta and al and, during the polymerization initiated by the PVR boron trifluoride ( $\text{BF}_3$ ) in the presence of ethylene glycol [12].

#### Effect of Temperature

From Figure 5 it is observed that the temperature has considerable influence on the polymerization therefore, an increase in temperature causes an increase in yield.

By increasing the temperature from 0 to 50 ° C, the yield increase from 15% to 74%.

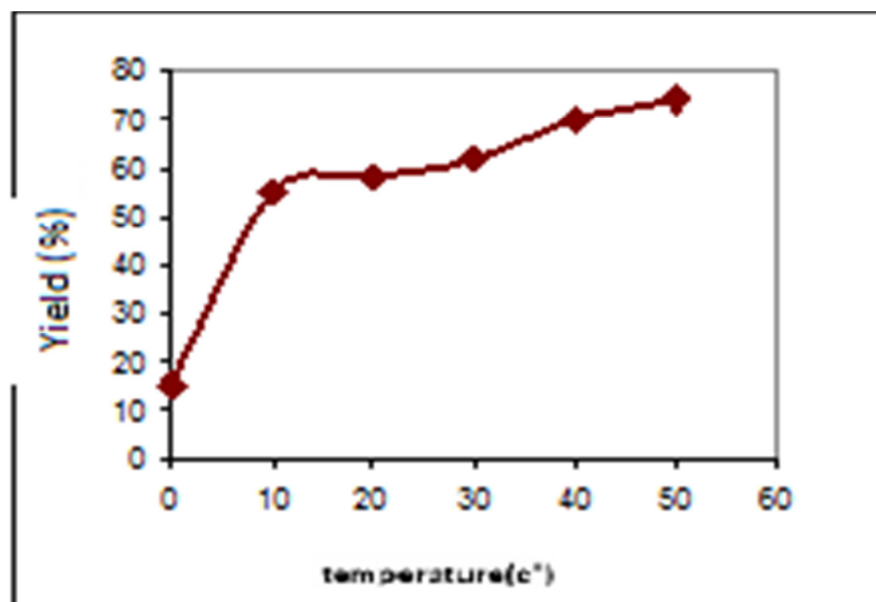


Figure 5. Effect of temperature on the yield of polymerization

#### 3.1.6. Effect of solvent

We Used a series of solvents with different dielectric constants: toluene ( $\epsilon = 2.38$ ), chloroform ( $\epsilon = 4.80$ ), acetonitrile ( $\epsilon = 37.5$ ), and dicloromethane ( $\epsilon = 9.1$ ).

The results are illustrated in figure 6.

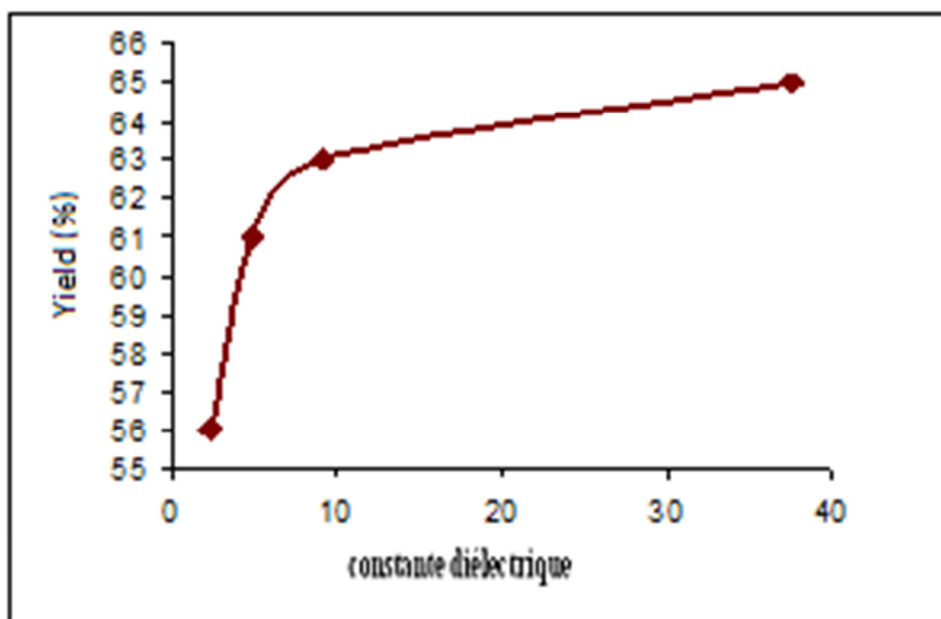


Figure 6. Solvent effect on the polymerization of OAPIN

We note that for this series of selected solvents, the yield is proportional to the dielectric constant, therefore solvents including high dielectric constant, promote the cationic polymerization of OAPIN. Similar results were found by Tsubokawa et al [13], in the polymerization of N-vinylcarbazole initiated by  $\gamma$ - poly (glutamic acid) and carbon black.

## CONCLUSION

In conclusion, we have found that maghnite  $H^+$  is effective as catalyst for the ring opening polymerization of POAPIN, which is a chemically and thermally stable catalyst having a proper mechanical resistance and non-toxic. The polymerization proceeds smoothly, and a simple filtration is sufficient to recover the catalyst; the structure of polymers was confirmed by  $^1H$ -NMR and IR.

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