

SYNTHESIS OF POLY(TETRAHYDROFURAN- CO-EPICHLOROHYDRIN) USING AN ECOLOGIC CATALYST MONTMORILLONITE (MAGHNITE-H+)

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Abstract. The copolymerization of Tetrahydrofuran (THF) with Epichlorohydrin (ECH) catalyzed by efficient and environmentally friendly catalyst called Maghnite-H⁺ was investigated, in the presence of a natural Algerian montmorillonite clay modified H₂SO₄, known as Maghnite-H, as proton source, a non-toxic and an efficient catalyst for cationic polymerization of many vinylic and hetero-cyclic monomers, this ecological catalyst replaces usual toxic catalysts such as Lewis and Bronsted acids, the oxonium ion of tetrahydrofuran (THF) and (ECH) propagated the reaction of copolymerization, the operating conditions were opted in order to obtain a maximum yield of the linear polymer and a high average molecular mass as well. We have studied the kinetic of the reaction by the effect of the time, the temperature, the amount of Maghnite-H⁺ and the proportion of monomers according to the changes in yield and the intrinsic viscosity, the structure of polymers obtained was confirmed by IR analysis. ¹H NMR, the average molecular mass and the polydispersity indices were determined by GPC, after these kinetic studies and analyzes obtained, it is possible to propose at the end a reaction mechanism of the copolymerization.

Keywords: green catalyst; tetrahydrofuran; epichlorohydrin; montmorillonite; copolymerization

Introduction

Polymerization of several monomers of cyclic ethers leads to polymeric materials that are produced on an industrial scale (McGrath, 1991). Among the most striking examples are polymers of (ECH) (Chanda & Roy, 2008; Bailey Jr & Koleske, 1990), or (THF) (Dreyfuss, 1982), the polymerization of THF with cyclic monomers, in particular those of cyclic ethers and acetals allows the synthesis of a number of unlimited products. From a technical point of view, they are characterized by the high mobility of their chain, the preservation of the flexibility both in low and high temperatures a remarkable resistance to

ozone (Gensturk et al., 2017). These poly ethers such as the poly (epoxide), poly (oxetane) and the poly (THF) are Very important materials with applications in all the domains, going of the car industry and the paper-maker to the cosmetic and biomedical applications (Bennabi et al., 2017).

Several studies have been carried out on the cationic polymerization of ECH and THF in the presence of homogeneous catalysts. By giving some examples of these catalysis, boron trifluoride ether complexes (Imoto & Aoki, 1961), sulfonic super acids ($\text{CF}_3\text{SO}_3\text{H}$, FSO_3H , and ClSO_3H), methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) (Masuda et al., 1976), Pd(II) and Ni(II) α -diimine catalysts (Na et al., 2016), Metal alkyls $\text{TiCl}_3\text{-Al(C}_2\text{H}_5)_3$, $\text{VCl}_3\text{-Al(C}_2\text{H}_5)_3$ (Otto & Paravano, 1964), Heteropolyacid, 12-phosphotungstic acid (PW12) (Zhu et al., 2010), Metal Complexes (Darensbourg et al., 2008), $\text{AlCl}_3/\text{SbCl}_3$ (Lu et al., 1996) and 2-iodoimidazolium salts (Takagi et al., 2017).

2-(Chloromethyl)oxirane (ECH) was also polymerized by a cationic ring opening polymerization reaction using hydroxyl-terminated poly butadiene as initiator in block polymerization reactions (Min & Jeung, 2018). And in another example, the synthesis of the multiblock copolymers tetrahydrofuran components, are synthesized in one step by “Janus polymerization”, a new synthetic protocol. Janus polymerization comprises anionic and cationic ring opening polymerization (Qiu et al., 2017).

However, most of these cationic catalysts used in the synthesis of these copolymers are expensive (Hagen, 2006). They may be toxic, corrosive and the separation of the initiators from the polymer is not always possible (Dubé & Salehpour, 2014). Therefore, the presence of toxic initiators has problems in the manufacture of polymers used (Liu, 2006). In the present work, cationic ring opening copolymerization of THF with ECH induced by maghnite- H^+ (Belbachir & Bensaoula, 2001), an eco-catalyst proton exchanged montmorillonite clay. This new non-toxic cationic solid catalyst (Moosavi, 2017) has exhibited higher efficiency via the cationic polymerization of vinylic and heterocyclic monomers (Kheroub et al., 2018), in the solid catalysts, several derivatives based on silica such as aluminium minerals and zeolites are reported to be effective for the ring opening reaction leading to 1,2-difunctionalized compounds from oxiranes (Iwasa et al., 2008; Zaharri et al., 2013). The treatment of acid-montmorillonite also leads to a redistribution of particle sizes and modifies the pore system. The results of studies have shown that bentonite clays (Maghnite- H^+) retain a significant portion of their adsorption properties, even after prolonged and intense thermo chemical treatment (Krupskaya et al., 2016), Maghnite- H^+ has been used as a catalyst in the synthesis of several polymers and copolymers (Bennabi et al., 2017).

The reaction can be proved by concordance with the analyses of the end product. A kinetic study will allow us to see the variation of the performance

and the intrinsic viscosity under different experimental conditions. This study will enable us to see the efficacy and the influence of Maghnite- H^+ in each reaction of these copolymerizations. We will know how is the condition to have the copolymer with good yield. A mechanism will be suggested for the resulting reaction of copolymerization induced by Maghnite- H^+ according to the discussion and the results of product analysis.

Experimental section

Material

ECH (99%) and THF (99%) were used as purchased from Aldrich. The Maghnite- H^+ (MMT- H^+) used in this work came from a quarry located in Maghnia (North West of Algeria) and was supplied by the company “ENOF” (Algerian manufacture specialized in the production of no ferric products and useful substances)

Preparation of Maghnite- H^+

The montmorillonite lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet (Zhu et al., 2010; Darenbourg et al., 2008; Lu et al., 1996). The protons carried by Maghnite- H^+ in the interlayer space induce cationic polymerization, and the montmorillonite sheets play the role of counter-anions (Fig. 1).

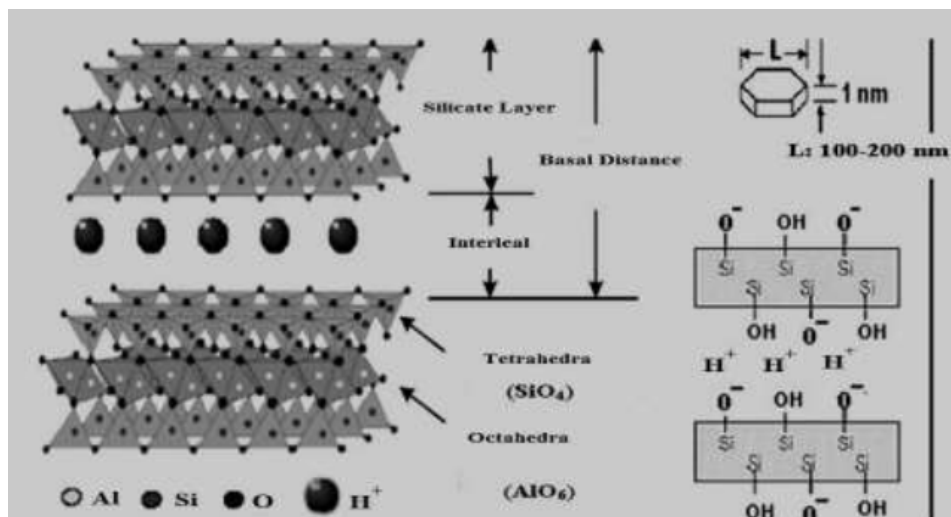


Figure 1. Schematic representation of Maghnite- H^+

The preparation of the Maghnite-H⁺ (0,23M) was carried out by using a method similar to that described by Belbachir & Bensaoula (2001). Indeed, the raw-maghnite (20 g) was crushed for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105°C for 2 h. The maghnite was then weighed and placed in an Erlenmeyer flask together with 500 ml of distilled water. The maghnite/water mixture was stirred using a magnetic stirrer and combined with sulfuric acid, until saturation was achieved over 2 days at room temperature, the mineral was washed with water until it became sulfate free and then dried at 150°C. The concentration 0,23M of sulfuric acid treatment solution was used to prepare 'Maghnite-H⁺ 0,23M'.

It has been found that there is an excellent correlation between the acid treatment and the catalytic activity of maghnite which results in the reduction of the octahedral content (Al₂O₃), and the increase of the proportion of silica (SiO₂). It should be pointed out that the best conversion monomer value was obtained with Maghnite-H + 0.23 M, in which there is a saturation of montmorillonite with protons without destruction of the catalyst structure (Belbachir & Bensaoula, 2001). For this reason, we used a concentration of 0.23 M.

Maghnite treated is hygroscopic; the presence of water trace makes him lose its effectiveness. For that, before each use, maghnite activated must be put in the drying oven with 105°C during two days, to eliminate the maximum of water.

Synthesis copolymer of ECH with THF

We carried out all the experiments in atmospheric pressure and without solvents. Into a small flask equipped with a magnetic bar, we introduced the THF and the ECH with the desired amount. We added quantity of Maghnite-H⁺ prescribed and we putted the whole under agitation. To give heat to the reactionals medium, one used an oil bath heating. The kinetic study was done by calculating the yield for the parameters: time, temperature, amount of catalyst, proportion of the monomers. Measurements of the intrinsic viscosity for some samples were made. The reactions of copolymerization were made in test tubes. The products obtained easily dissolves in the THF. Maghnite-H⁺ can be easily separated from the polymer by filtration. The solution was then dried by evaporation and the product was a viscous liquid with a brown colour.

In contrast to the more usually used catalyst and regenerated by heating to a temperature above 100°C. To calculate the yield, in the case of polymerization in chain, we divided the mass of polymer obtained by the initial mass of the monomers.

Characterization

An investigation was devoted to the analysis of the products from the experiments. The characterization was made using many analyses. Measurement

of ^1H -NMR spectra was conducted in CDCl_3 solution under ambient temperature on an AC 300 MHZ Bruker (USA) spectrometer using tetramethylsilane (TMS) as internal standard.

IR absorption spectrum was recorded on ALPHA FT-IR Bruker (USA) spectrometer with diamond ATR.

Gel permeation chromatography (GPC) Waters 510 HPLC Pump (USA) was performed using THF As a solvent, this technique has made it possible to determine the average molar masses (in number and in mass) of the polymers and to give the polydispersity index. The solvent used is THF with a flow rate of 1 ml/min. The molar masses are measured against polystyrene standards.

Viscosimetric analysis is performed and the measurements were made on a capillary viscometer, the viscometric (VISCOLOGIC TL1 Sematech® USA) chambers comprise a capillary type Ubbelohde dilution. This method allows experimental determination of molar mass viscosimetric polymer. Intrinsic viscosity and M_v are bound by Mark-Houwink's law: $[\eta] = k.M_v^a$, (k and a are specific constants for polymers, solvent and temperature).

Results and discussion

Interpretation of ^1H NMR analysis

Fig. 2 given the ^1H -NMR spectrum of the copolymer, the following chemical shifts were observed (Table 1).

A signal (b,c) located at $\delta = 1.62$ ppm corresponding to the two ethylenes in position 3 and 4 of THF ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$). The intense peak (d,a) at $\delta = 3.41$ ppm was assigned to the two ethylenes in position 2 and 5 of THF. The protons (CH_2) of ECH signal (g) appear at $\delta = 3.53$ ppm for (CH_2-Cl), the peak (e) appears to $\delta = 3.59$ ppm corresponds to the proton for CH_2-O . The peak (f) at $\delta = 3.96$ ppm was assigned to ($-\text{CH}-\text{O}$). The CDCl_3 appears at $\delta = 7.279$ ppm. Arguably singlet appeared at $\delta = 2.46$ ppm was due to the OH end of secondary products.

It was not already obvious to prove by NMR that there were no traces of monomers for analyzing polymer simple. The interpretation of NMR spectra of polymer solutions generally follows the same approach as for smaller molecules (Brandolini & Hills, 2000). But here, no traces of monomers can be proven in the samples analyzed. Absence of the two peaks of the ECH monomer from 2.6 to 3 ppm assigned CH_2 linked to the ring oxygen had disappeared. This proves that the ring opening polymerization of the ECH had happened at this level. And there weren't other reagents which remained in the analyzed samples, because the ECH was the last reagents drawn aside from the product during drying by its dominant boiling point. Something else, the reaction of copolymerization can be proven here easily:

We know that the ring opening polymerization of THF by Maghnite- H^+ lonely it was impossible, but when the AA was added, we will have Poly

(THF) (Ferrahi & Belbachir, 2004). THF was present in polymeric form in the ^1H -NMR spectrum (Fig. 2) of the purified sample from the reaction, these two reasons proved that actually had got a copolymer.

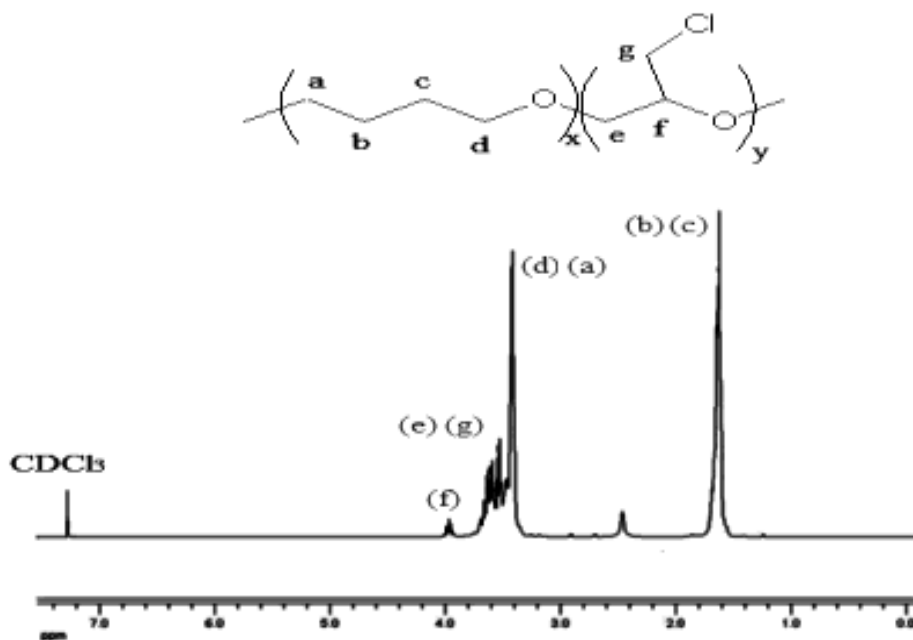


Figure 2. ^1H -NMR (300 MHz) in CDCl_3 of Poly (ECH-co-THF)

Table 1. Results obtained by ^1H -NMR

Index	monomer	Nature of the proton	Chemical Displacement δ (ppm)
d, a	THF	$-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$	3,41
b, c	THF	$-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$	1,62
g	ECH	$-\text{CH}_2-\text{Cl}$	3,53
e	ECH	$-\text{CH}_2-\text{O}-$	3,59
f	ECH	$-\text{CH}-\text{O}-$	3,96

Interpretation of infrared analysis

Spectroscopy (IR) is one of the most important methods of analysis used in the analysis of polymers (Holland-moritz & Siesler, 1976), Infrared analysis (Fig. 3) of purified polymer had given the following results.

The presence of the ether function was shown by the band at 1090.98 cm^{-1} . Binding (CH) in the methylene chain of the polymer was shown in three areas: at

1431.62 cm⁻¹ to shear deformation at 2939.24 cm⁻¹ asymmetrical stretching and 2863.73 cm⁻¹ for symmetrical. The strong band to 742.61 cm⁻¹ corresponded to the bond (C-Cl).

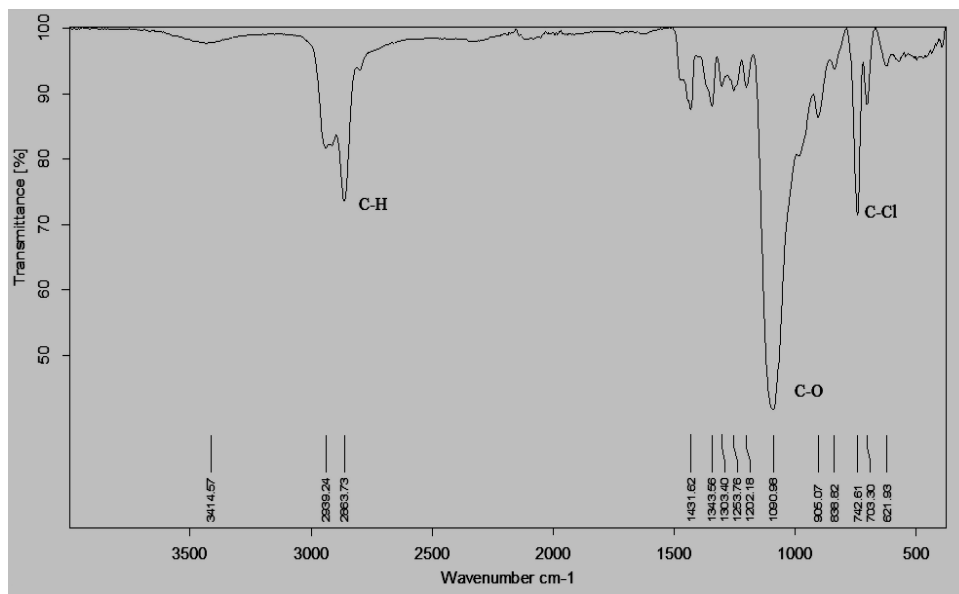


Figure 3. IR spectrum of Poly(ECH-co-THF)

Interpretation of gel permeation chromatography (GPC) analysis

As can be expected, the properties of the polymers are directly related to their size, shape, composition and uniformity (Aaserud et al., 1999; Hammond et al., 1975). Any synthetic polymer is a mixture of molecules of different sizes and molecular weights depending on the number of repeating units of the monomer incorporated in its structure (Oadian, 2004).

The GPC makes it possible to give the distribution of the molar masses as well as the Mn, the Mw and the polydispersity index of the polymer analyzed.

It also makes it possible, as in our case, to confirm the production of the copolymer and not a mixture of homopolymers. The following figure gives the GPC analysis of a sample of poly (THF-co-ECH).

The presence of a single band confirms the copolymer production and excludes having a mixture of two homopolymers which normally have to appear in two strips (Table 2).

The molar mass distribution is very narrow. This means that the strings Obtained are of neigh boring molar masses (Fig 4).

Table 2. Results obtained by GPC

Mn (g/mol)	Mw(g/mol)	I
22 265	28 156	1.2646

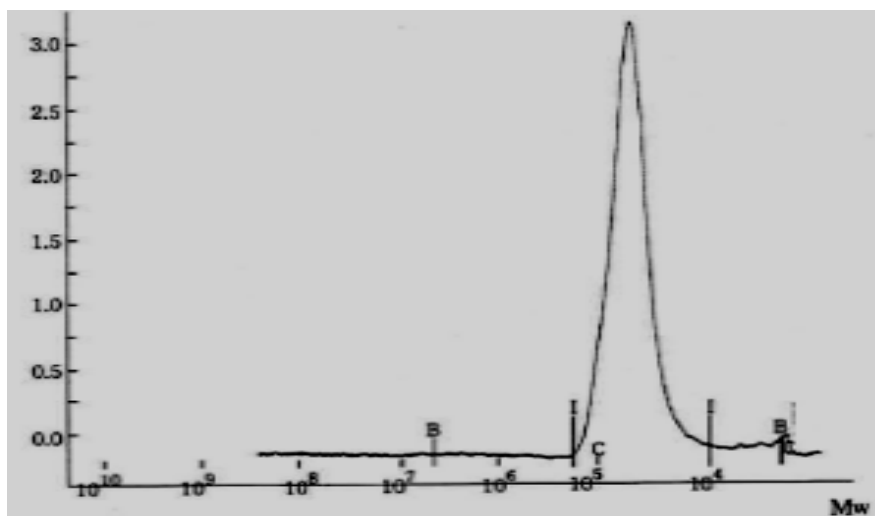


Figure 4. GPC curve of poly (ECH-co-THF) prepared with amounts Equimolar, 10% Maghnite-H⁺, T = 20 °C

Kinetic study of copolymerization

Effects of time

In Fig 5, we had seen that the evolution of the performance was very slow at the beginning of the copolymerization and accelerates from 6h of the reaction with a yield of 10.80%. This may be related to the initiation was slow as compared to propagation. A slight slowdown in performance was perceived and can be explained by the difficult movement of molecules on a formation of high molecular weight chains that increases the viscosity of the medium. This was happening in the final phase of the reaction (Moore Jr, 1959).

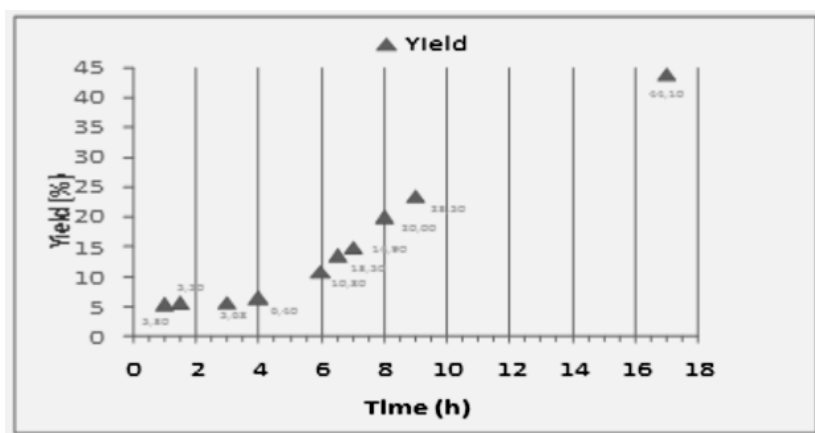


Figure 5. Effects of time in the yield of the copolymerization

Effects of the temperature

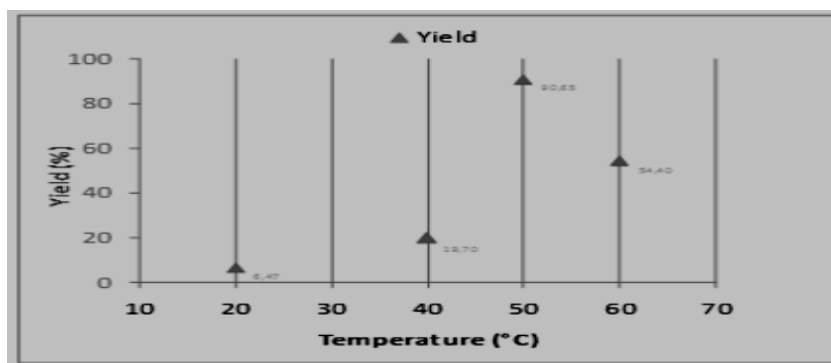


Figure 6. Effects of temperature in the yield of the copolymerization

The yield increases slowly from 20 °C to 40 °C, while it touches a maximum of 50 °C (Fig 6). This was due to the change in the balance (propagation / depropagation) for the formation of polymer. Reduction in yield at $T = 60$ °C was explained by the fact that the reaction was limited by the action of the temperature of the ceiling, where the rate of polymerization equals the rate of depolymerization (Höcker & Keul, 1995; Höcker, 2006).

Effects of the molar fraction of the monomers

The results clearly show the evolution of the performance of the copolymerization according to the molar fraction (Fig 7). It reached a maximum of 97.30% for the molar fraction 0.2 of THF. The yield decreases before and after this fraction.

The viscosity increases with the molar fraction of THF. We note that there was a large gap between the intrinsic viscosities of the two homopolymers.

With the Maghnite-H⁺, the reaction was done in a 16 both shorter time benefiting an additional yield of 30% and a viscosity 4 times higher at 50 °C compared to results obtained using Al(C₂H₅)₃-H₂O-ECH [29], for the same fraction of THF (25%), knowing they did the reaction at 20 °C.

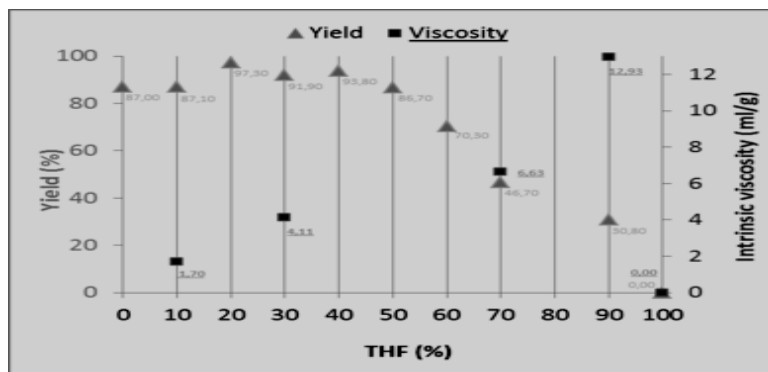


Figure 7. Effects of the molar fraction of the monomers in the yield and intrinsic viscosity of the copolymerization

Mechanism of the copolymerization

According to the foregoing discussion and the results of product analysis, the mechanism below may be suggested for the resulting reaction of copolymerization induced by Maghnite-H⁺ (Fig 8). Protons carried by montmorillonite sheets of Maghnite-H⁺ induced the polymerization; these montmorillonite sheets take place as counter-anions.

It should be remembered that occasionally, at the conditions when monomer cannot undergo homo polymerization, it may participate in copolymerization (Tsu-da & Yamachita, 1966).

Here, we had find the same phenomenon with THF. With the Maghnite-H⁺ as initiator, a small amount of acetic anhydride (AA) was required for the formation of PTHF (Ferrahi & Belbachir, 2004). But in our copolymerization, the (AA) was not essential.

On the whole copolymerization of ECH and THF under the conditions which we investigated obeys the laws of a cationic process. The typical mechanism of cyclic ethers polymerization was the active chain end (ACE) mechanism (McGrath, 1991).

The first stage was the protonation of ECH. Then a nucleophilic attack of an oxygen atom in a monomer molecule on a carbon atom in α -position to an oxygen atom (CH₂-O) of the protonated ECH (due to the steric effects) bearing formally the

positive charge in a tertiary oxonium ion located at the chain end. The formed ions oxonium take place in the vicinity of the counter-anion carried by montmorillonite sheets.

According to the bibliography (Saegusa et al., 1964), the ECH was initiated first and after it was essentially exhausted. The resulting species acted as a macro initiator and initiated the cationic polymerization of THF. The stage of homo polymerization of ECH began when the THF had been consumed in the copolymerization.

Conclusions

The spectrometric analyses $^1\text{H-NMR}$ as well as IR have made it possible to highlight the structure of copolymer and these results were in agreement with the former studies. Obtaining copolymer proves that the oxoniums ions of ECH initiated the reaction of copolymerization. An intermolecular transfert was observed in this reaction of copolymerization.

The reaction rate increases with temperature and amount of catalyst to the ceiling temperature of this reaction which is around 50°C .

The Maghnite- H^+ has a great catalytic activity. It allowed us to obtain extremely pure copolymer in good yield by following a simple experimental and safely condition. The results obtained in this work like in the work undertaken by Belbachir & Bensaoula (2001) shows well that this ecological catalyst is advantageous for the reaction of polymerization.

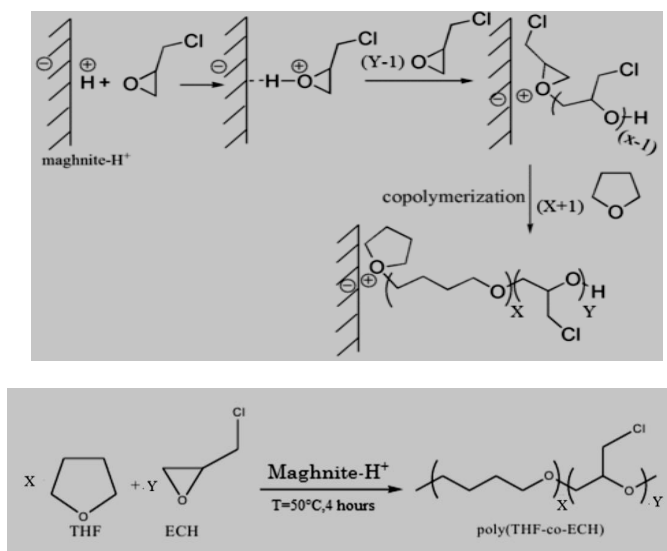


Figure 8. Mechanism suggested for the copolymerization of ECH with TH

Copolymerization reaches a maximum of 97.3 % of yield with 20% of THF and 80% of ECH at 50°C in 4 hours. We can notice the ease and cost-to carry out this reaction on an industrial scale.

The copolymerization between these different comonomers, can lead to a product whose entire physical, mechanical and chemical properties are news. Research on the physicals and chemicals properties could be carried out in order to find applications for this product: (a) three-membered ring compound might be added to a four- or five-membered ring compound to reduce the tendency of the polymer from the larger ring size to crystallize or to lower its melting temperature; (b) THF might be copolymerized with an energetic monomer like 3,3-bis(azidomethyl) oxetane to improve processing and modify its glass transition temperature.

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