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Cationic ring-opening copolymerization of propylene oxide with tetrahydrofuran by acid exchanged montmorillonite clay

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ABSTRACT

The copolymerization of propylene oxide (PO) with tetrahydrofuran (THF) catalyzed by Maghnite- H^+ ($Mag-H^+$) was investigated. $Mag-H^+$, a nontoxic catalyst for cationic polymerization of vinylic and heterocyclic monomers, is a montmorillonite silicate sheet clay. This catalyst was prepared through a straight forward proton exchange process. It was found that the copolymerization in bulk is initiated by $Mag-H^+$ at room temperature. Various techniques, including H^1NMR , IR, and Ubbelohde viscometer were used to elucidate structural characteristics of the resulting copolymers. The effects of the amount of $Mag-H^+$ and propylene oxide were studied. The copolymerization yield increased as the proportions of catalyst and propylene oxide were increased. Finally, a mechanism for the reaction was proposed.

Keywords: Cationic polymerization, Ring opening, Maghnite, Montmorillonite, Cyclic ethers, Propylene oxide, Tetrahydrofuran.

INTRODUCTION

The commercially important elastomers are amorphous homopolymers of epichlorohydrin, as well as copolymers and terpolymers of epichlorohydrin, ethylene oxide, propylene oxide, and allyl glycidyl ether. Polyether elastomers are used in automotive and industrial applications that require materials with low gas permeability, retention of flexibility at both low and high temperatures, and stability upon extended exposure to heat, hydrocarbons, and ozone [1].

A variety of reagents will catalyze the ring-opening oligomerization or polymerization of epoxides [2], including metal alkoxides [3], tin reagents [4], hydrolyzed zinc and cadmium alkyls [5], heterometallic cyanide complexes (e.g. $Zn_3Co(CN)_6$) [6], calcium amide-alkoxides [7], and neutral and cationic aluminum complexes supported by chelating ligands such as porphyrins [8], salen [9,10], diamidoamines [11], biphenolates [12], and others [13]. The inconveniences of many of these catalysts include high cost, poor polymerization activity, and generally, they are toxic. In order to avoid these disadvantages, acid-treated clays mineral, green catalysts, such as montmorillonite or kaolinite can be used as an alternative for the same reactions. Thus, acid-treated clays react as heterogeneous acid catalysts or catalytic supports. They were easy removal from the product. The proton-exchanged clays have both Brønsted and Lewis acid sites in the interlamellar zone and so are characterized by promoting acid-catalyzed reactions [13]. There are many examples of Brønsted acid catalyzed reactions carried out with commercially acid-treated montmorillonite catalysts [14-17]. Acid-treated clays mineral have been also successfully used as catalysts in polymerization of vinyl or heterocyclic [18-20].

Natural Maghnite has low catalytic activity but it is relatively easy to convert it into catalysts by a simple acid treatment giving thereby $Mag-H^+$. $Mag-H^+$ is a green catalyst, it was successfully used in cationic polymerization of

vinyl monomers and heterocyclic monomers [21-27].

In this article propylene oxide (PO) was selected for ring opening copolymerization with Tetrahydrofuran (THF), using Maghnite-H⁺ as catalyst. One advantage of copolymerizing THF with PO is the higher yield of polymers achievable compared to homopolymerization alone [28]. Other advantages included better elastomeric properties of polyurethanes compared to elastomers derived from PO homopolymers or PO-EO copolymers [29].

Moreover, this method has a double benefit, the first is that the catalyst can be easily separated later from the polymer product and regenerated by heating at a temperature above 100 °C and the second is the non-use of solvent. Indeed, the use of solvents produces largest amount of auxiliary waste in polymer science. Due to the fact that sustainable chemistry is becoming more and more important in polymer research, alternative reaction media have been investigated in order to eliminate, reduce or replace the use of organic solvents.

MATERIALS AND METHODS

2.1. Samples

Maghnite-H⁺, a montmorillonite silicate sheet clay, was obtained from the western part of Algeria and delivered by the National Company for Non-ferrous Mining Products ENOF. It was prepared according to the process described by Belbachir *et al.* [30]. Indeed, the raw-Maghnite (20 g) was crushed for 20 min using a prolabo ceramic balls grinder. It was then dried for 2 h at 105 °C. The Maghnite was 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 0.25 M sulphuric acid solution, until saturation was achieved over 2 days at room temperature, the mineral was then washed with distilled water to become sulphate free and then dried at 105 °C.

Tetrahydrofuran (THF 99%), 1,3-Dioxolane (DXL 99%), Propylene oxide (PO 99%), Epichlorhydrin (ECH 99%) and Chloroform (99%) were obtained from Aldrich and used as received.

2.2. Characterization

2.2.1. Characterization of Maghnite-H⁺.

The BET surface area and pore volume of sample were determined by Nitrogen sorption at 77 K using an ASAP 2020 V3.04 E from Micromeritics.

X-ray fluorescence (XRF): the chemical compositions of raw and acid activated Maghnite were determined by XRF using a PW 2400 Philips Analytical wavelength-dispersive sequential XRF spectrometer with SuperQ PANalytical software.

X-ray diffraction (XRD): the XRD spectrum was performed on oriented samples with a Bruker AXS D8 Advance diffractometer equipped with LynxEye linear detector, with Co K α 1 radiation ($\lambda=1.54056$ Å) and a scanning interval of $2\theta = 0^\circ$ to 70° and a scanning speed of $0.02^\circ/\text{s}$, at room temperature.

FTIR: the FTIR spectrum was recorded on an Alpha FTIR Bruker spectrometer ($400\text{--}4000\text{ cm}^{-1}$).

2.2.2. Characterization of copolymers

¹H NMR: the ¹H NMR spectrum was recorded at room temperature on a 300 MHz Bruker Avance spectrometer using CDCl₃ as solvent.

FTIR: the FTIR spectrum was recorded on an Alpha FTIR Bruker spectrometer ($400\text{--}4000\text{ cm}^{-1}$).

Intrinsic viscosity: viscosity measurements were carried out with an Ubbelohde capillary viscometer (Viscologic TI1, version 3-1 Semantec), in HFIP at 30 °C.

Gel permeation chromatography (GPC): The molecular weight and its distribution were determined by Gel permeation chromatography, using a Spectra physics RI SP8430 equipped with a polystyrene gel column (96000) and with tetrahydrofuran (THF) as an eluent at a flow rate of 0.80 ml/min at 25 °C.

2.3. Copolymerization of tetrahydrofuran with propylene oxide

The copolymers were synthesized by cationic ring opening polymerization of tetrahydrofuran (THF) with propylene oxide. The bulk copolymerization was carried out in sealed tubes at room temperature (20 °C). Each mixture was prepared with a weighted quantity of Mag-H⁺ dried just before use for 1h in a drying oven at 100 °C. Each tube contains a mixture of 7.21 g (0.1 mol) of THF, 5.8 g (0.1 mol) of PO and a certain percentage by weight of Mag-

H⁺/monomers. The molar ratio (*f*) of THF to PO ($f = n_{\text{THF}}/n_{\text{PO}} + n_{\text{THF}}$) was kept constant in all tubes. The mixture was stirred with a magnetic stirrer. When the reaction time was over, the reaction mixture was cooled. Purification and removal of unreacted monomer and low molecular weight polymers were carried out by dissolving the product in chloroform (CHCl₃) and filtering to eliminate the Mag-H⁺. Then, chloroform was removed by evaporation.

RESULTS AND DISCUSSION

The cationic ring opening copolymerization of THF with PO was examined in the presence of Mag-H⁺ powder in bulk at room temperature (Scheme 1). The polymers were obtained as highly viscous oils; similar results are obtained by H. Thomas *et al.* [31]. The results are shown in Table 1.

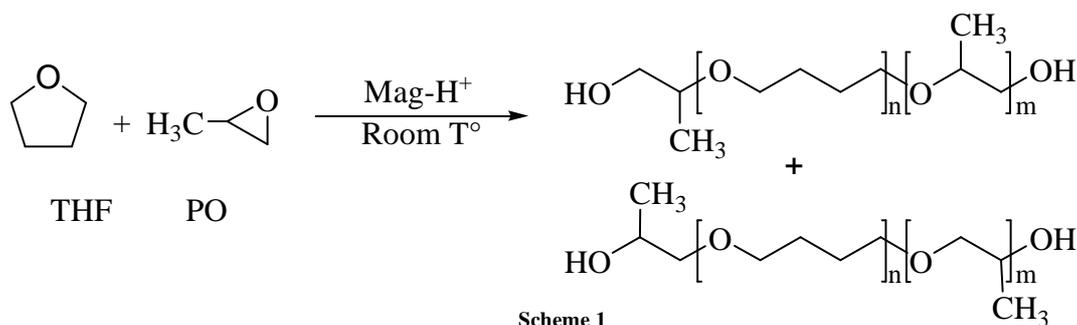


Table 1: Copolymerization of THF with epoxide induced by Mag-H⁺ (t = 24h)

<i>f</i>	m _{PO} (g)	m _{THF} (g)	m _{Mag-H⁺} (g)	Conversion%	M _n	M _w	I=M _w /M _n
0.9	0.58	6.45	0.703	23	991	2634	2.66
0.5	5.8	7.21	1.301	89	1050	3033	2.89
0.1	5.22	0.72	0.594	41	696	1446	2.46

3.1. Characterization of Maghnite-H⁺.

The best value of monomer conversion was obtained with Maghnite-H⁺ 0.25 M, in which there is a complete saturation of montmorillonite with protons without destruction of catalyst structure [30].

Mag-H⁺ was found to have a BET surface area (SSA) of 59.45 m²/g, an average pore diameter of 62.46 Å and total pore volume of 0.00772 cm³/g. The SSA of Mag-H⁺ is close to that (61 m²/g) obtained by Macht *et al.* [32] for montmorillonite.

The chemical compositions of Mag-H⁺ was given in table 2. Results show that the alumina and silica oxide are present in major quantities while other minerals are present in trace amounts and that Maghnite clay contains mainly Al³⁺ with some Fe³⁺ and Mg²⁺ as octahedral cations and Ca²⁺, K⁺ and Na⁺ as exchangeable interlayer cations.

Table 2: Chemical composition of raw Maghnite and Maghnite-H⁺

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	PF*
Raw Maghnite	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	11
Maghnite-H ⁺	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	11

*PF: Pert in Fire

The XRD pattern of the acid-treated Maghnite (figure 1) shows peak positions, observed in the range 2θ, 0–40°, characteristic of montmorillonite (table 3).

Table 3: X-ray characteristics of Maghnite-H⁺

d _{hkl} (Å)	hkl
15.21	001
4.45	110
2.57	200
1.67	009
1.49	060

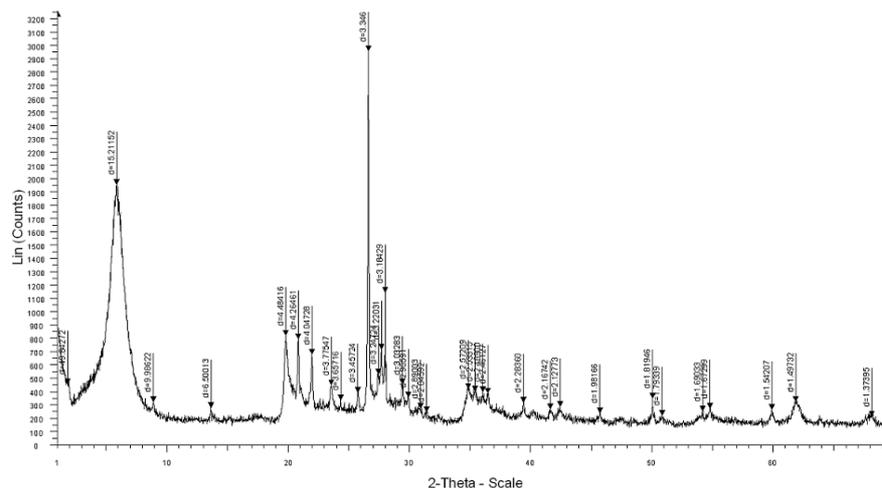


Figure 1: X-ray Power Diffraction of Maghnite-H⁺

Figure 2 shows the FTIR spectra of acid activated Mag-H⁺, all montmorillonite characteristic bands are present (Table 4). FTIR Spectra are in good agreement with literature [33].

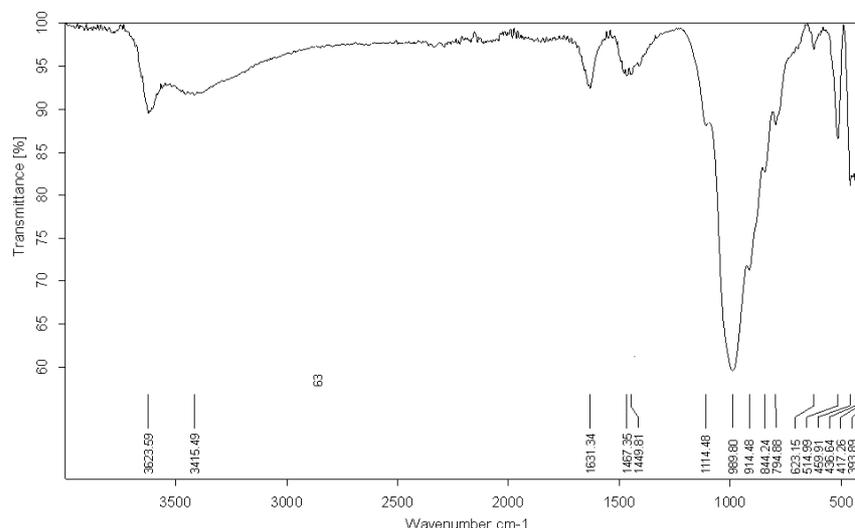


Figure 2: FTIR Spectra of Maghnite-H⁺

Table 4: FTIR results of Mag-H⁺

Wavenumber cm ⁻¹	Attribution
3624	Stretching vibrations due to hydroxyl group bonded with Al ³⁺ cations
3415	OH groups stretching vibration of physisorbed water molecules
1631	OH ₂ bending of water molecules due to hydration
1450	absorption of calcite
1114	Si O stretching, out-of-plane
990-1006	Si-O stretching in tetrahedral sheets
914 and 844	Al ₂ OH stretching, AlFeOH and AlMgOH hydroxyl bending vibrations
623	ascribed to the perpendicular vibration of Al-O
515-460	stretching and bending vibrations of the Si-O-Al (Al in octahedral) and Si-O-Si groups respectively

3.2. Copolymer Characterization

The Mw, Mn and polydispersity of the copolymer were measured by gel chromatography (GPC) (table 1). Results show that the PO is more reactive than THF.

Figure 3 shows the ¹H NMR spectra of the poly (THF-co-OP). According to the work published by Hamilton and Semlyen [34] and Oguni *et al.* [35]. The copolymer (poly(THF-co-PO)) (scheme 1) reveals characteristic resonance lines for the methyl groups of the PO (CH₃) repeating units at δ= 1.1 ppm, the central methylene groups of THF at δ = 1.78 ppm, and all other methylene (groups of THF and PO) adjacent to the oxygen atom as a complex signal at δ = 3.5-3.8 ppm. The chain end proton of the secondary hydroxyl (CH-OH) appears at 2.4 ppm.

For a preview on the structure of the copolymer, FTIR spectra of the copolymers were recorded. Firstly, we observe the disappearance of the characteristic band of the epoxy function located between 890 and 900 cm^{-1} . This is evidence that the polymerization takes place by ring opening. All copolymers show absorption bands between 2850-3000 cm^{-1} 1082-1113 cm^{-1} corresponding, respectively to stretching vibrations of aliphatic C-H of the methylene and to the C-O-C stretching vibration. Finally, all copolymers show absorption at around 3480 cm^{-1} assigned to stretching vibrations of hydroxyl of chain end.

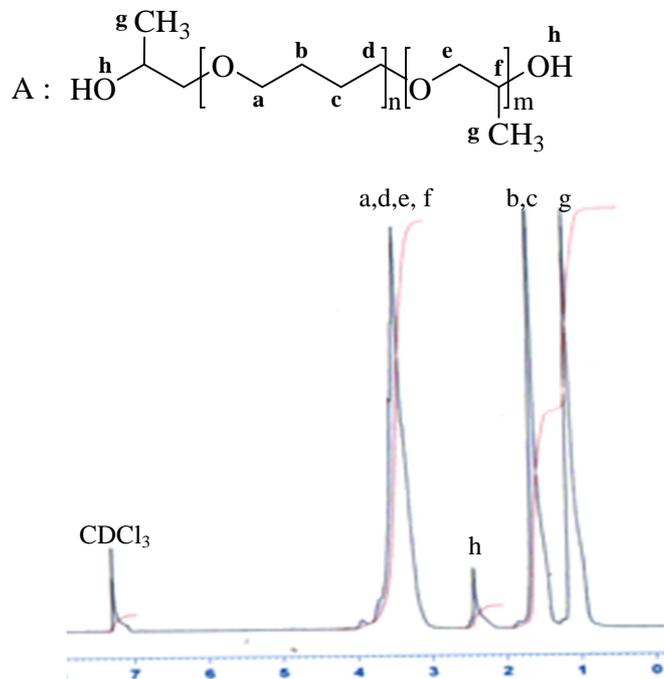


Figure 3: ^1H NMR spectra in CDCl_3 of the poly (THF-OP) ($f = 0.5$).

3.2. Effect of the Amount of Mag-H^+ on the copolymerization

The cationic copolymerization of THF with OP initiated with Mag-H^+ was carried in bulk. Figure 4 shows the effect of the amount of catalyst on the yield copolymerization. As can be noted in this figure, the copolymerization rate increased with the amount of Mag-H^+ . These results clearly indicate that an optimal rate of reaction is obtained at room temperature in bulk, this phenomenon is probably the result of number of initiating active sites responsible of inducing polymerization, and this number is proportional to the catalyst amount used in reaction. Similar results are obtained by Belbachir *et al.* [23, 36], and Njopwouo *et al.* [37], in the polymerization of N-vinyl pyrrolidone and THF by Mag-H^+ and the polymerization of styrene by montmorillonite, respectively.

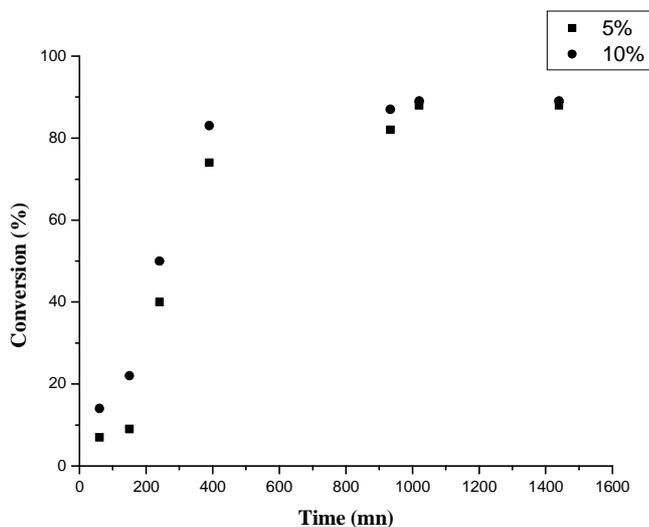


Figure 4: Effect of Mag-H^+ proportion on the yield of copolymerization of THF with PO. ($f = 0.5$)

In contrast, as depicted in Figure 5, the viscosity intrinsic is inversely proportional to the amount of Mag-H^+ . The viscosity increases up to 16 hours of reaction beyond a reduction of the latter is observed, indicating a depolymerization. This result is in good agreement with the proposal that Mag-H^+ is present as the active initiator species since the number of those species should be related to their surface area. Similar results are obtained by Yahiaoui *et al.* [38], and Crivello *et al.* [39], in the polymerization of cyclohexene oxide by Mag-H^+ and by Cobalt respectively.

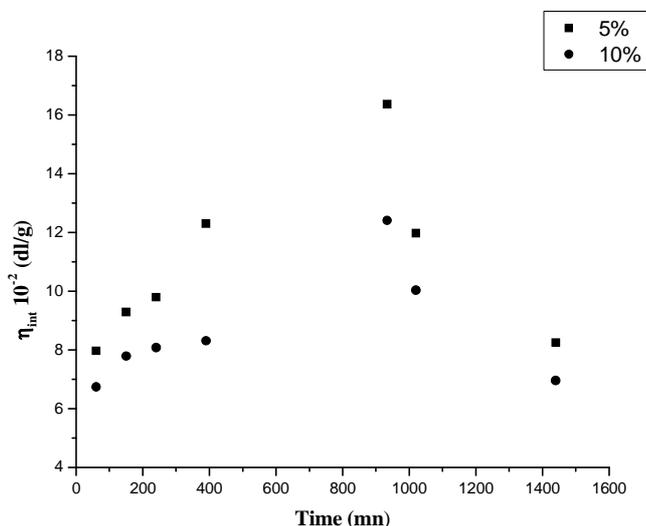


Figure 5: Effect of Mag-H^+ proportion upon the intrinsic viscosity ($f = 0.5$).

3.3. Effect of the molar fraction of THF on Copolymerization

Figure 6 shows that the conversion increases as amount of epoxide increases. Result shows that increasing of the propylene oxide amounts gave higher conversions. To a molar fraction equal to 1, the polymerization of THF does not occur, this shows that the PO is the first initiated. Results are in agreement with those obtained by Budreckiene *et al.* [40] which have copolymerized THF with 9-(2,3-epoxypropyl) carbazole.

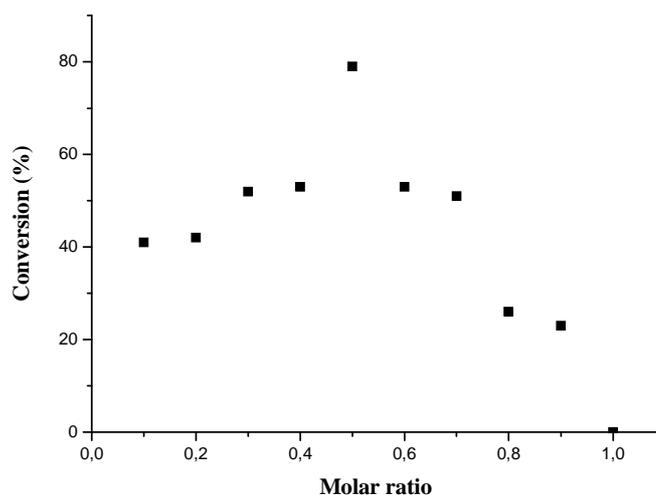


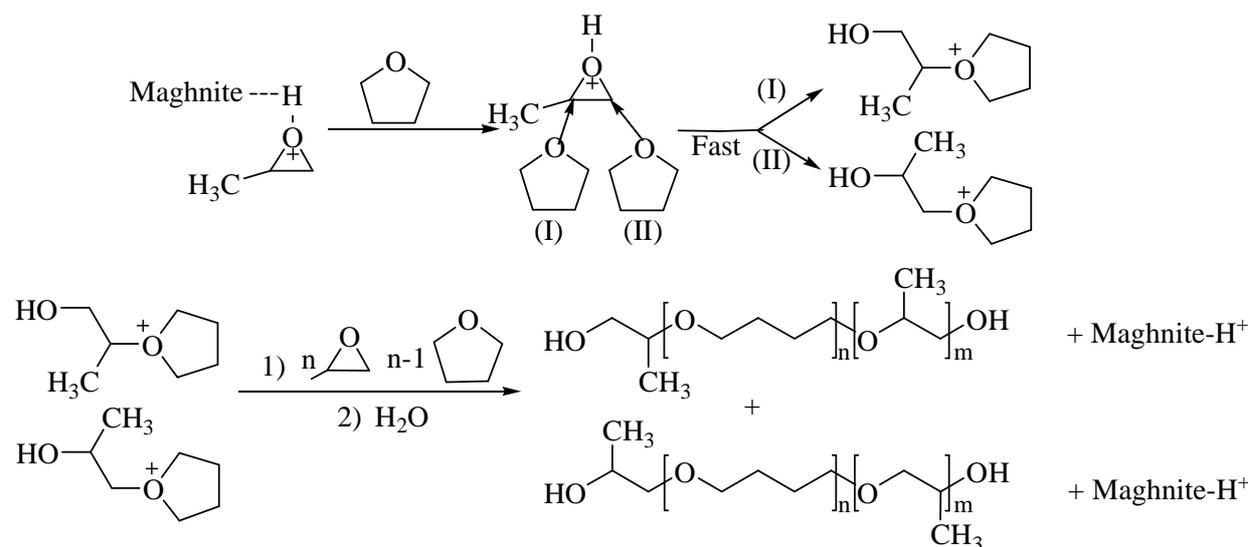
Figure 6: Effect of THF/PO molar ratio upon the conversion (% $\text{Mag-H}^+ = 10$, $t = 24\text{h}$).

3.4. Mechanism of the reaction

According to the foregoing discussion and the results of product analysis, we may suggest a cationic mechanism for the resulting reaction of copolymerization of THF with OP induced by Mag-H^+ (Scheme 1 and Scheme 2). Protons

carried by montmorillonite sheets of Mag-H⁺ induced the cationic polymerization; these montmorillonite sheets take place as counter-anions.

In the copolymerization of THF with PO, The first stage (initiation), both PO and THF can coordinate with the Mag-H⁺ generating complex with THF and PO. However, complex with THF cannot undergo initiation due to its stable five-membered secondary oxonium ion and is subject to nucleophilic attack Mag-H⁺ forming an active center [41]. The more highly strained complex with PO has a much higher reactivity. The α - or β -bond cleavage of the activated PO ring leads to complexes II or III, respectively (Propagation then take place by conventional cationic ring opening mechanism). Termination was caused by H₂O presented as adsorbed molecules in the Mag-H⁺ surface.



CONCLUSION

Maghnite-H⁺, proton exchanged montmorillonite clay is an effective initiator for the ring opening copolymerization of cyclic ethers. In the copolymerization, the solid catalyst was thought to act as an acid to generate cation species. Actually, the efficiency of the copolymerization reflected the Lewis acidity of Maghnite-H⁺. Two main advantages were shown in the copolymerization system using the solid acid Maghnite-H⁺, that the catalyst could be removed from the mixture of the products by simple filtration and recycled without a loss of catalytic activity.

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