



A new synthetic approach synthesis of bis-macromonomers of polyepichlorhydrin by exchanged montmorillonite

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ABSTRACT

The polymerization of epichlorhydrin (ECH) catalyzed by Maghnite-H⁺; (Mag-H⁺), a montmorillonite sheet silicate clay exchanged with protons, was investigated. The cationic ring-opening polymerization of epichlorhydrin was initiated by Mag-H⁺ at different temperatures (20, 30, 40, 50 and 60°C) in bulk and in a solvent. The effects of the amount of Mag-H⁺ and the temperature were studied. The polymerization rate and the average molecular weights increased with an increase in the temperature and the proportion of the catalyst. These results indicated the cationic nature of the polymerization and suggested that the polymerization was initiated by proton addition to the monomer from Mag-H⁺. Moreover, we used a simple method, in one step in bulk and in solution at room temperature (20°C), to prepare a telechelic bismacromonomer: α,ω -bisunsaturated polyepichlorhydrin. The telechelique polymer was characterized by means of ¹H-NMR, FT-IR spectroscopy, UV and GPC.

Key words: Maghnite, Montmorillonite, Catalyst, Epichlorhydrin, Macromonomer, Polyepichlorhydrin, Methacrylic Anhydride.

INTRODUCTION

Macromonomers (defined as polymers with polymerisable entities at one or both chain ends and generally low molar masses) were shown to copolymerise with low molar mass monomers more than 40 years ago [1]. They were used for some applications [2,3].

Macromonomers have been employed for macromolecular engineering [4,5]. Macromonomers with various chemical structures are now accessible [6]. They can either be homopolymerised to yield comb polymers or copolymerised with a large number of comonomers to yield graft copolymers.

Graft copolymers are of interest as coatings, adhesives, emulsifiers, moisture retention agents, biomaterials, etc [7,8].

Numerous examples of macromonomer synthesis by different polymerization processes and extensive studies on their copolymerization behavior have been reported.[9–12] Nevertheless, the cationic initiators and catalysts used for these synthesis are expensive and often toxic either because of side-products or heavy metals such as antimony, chromium, mercury, etc. Frequently, these initiators require high pressure and very high or very low temperature to achieve controlled polymerization. Therefore, the presence of toxic impurities precludes the use of the polymers prepared in biomedical applications.

There is still a great demand for heterogeneous catalysis under mild conditions and in environmentally friendly processes. Montmorillonites, a class of inexpensive and noncorrosive solid acids, have been used as efficient

catalysts for a variety of organic reactions. The reactions catalyzed by montmorillonites are usually carried out under mild conditions with high yields and high selectivity's, and the workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused [13,14].

In the present work, we present a new approach to design telechelic poly(Epichlorhydrin) (PECH) bis-macromonomers in one shot, namely by the polymerization of epichlorhydrin (ECH) in the presence of methacrylic anhydride (MA) and catalyzed by Mag-H⁺. This catalyst can be easily separated from the polymer product and regenerated by heating at a temperature above 100°C [15]. The effects of different synthesis parameters on Epichlorhydrin conversion, such as the amount of Mag-H⁺, monomer, methacrylic anhydride, temperature, solvent and time are discussed, together with the mechanism of polymerization.

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 ¹³C nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl₃. Tetramethylsilane (TMS) was used as the internal standard in these cases. Average molecular weights and molecular weight distributions of the different polymers were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5µm Guard, 50x7.5 mm) followed by 2 columns (Polymer Laboratories, 2 PL gel 5µm MIXED-D columns, 2x300x7.5 mm), with a SpectraSYSTEM RI-150 and a SpectraSYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1mL.min⁻¹ at 35°C. Polystyrene standards (580-483.103 g.mol⁻¹) were used to calibrate the SEC.

2.2. Materials

1,2-Epoxy-3-Chloro Propane (Epichlorhydrine, ECH, (Merck)), was dried over calcium hydride and distilled under reduced pressure before use. Dichloromethane 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⁺ ions using 1M NaCl solution, then the protonated forms of montmorillonite (Mag-H⁺) 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 BaCl₂. The Mag-H⁺ 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)⁻¹ of dried clay and 786 m².g⁻¹ respectively.

2.3. Chemical synthesis

Polymerizations were performed with or without dichloromethane at 20 °C. The procedure was identical in both cases, involving slow addition of ECH to the stirred bulk containing catalyst methacrylic anhydride. Prior to use, Mag-H⁺ was dried at 120 °C overnight and then transferred to a vacuum desiccator containing P₂O₅ to cool to room temperature overnight. An example reaction is detailed here. After charging the reaction vessel with ECH and methacrylic anhydride, the catalyst (10% w/w to monomer) was added. At the end of the reaction, the resulting mixture was filtered to remove the clay and then slowly added to methanol with stirring. This process was repeated three more times and then the polymer was dried in a vacuum oven prior to submission for GPC, ¹H- and ¹³C-NMR analysis. The yield was calculated from the weight of the obtained polymer.

Table 1 Chemical composition of the catalyst

Species	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	As	L.O.I.*
% (w/w)	69.4	14.7	1.2	1.1	0.3	0.5	0.8	0.2	0.05	11

*L.O.I: loss on ignition at 900°C in wt %.

RESULTS AND DISCUSSION

3.1. Procedure for lead determination method

3.1.1. DRX Spectroscopy

As described in the Introduction, we have recently reported that the ring-opening polymerization of 1, 2-propylene oxide (PO) by primary alcohol in the presence of Mag-H⁺ satisfactorily proceeds to give linear polyPO with the controlled $\overline{Mn} < 3200$. The key feature of this polymerization may be the acidity of the added Mag-H⁺, which is not as large to polymerize the monomer by itself but is sufficient to activate the monomer. To extend this facile method to others epoxies, we performed the ring-opening polymerization of ECH to examine the \overline{Mn} and \overline{DPn} of the polymer. Tables 2 summarize the results of the polymerization of ECH with methacrylic anhydride in the presence of Mag-H⁺ as catalyst. The polymerization did not proceed with methacrylic anhydride alone, the addition of Mag-H⁺ was quite effective to give polyECH macromonomers (EA) quantitatively.

Polymerization conditions for the synthesis of macromonomers of ECH polymers are shown in Table 2. An ethylenically unsaturated modifier, AM, is employed to replace a conventional modifier such as ethylene glycol or water [16, 17].

As shown table 2, when the ratios of monomers to initiator are ≤ 10 , the \overline{DPn} values of the product polymers are in good agreement with the calculated values (entries EA1,EA2, EA3 in Table 2). With increasing the ratios of monomer to initiator than 10, the \overline{DPn} values become smaller than the calculated values (entries EA4, EA5 in Table 2). These observations are probably due to the presence of moisture in the polymerization system at the larger monomer/initiator ratios. Kadakowa *et al* [18] obtain similar results in the polymerization of lactones by Sn-montmorillonite in the presence of ethanol as initiator.

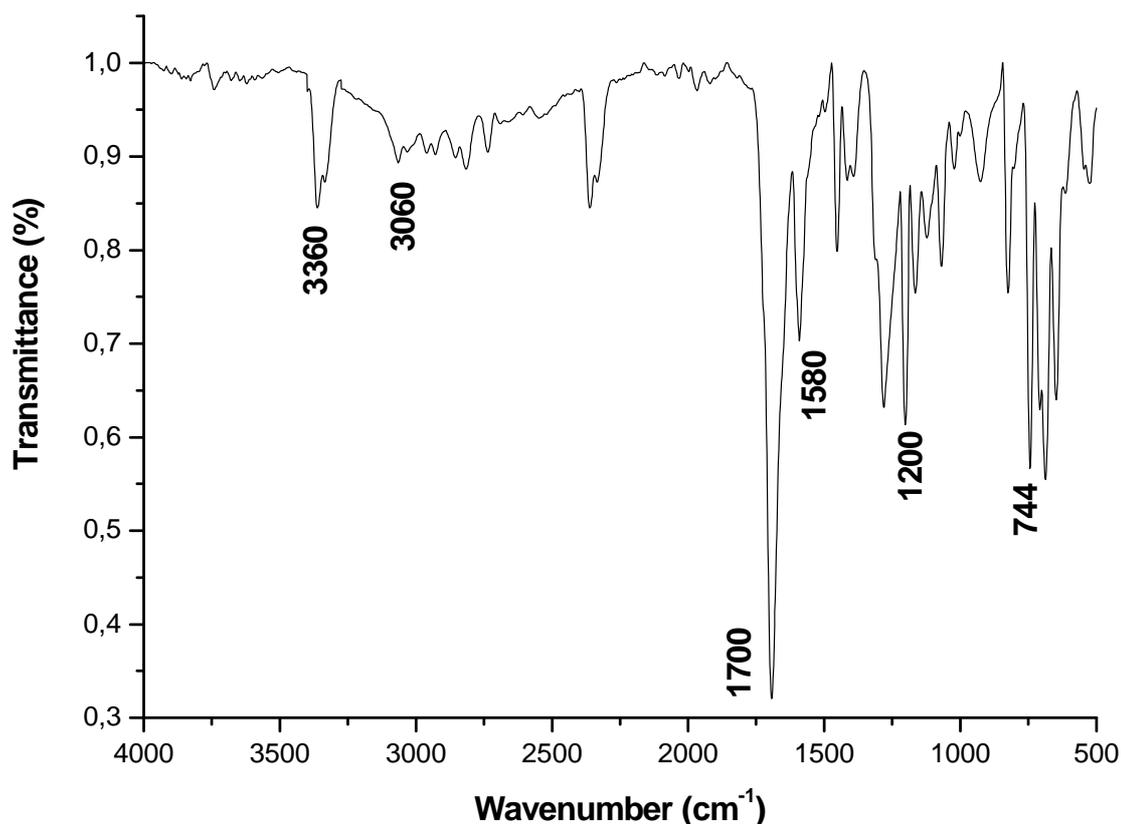


Figure 1: Infrared spectroscopic analysis of PECH functionalized

Table 2 Synthesis conditions of the polyECH macromonomers (EA); T = 20 °C, Time = 24 h

Entry	[ECH]₀/[MA]₀	Conversion (%)	\overline{Mn}_a	\overline{Mn}_{NMR}	\overline{Mn}_{Theo}	\overline{DPn}	$\overline{Mw}/\overline{Mn}$
EA1	3	30	210	210	217	2.87	1.20
EA2	5	35	270	280	296	4.71	1.17
EA3	10	50	590	580	596	9.78	1.25
EA4	15	69	980	960	1090	14.76	1.3
EA5	20	77	1370	1340	1558	19.74	1.36

a: Determined by GPC.

The structures of macromonomers have also been determined by ¹H-NMR, FT infrared and GPC. NMR and IR spectra of macromonomers show characteristic chemical shifts absorptions, respectively, corresponding to polyECH glycol [19] and the incorporation of the unsaturated methacrylate end groups of the initiator. FT infrared spectrum of methyl methacrylate-terminated macromonomers (Fig 1) show absorptions at 1580 and 3080 cm⁻¹ and 1700 cm⁻¹ for the C=C and C=O stretching of the methacrylate group.

Chemical shifts of ¹H NMR spectrum of macromonomer corresponding to the terminal unsaturated groups are shown below:

For macromonomer EA2 the signals a and b, at $\delta = 5.82$ -6.22 ppm (ABX) are assigned to methacrylate group. The relative intensity of these signals was 1:1, indicating that the polymerization was initiated by methacrylic anhydride with incorporation of the methacrylic end group at the initiating site of the polymer chain. The degree of polymerization (\overline{DPn}), therefore, was calculated by the integrated ratio of the signal due to the protons end group to the signals due to the polymer main chain. Signals c and i at 1.7 ppm are assigned to methyl protons linked to methacrylic group. Signals d, e, f, g and h at 3-4 ppm are assigned to methylene and methine protons linked to oxygen and chloride atoms (Figure 2)

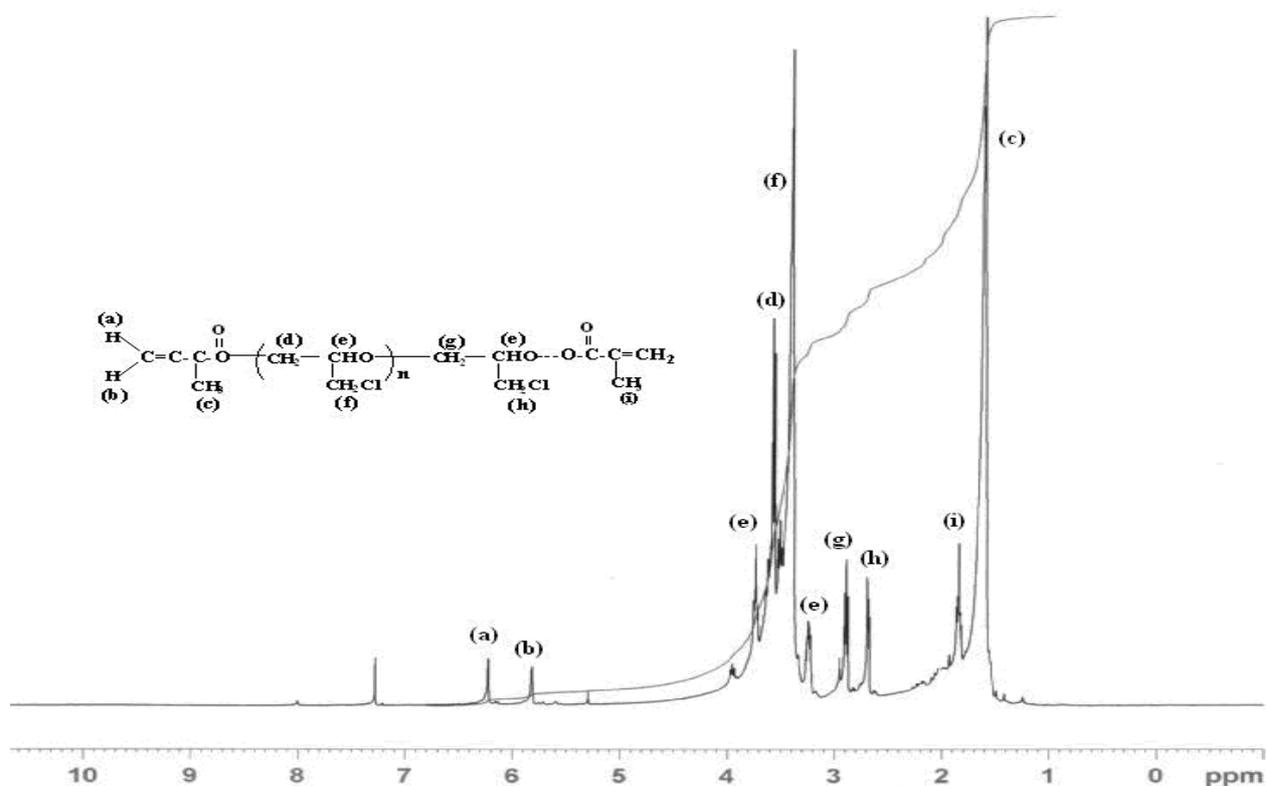


Figure 2: ¹H NMR spectrum (200 MHz) of PECH α, ω diméthacryloyl in $CDCl_3$

The molecular weights of the macromonomers calculated based on NMR spectroscopy were in agreement with the molecular weights obtained by GPC (Table 2 and figure 3). These results may strongly support the presence of 2

méthacryloyl group per molecule. One notes that the GPC molecular weight distribution of bis-unsaturated PECH (Fig. 3a) is very different from those of PECH (Fig. 3b) [19], which contained high proportions of low molecular weight, presumably cyclic oligomers. The polydispersities ($PD = \overline{M}_w / \overline{M}_n$) as determined by GPC were relatively narrow ($PD \leq 1.36$), which is agreement with a “living” polymerization process with fast initiation. This shows that the polymerization products in the present case are linear polyethers similar to those of Bacskai [20] and those of Malhotra [21].

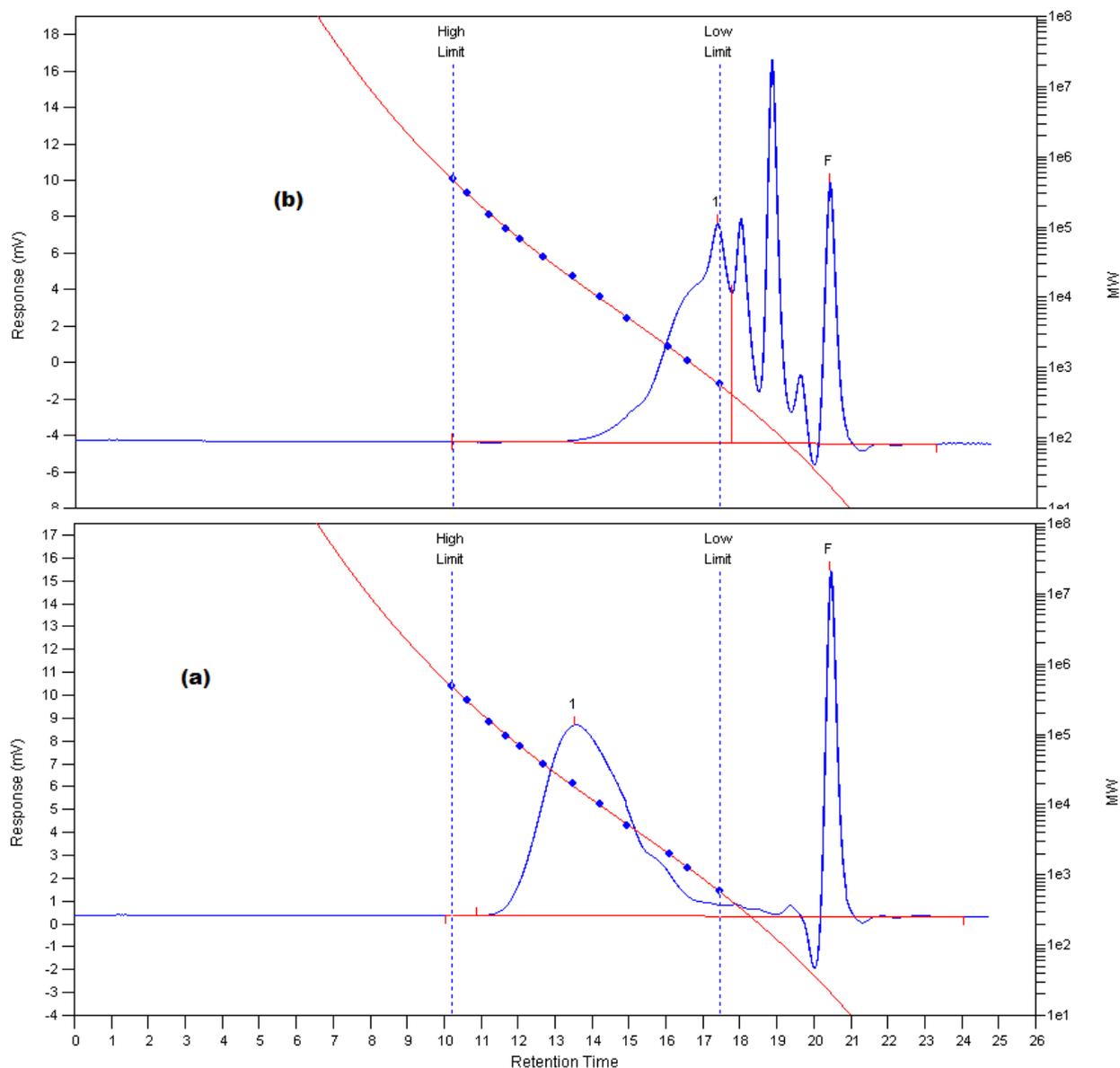


Figure 3: GPC chromatograms of: (a) PECH α, ω diméthacryloyl et (b) PECH

4. Kinetic study

4.1. Effect of amounts of Mag-H+

Fig. 4 show the effect of maghnite/monomer weight ratio on the yield of bis-unsaturated PECH. Indeed, using various amounts of maghnite-H+ 1,3, 5,7, 10, 15, and 20% by weight, the polymerization of ECH was carried in bulk at room temperature for 24h. It can be noted that increasing the weight ratio maghnite-H+/ECH also increases the yield of polymer. This phenomenon is probably the result of the number of “initiating active sites” responsible for inducing polymerization, this number is dependent on to the catalyst amount used in the reaction. Similar results are obtained by Yahiaoui *et al* [19, 22], and Njopwouo *et al* [23], in the polymerization of epichlorohydrin and propylene oxide by Mag-H+ and the polymerization of styrene by montmorillonite-H+, respectively. This result shows the effect of maghnite-H+ as a cationic catalyst. The use of a higher amount of clay caused a decrease of the yield of the reaction.

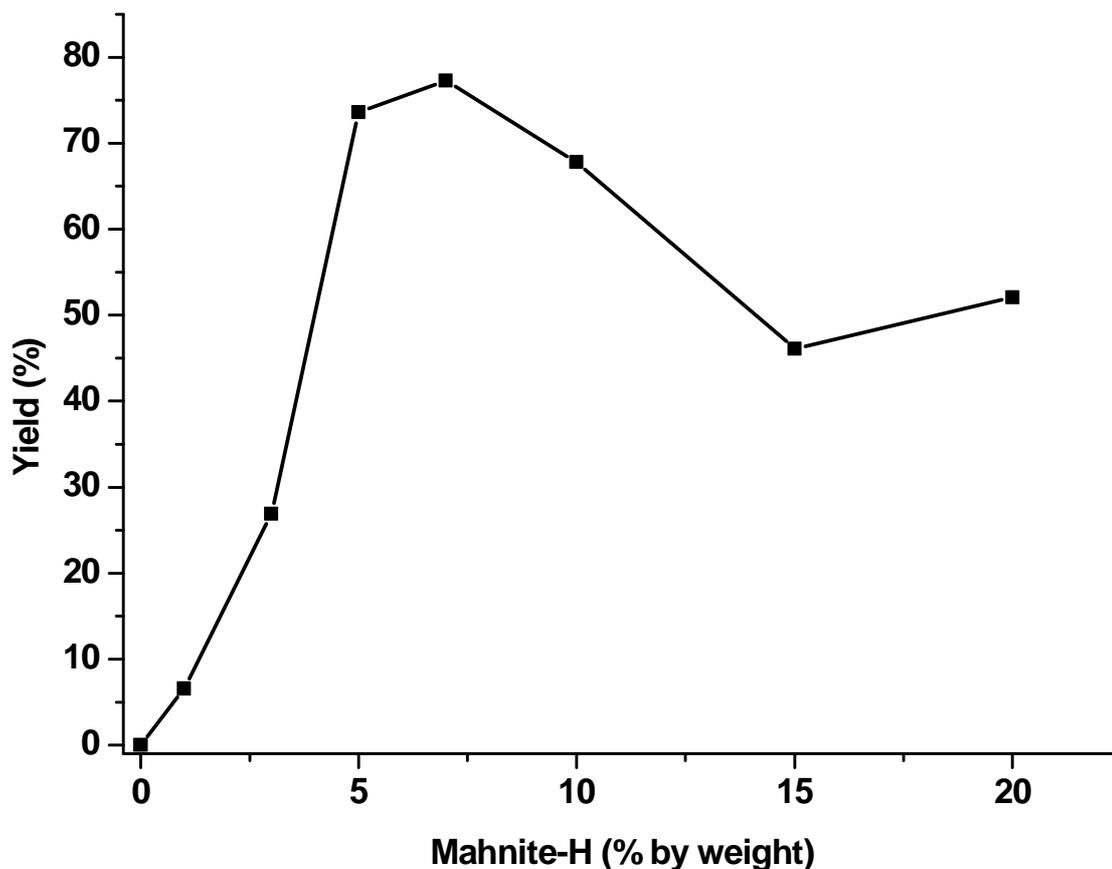


Figure 4: Effect of the amount of Mag-H on the yield of bis-unsaturated PECH

Polymerization using a weight ratio maghnite-H+/ECH of 10% was carried out at room temperature and the reaction was monitored at various times to study the evolution of monomer conversion and the molecular weight of the polymer with reaction time. The results are given in fig 5 and Table 3. The molecular weight increases with polymerization time and reaches a maximum after 8 h. The results show that after this time, the molecular weight decreases. This result suggests that chain transfer causes degradation and formation of cyclic oligomers and consequently may cause a decrease in the molecular weight. On the other hand, the monomer conversion increases with time and it can be noted that initially the polymerization proceeds very slowly; this can be considered as an induction period (8h), which consumed approximately 18% of the monomer. At the end of this period, the polymerization process becomes faster to reach a maximum of 77,24 % in 24 hours.

Table 3: Kinetic evolution of ECH polymerization a initiated by maghnite-H+ (Maghnite-H+/ECH weight ratio =10%)

Time (h)	1	2	4	6	8	16	18	20	24
Yield (%)	11.15	10.57	15.2	16.10	18	42.11	49.70	54.98	77.24
Mv	3383	3500	4110	4245	4382	4150	3960	3845	3795

4.2. Temperature effect

Using ECH mixture with methacrylic anhydride (20%) and 7 % [Monomer / Mag-H+] (w/w), the polymerization was carried out at 20, 30, 40, 50 and 60°C. In the absence of Mag-H+ no polymerization could be detected. In the presence of Mag-H+, however, the polymerization was initiated. Fig. 6 shows that polymerization temperature has much influence on the yield of bis-insaturated PECH. The yield increased with the temperature rising from 20°C to 60°C and reached a high conversion of 87% at 60°C.

we have found that the polymer molecular weight increase, depending on the polymerization temperature, in the following order: 20°C >30°C >50°C >70°C. Namely, the result indicates that the increase in the polymer molecular

weight is enhanced by increasing the polymerization temperature. This is because increasing the temperature causes an increase in the rate of propagation reaction of the growing polymer cation [24, 25]. (Fig. 7).

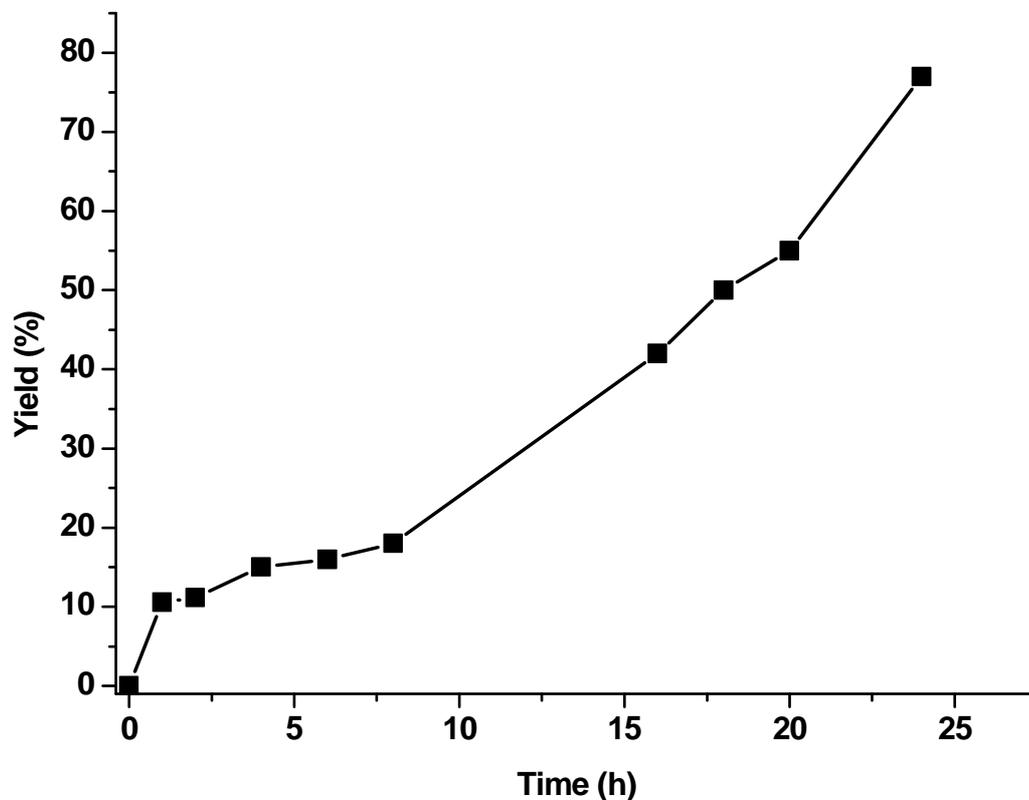


Figure 5: Effect of the reaction time upon the yield of bis-unsaturated PECH

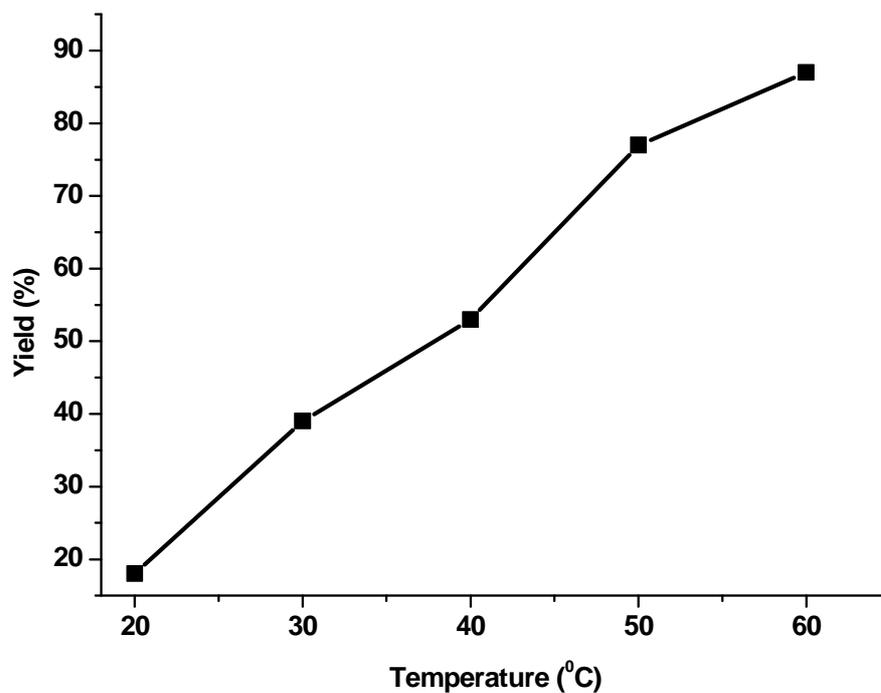


Figure 6: Temperature effect on the poly ECH bis-unsaturated yield “7 % of Mag-H⁺ for 6h”

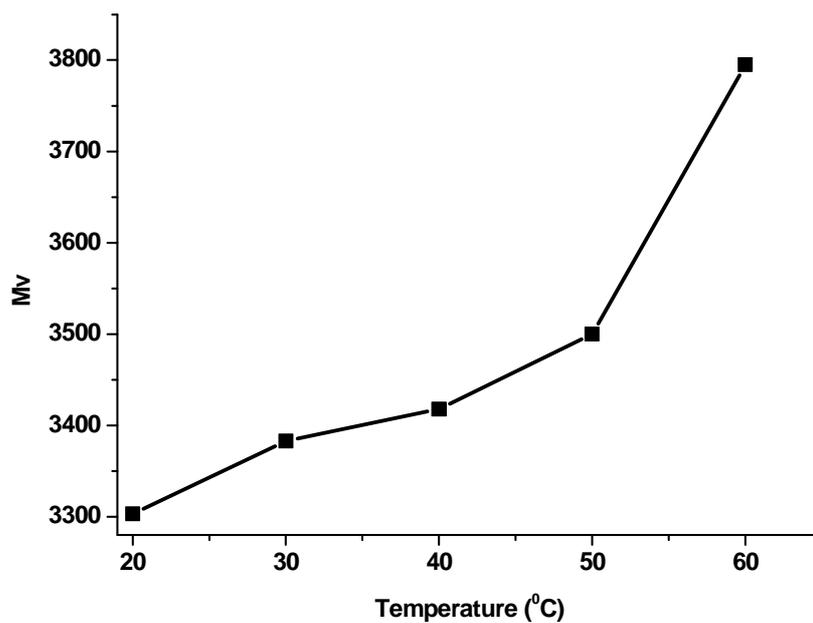


Figure 7: Temperature effect on the poly ECH bis-unsaturated molecular weight “7 % of Mag-H+ for 6h”

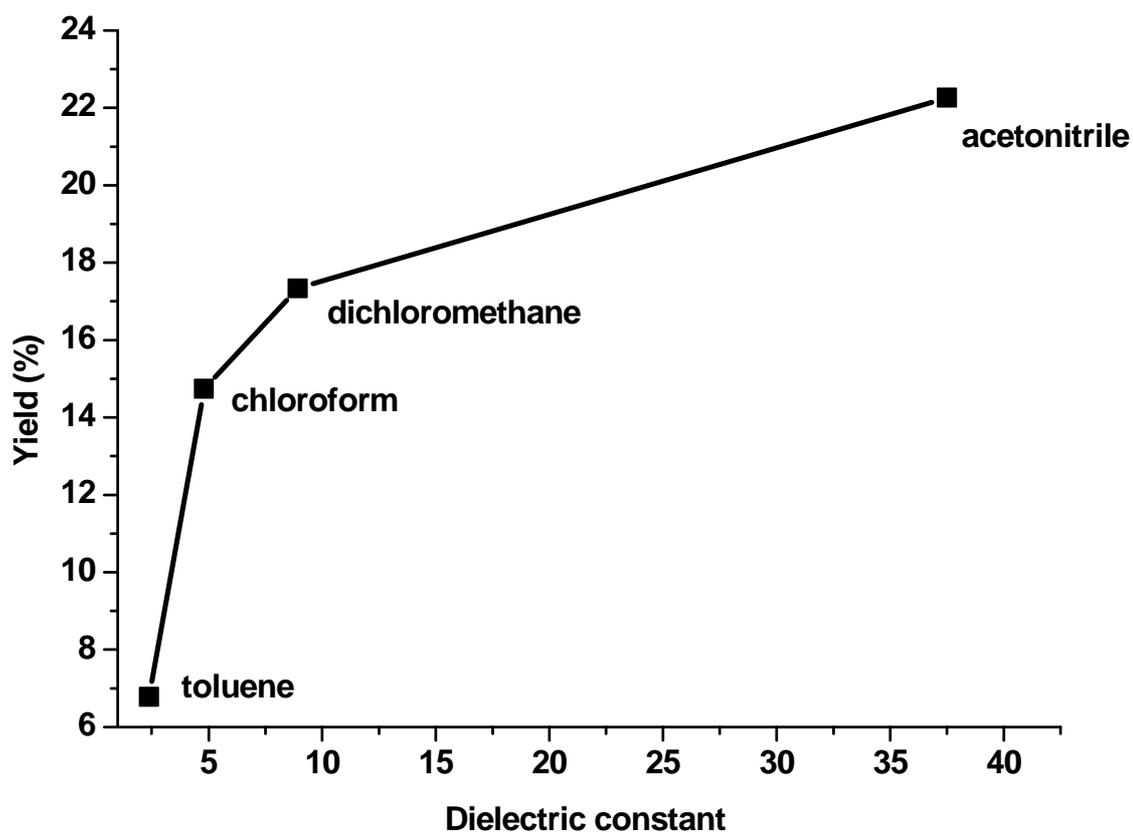


Figure 8: Effect of solvent on the polymerization of ECH, catalyzed by Mag-H

4.3. Effect of solvent on the polymerization

The influence of solvent on the polymerization was presented on fig 8. The data showed that the polymerization reaction proceeded better in acetonitrile. The rate of polymerization in acetonitrile ($\epsilon = 37.5$) was found to be much higher than that of chloroform ($\epsilon = 4.80$), dichloromethane ($\epsilon = 8.93$), and toluene ($\epsilon = 2.38$). The chain transfer of growing polymer cation to monomer takes place more easily in nitrobenzene than in toluene. Similar results was found, by Tsubokawa et al. [26–28], in the cationic polymerization of N-vinylcarbazole initiated successively by g-poly (glutamic acid), carbon fiber and carbon black.

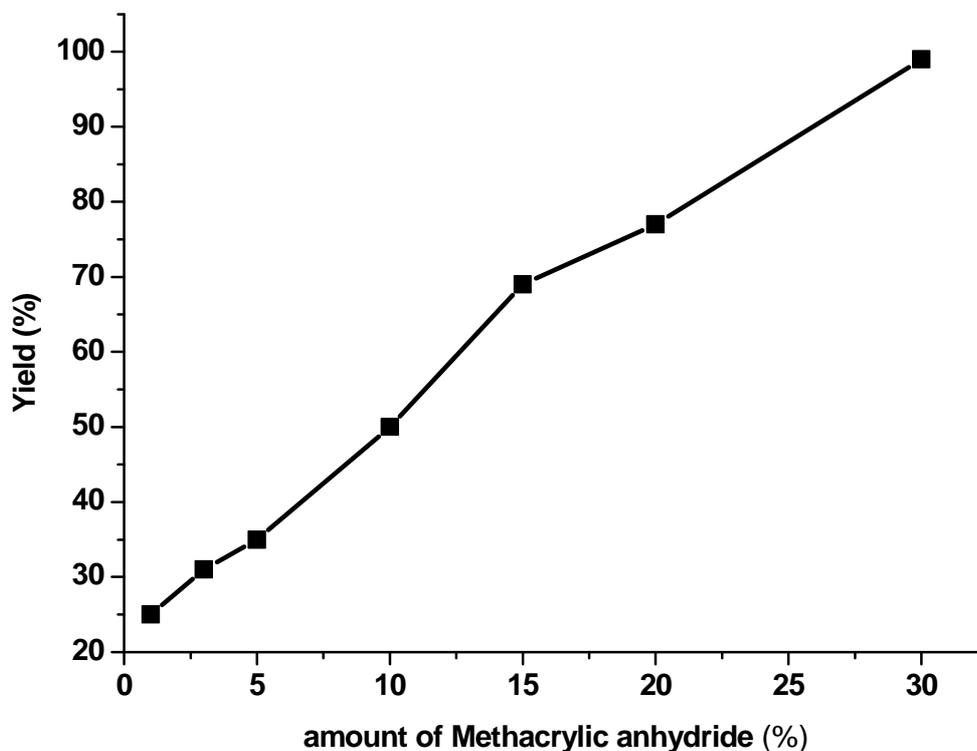
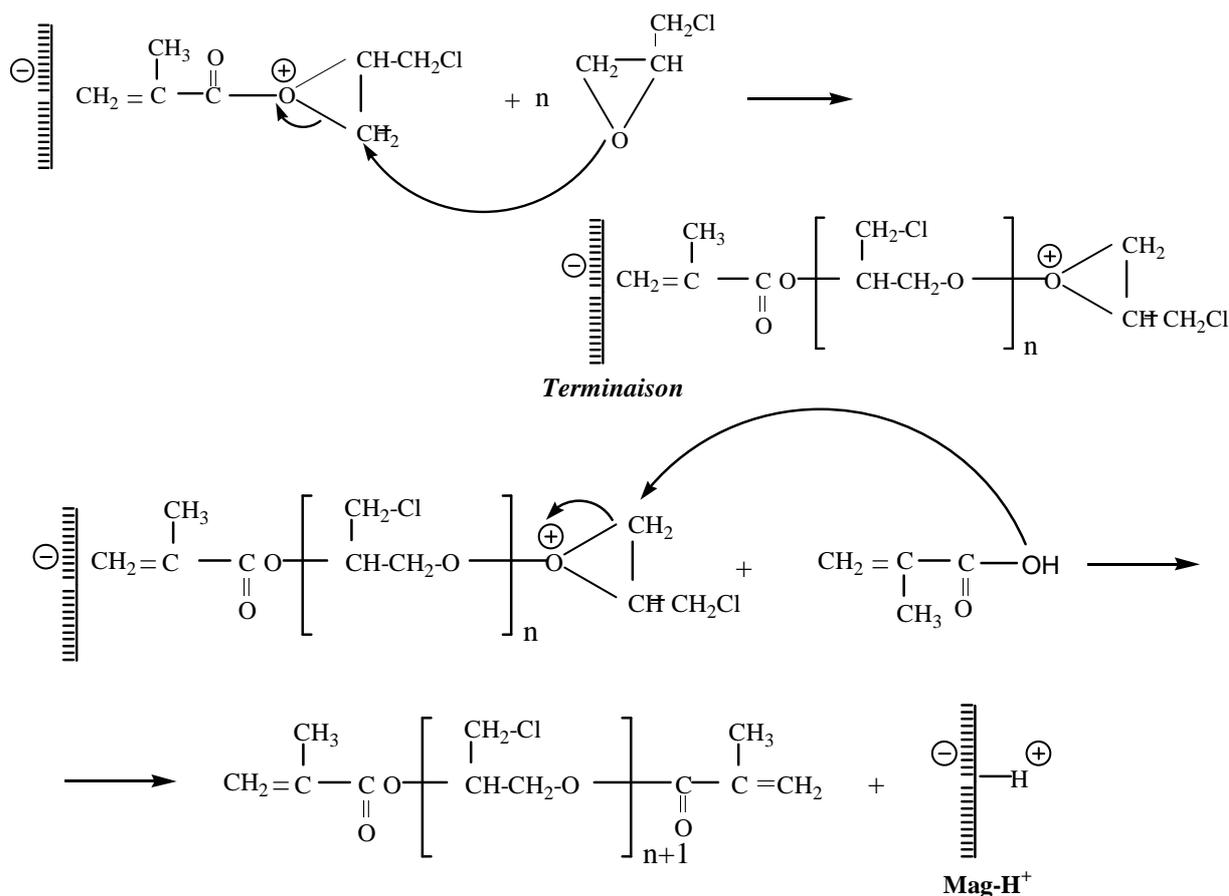


Figure 9: Effect of the ratio ECH / AM on the polymerization yield

4.4. Effect of Epichlorohydrin and methacrylic anhydride contents

According to Figures 9 and 10, synthesis of α,ω -bisunsaturated PECH with different amounts of ECH and methacrylic anhydride showed similar profiles, although the molecular weights and yields of the compounds were different. When the concentration of AM is increased, the yield of the product increases and the average molecular weight, determined by viscosity measurement, decreases. This means that the growing reaction proceeds faster when using a small monomer concentration. Lutz et al [29] obtains similar results, in the polymerisation of (1.3DXL) by Maghnite-H⁺ in the presence of methacrylic anhydride.



1. We have shown that Maghnite 0.23M treated in an acid medium; catalyses the polymerization of epichlorohydrin.
2. The catalytic activity of formed polymers, as measured by the conversion rate, depend on the catalyst proportion in the reaction medium and the reaction temperature.
3. Polyepichlorohydrins were produced by a very simple procedure.
4. Through simple filtering the clay can be separated from the reaction mixtures.
5. Moreover this acidic clay is inexpensive, stable and non corrosive.

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