Int. J. Mol. Sci. **2003**, *4*, 548-561

International Journal of
Molecular Sciences
ISSN 1422-0067

www.mdpi.org/ijms/

An Acid Exchanged Montmorillonite Clay-Catalyzed Synthesis of Polyepichlorhydrin

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Received: 8 April 2003 / Accepted: 2 September 2003 / Published: 30 September 2003

Abstract: "Maghnite", a montmorillonite sheet silicate clay, exchanged with protons to produce "H-Maghnite" is an efficient catalyst for cationic polymerisation of many heterocyclic and vinylic monomers (Belbachir, M. *U.S. Patent.* 066969.0101 –2001)**.** The structural compositions of both "Maghnite" and "H-Maghnite" have already been determined. Epichlorhydrin monomer, which is polymerizable by a cationic process (Odian,G. *La Polymerisation: Principes et Applications*; Ed.Technica: New York, 1994; pp 222-226), was used to elucidate the polymerization cationic character. The polymerization was performed under optimum conditions at 20°C. Experiments revealed that the polymerisation induced by "H-Maghnite" proceeds in bulk. In bulk polymerization, Epichlorhydrin conversion increases with increasing "H-Maghnite" concentration and temperature.

Keywords: Maghnite, Montmorillonite, Catalyst, Epichlorhydrin, Epoxides, Polyepichlorhydrin, Ring Opening Polymerization.

Introduction

Clay catalysts have been shown to contain both Brönsted and Lewis acid sites [1-2], with the Brösted sites mainly associated with the interlamellar region and the Lewis sites mainly associated with edge sites. The acidity of ion-exchanged clays is very much influenced by the quantity of water between the sheets. If the clay is heated (to around 100°C) so as to remove most of the interlamellar water until only 'one layer' of water remains, at about 5% total water level, the Brönsted acidity increases markedly [3-4] to that of a very strong acid. Heating to a higher temperature (at around 200-

300°C) results in the collapse of the clay interlayer structure as the water is driven out, resulting in a decrease in Brönsted acidity but an increase in Lewis acidity. Further heating (to around 450°C and above) results eventually in complete dehydroxylation of the aluminosilicate lattice, producing a completely amorphous solid that retains Lewis acidity.

Organic chemists, with synthesis in mind, have so far confined their interests to expandable montmorillonite clays[5-7], and almost all of their clay catalysts have been either (a) acid-treated clays such as K-10 [8], or ion-exchanged clays such as $Al^{3+,}$ Cr^{3+} or H^{+} exchanged Wyoming or Texas bentonites [9].

The acid-treated and cation exchanged clays can be simply regarded as solid acids and act as heterogeneous catalysts, with all of the advantages of easy removal of the catalyst from the product. Acid-treated clays, because of their increased surface area and swelling properties, have also been widely used as solid supports for inorganic reagents such as potassium permanganate [10], thallium(III) nitrate [11] and both copper(II) and iron(III) nitrates [12].

The ion-exchanged clays have mostly Brönsted acidity in the interlamellar zone and so are characterised by promoting acid-catalysed reactions often of a bimolecular type between protonated and neighbouring unprotonated reactants [13]. These exchanged montmorillonites have been successfully used as catalysts in polymerization reactions [14].

The present study is also concerned with polymerization and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay called "Maghnite" via Epichlorhydrin polymerization to exhibit the cationic character of the reaction [15]. The aim of this research is to extend the scope of other promising new field of polymer synthesis by the use of another catalyst system that has been shown to exhibit a higher efficiency.

This paper concerns detailed analyses of "raw-Maghnite", "H-Maghnite" and polymerization products, and the effect of the catalyst reaction and temperature on Epichlorhydrin conversion.

Experimental Part

Materials

1) 1,2-Epoxy-3-Chloro Propane (Epichlohydrine, ECH, (Merck)), was distilled (bp 113.0 –113.5°C) from calcium hydride and stored.

2) Dichloromethane (DCM) was washed successively with conc. sulfuric acid, distilled water, 5% aqueous Sodium hydroxide, and distilled and dried over anhydrous calcium chloride. DCM was distilled (bp 40°C) from calcium hydride and stored.

3) Toluene was washed successively with con. sulfuric acid, distilled water, 5% aqueous Sodium hydroxide, and then dried over anhydrous Magnesium sulfates. Toluene was distilled (bp 110°C) and stored.

4) Methanol was used as received.

5) Number-average molecular weight (Mv) and intrinsic viscosity (η) measurements were performed at 35 °C in toluene using a capillary viscometer SEMATECH (VISCOLOGIC TL1). The sample concentration was 1 mg/ml.

6) Gel permeation chromatography (GPC) was performed using a Waters model 200 instrument equipped with a set of four styragel columns (10^3 Å, 10^4 Å, 1.5 10^5 Å and 3.10^6 Å). The flow rate of tetrahydrofuran was 1 mL/min and the sample concentration was 2 mg/ml. The GPC columns were calibrated using a set of nine narrow-distribution polyethylenoxide standards.

7) The mass loss was measured by Thermogravimetric Analysis (TGA) performed in a nitrogen atmosphere using a Dupont model 9900 thermal analyzer. The heating rate was 20°C min^{-1}.

8) 0.05M, 0.10M, 0.15M, 0.20M, 0.25M, 0.30M and 0.35M sulfuric acid treatment solutions were used to prepare "H-Maghnite 0.05M", "H-Maghnite 0.10M", "H-Maghnite 0.15M", "H-Maghnite 0.20M","H-Maghnite 0.25M","H-Maghnite 0.30M" and "H-Maghnite 0.35M" respectively. "H-Maghnite XM", the acid form of "raw-Magnate", is prepared by shaking the raw material (raw- H-Maghnite) with a solution of sulfuric acid at room temperature until saturation is achieved over a two-day period, The cation-exchanged clay was filtered, resuspended in deionized water continuously until no sulfate ions were detected in the filtrate by $BaCl_2$; isolated by filtration; dried in an oven at 105°C and then finely ground. The clay cation exchange capacity (CEC) was found to be 84 mEq/100g of dried clay.

"Maghnite" and "H-Maghnite" characterization

1) Samples for XRF analysis were prepared using the LiB_4O_7 fusion method. The resulting beads were analyzed on a Philips PW 2400XRF spectrometer in the Laboratory of Inorganic Chemistry, Granada University, Spain.

2) XRD profiles for pressed powder samples were recorded on a Philips PW 1710 diffractometer using Cu-K α radiation (λ =1.5418 Å).

3) IR absorption spectra were recorded on an ATI Matson FTIR N°9501165 spectrometer using the KBr pressed-disc technique where a 0.5mg sample was added to 300mg KBr and mixed for 3min in a vibratory grinder prior to pressing into a 13mm disc.

4) High-resolution solid-state ^{29}Si and ^{27}Al MAS NMR spectra of untreated (raw-Maghnite) and acid-treated (H-Maghnite0.25M) samples were recorded on a Brüker ASX 500 spectrometer at 59.6 and 130.3 MHz respectively. The sample spinning frequency was 4 KHz for ^{29} Si and 11.5 KHz for ^{27}Al. Chemical shifts of ^{27}Al are referred to $[Al(H_2O)_6]^{3+}$ as external reference.

Procedure and polymer characterization

Polymerizations were carried out in stirred flasks at 20 °C. The catalyst was dried in a muffle oven at 120°C over night and then transferred to a vacuum desiccator containing P_2O_5. After cooling to room temperature under vacuum, the mineral was added to 10g of Epichlorhydrin which was

preliminary kept in a stirred flask at 20°C. The resulting mixture was dissolved in CH_2Cl_2. Adding water stopped the polymerization. At the required time, an aliquot of the reaction mixture was then taken in such a manner as to exclude any clay mineral. The organic phase was separated by decantation and slowly added to methanol while stirring. The precipitated polymer was filtered and dried under vacuum. The polymers were redissolved in CH_2Cl_2 and precipitated in methanol for characterization and molecular weight measurements. The conversion rate was calculated from the weight of the obtained polymer.

Results and Discussion

Catalyst structure

Various methods of analysis, such as ^{27}Al and ^{29}Si MAS NMR, show that "Maghnite" is a montmorillonite sheet silicate clay. The elementary analysis of selected samples obtained using XRF and monomer conversions obtained from the reaction of 1g of each sample with 10g of Epichlorhydrin for 7 hours in a bulk polymerization at 20°C, are shown Table 1.

It is necessary to report that the best value of Epichlorhydrin conversion is obtained with "H-Maghnite 0.25M". We thus selected this sample to study the effect of catalyst proportions and temperature on Epichlorhydrin polymerization. Acid treatment of "Raw-Maghnite" caused a reduction in octahedral Al_2O_3 content with an increase in the proportion of silica (SiO_2) observed. The polymer yield decrease implies that the Maghnite original structure was not preserved (destroyed) after acid treatment at a concentration > 0.25 M.

Table1. Elementary compositions of Protons exchanged samples "H-Maghnite"

Sample	Composition in wt%											Poly(ECH)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	As	FL*	Yield %
Raw-Maghnite	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	0.05	11	00
H-Mag0.05M	70.75	14.67	1.05	0.30	1.01	0.49	0.78	0.16	0.75	0.04	10	2
H-Mag0.10M	71.00	14.60	1.00	0.30	0.98	0.39	0.78	0.16	0.55	0.04	10	3
H-Mag0.15M	71.58	14.45	0.95	0.29	0.91	0.35	0.77	0.15	0.42	0.03	10	8
H-Mag0.20M	71.65	14.20	0.80	0.28	0.85	0.30	0.77	0.15	0.39	0.01	10	11.2
H-Mag0.25M	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11	56
H-Mag0.30M	73.20	13.85	0.70	0.27	0.78	0.20	0.76	0.13	0.31	0.02	9.78	25
H-Mag0.35M	75.31	13.52	0.71	0.26	0.78	0.18	0.75	0.13	0.32	0.01	8.03	20

*FL: Flame Loos.

The x-ray powder diffraction profiles (Figure 1 and Table 2) exhibited the presence of other crystalline phases such as quartz, feldspath and calcite in "raw-Maghnite". Under acid treatment, all trace of calcite was removed in "H-Maghnite". The increase in basal spacing from 12.5 Å in "raw-Maghnite", characteristic of a single water layer between the sheets, to a 15.02 Å value in "H-Maghnite" — for two interlamellar water layers — reflects the changes in interlayer cation and its associated hydration state as a result of the acid treatment [16].

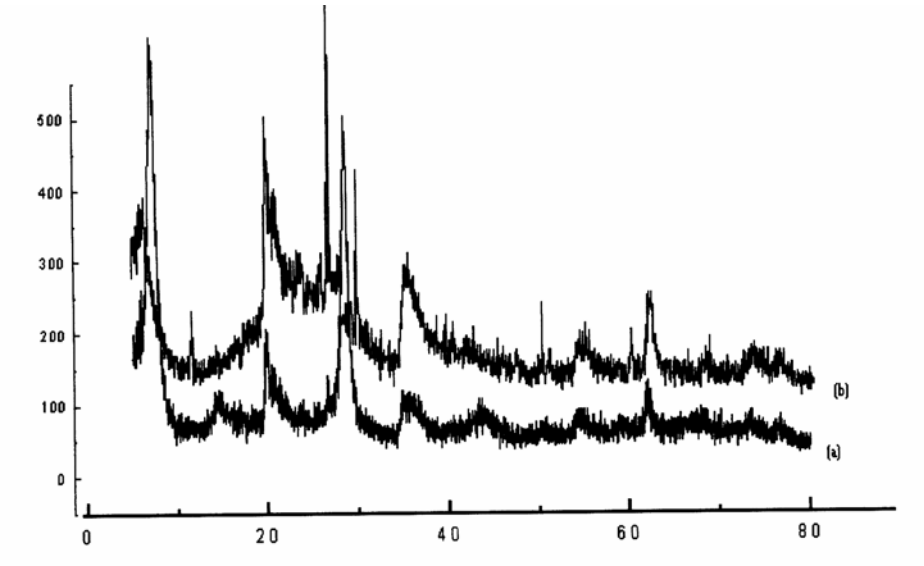


Figure 1. X-ray powder Diffraction of (a) "Raw-Maghnite" and (b) "H-Maghnite0.25M"

Table 2. XRD characteristic of Raw-Maghnite and H-Maghnite0.25M.

Samples	d_{hkl} (A°)	hkl	Nature of sample
Raw-Maghnite	12.50	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	,,	Quartz
	3.35	,,	Quartz
	3.21	,,	Feldspath
	3.03	,,	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite
H-Maghnite0.25M	15.02	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	,,	Quartz
	3.35	,,	Quartz
	3.21	,,	Feldspath
	3.03	,,	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite

The effects of the acid activation process on the FTIR spectrum of the treated Maghnite (Fig. 2) are summarized as follows: The intensity of the absorption band at 3630 cm^{-1} (AlAlOH coupled to AlMgOH stretching vibrations) decreases with acid treatment. The bands at 3425 cm^{-1} and 3200 cm^{-1} (absorption of water interlayer) become more diffuse with acid treatment [17]. The intensity of the Si-O out of plane and Si-O-Si (2 bands) in plane stretching bands at 1116, 1043 and 999 cm^{-1} are not affected by acid treatment. The AlAlOH (920 cm^{-1}), $AlFe^{3+}OH$ (883 cm^{-1}) and AlMgOH (846 cm^{-1}) deformation bands decrease with acid treatment. The intensity of the band at 796 cm^{-1} increases with treatment and reflects alterations in the amount of amorphous silica in accordance to the findings of others workers [18,19]. The intensity of the band at 628 cm^{-1} (either Al-OH or Si-O bending and / or Al-O stretching vibration) gradually decreases with acid treatment in good agreement with the findings of Komadel [20]. The intensity of the band at 467 cm-1 (Si-O-Al and Si-O-Mg coupled to OH vibrations or Si-O bending vibrations) is essentially unchanged.

The ^{27}Al MAS NMR spectra of both Raw–Maghnite and H-Maghnite-0.25M (Fig. 3) show Aluminum in two tetrahedral environments, with resonances centered at 60 and 68 ppm, in addition to the main contribution from the octahedral aluminum at 2.9ppm. These values and assignments concur with those published in the literature [21,22].

The ^{29}Si MAS NMR spectra for the Raw-Maghnite and H-Maghnite 0.25M are shown in Fig 4. The dominant resonance at – 93.5 ppm corresponds to Q 3 (OAl) units, i.e. SiO_4 groups crosslinked in the tetrahedral sheets with no aluminum in the neighboring tetrahedral [21]**.** The resonance at –112 ppm corresponds to three-dimensional (3D) silica with no aluminum present and is generally labeled Q 4 (OAl) [16,23,24].

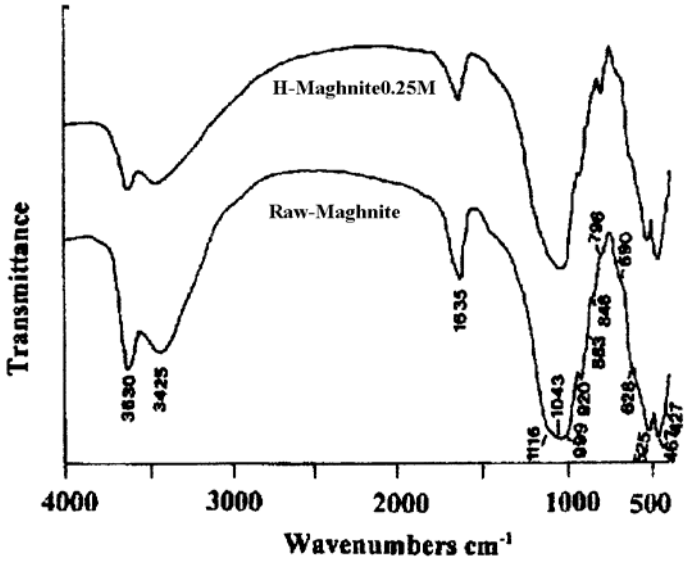


Figure 2. IR Spectra of (a) untreated Clay "Raw-Maghnite" and (b) Acid treated Clay "H-Maghnite0.25M"

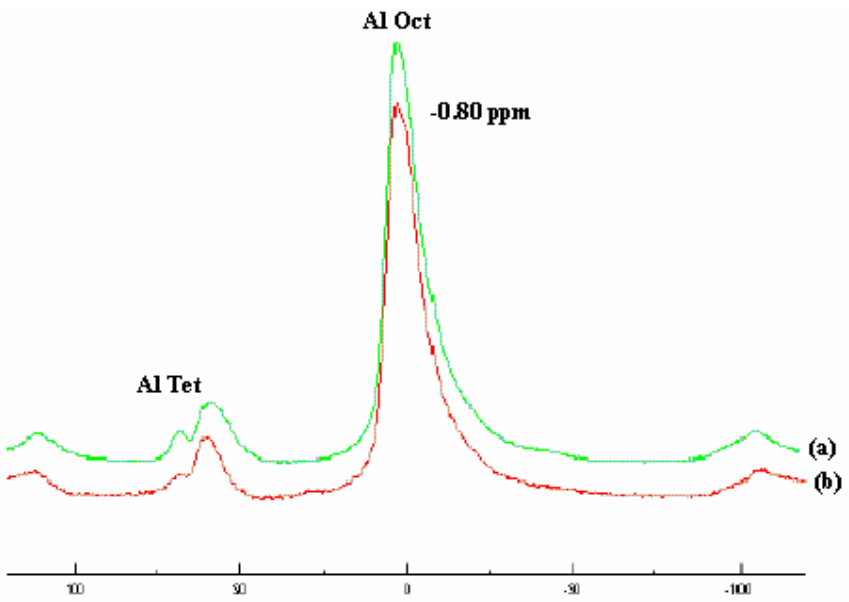


Figure 3. ^{27}Al MAS NMR spectra of (a) "Raw-Maghnite" and (b) "H-Maghnite0.25M"

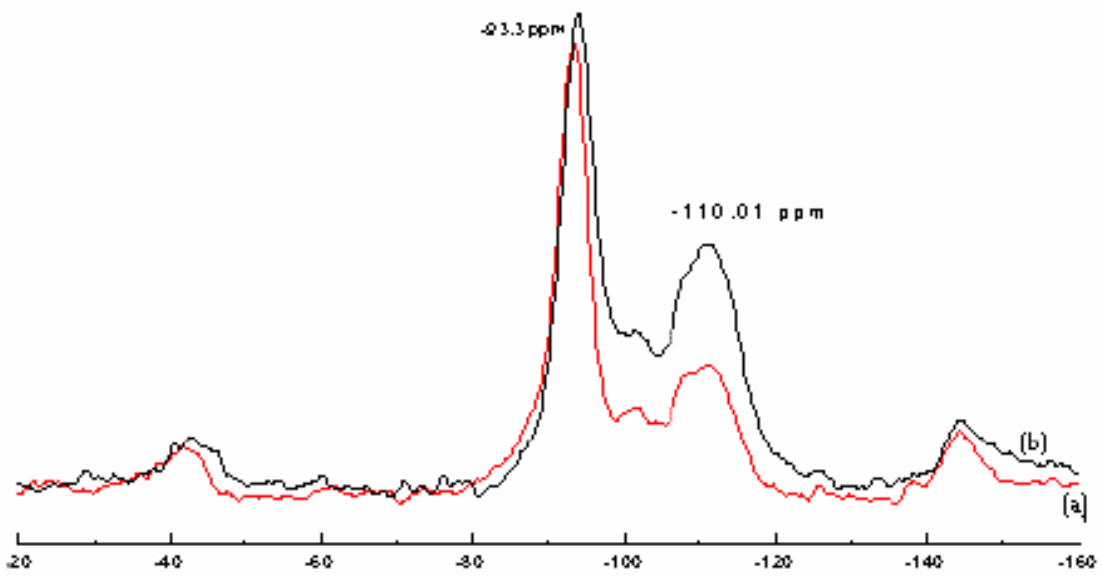


Figure 4. ^{29}Si MAS NMR spectra of (a) "Raw-Maghnite" and (b) "H-Maghnite0.25M"

Polymerization and products characterization

The experimental results from Epichlorhydrin polymerization induced by "H-Maghnite0.25M" are reported in Table 3. For all these experiments the temperature was kept constant at 20 °C for 7 hours.

Table 3. Polymerization of Epichlorhydrin induced by the "H-Maghnite0.25M"

Experiment	ECH (g)	"H-Maghnite0.25M"(g)	Yield %	Mv	M_n	M_w
1	10	1	56	4012	2435	4385
2	10	0.5	12	4245	3458	5390

Effect of "H-Maghnite0.25M" proportion

We can see from Fig. 5 and Table 3 that the monomer conversion rate increases with increasing "H-Maghnite0.25M" proportion (experiments 1,2). This led to a series of detailed experiments in which the time dependence of the conversion of Epichlorhydrin was measured for various catalyst amounts. Table 4 and Figure 5 show that increasing the "H-Maghnite0.25M" yielded higher Epichlorhydrin conversion. This is probably the result of an increase in the number of "initiating active sites" responsible for inducing polymerization; this number is proportional to the catalyst amount used in the reaction.

In all cases we also observed that for each catalyst concentration, the polymerization rate became constant at a higher conversion. A possible explanation is probably related to that the protonation equilibrium between the monomer and polymer- the latter becoming more important with the chain length [25].

The results obtained and presented on Table 3 show that contrary to the conversion rates, the molecular weight decreases with the catalyst concentration. A possible explanation can be: Propagation takes place through nucleophilic attack of the monomer onto an end-standing cyclic oxonium ion. Nevertheless, a specific character of (Epichlorohydrin) lies in its lower nucleophilicity as

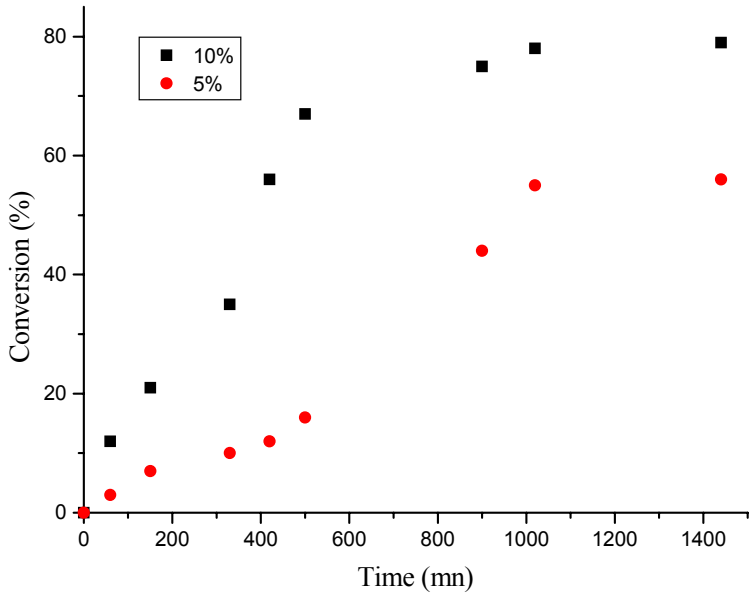


Figure 5. Effect of catalyst proportion on the conversion of Epichlorhydrin.

Table 4 Epichlorhydrin conversions with time : for 10g of Epichlorhydrin, the amounts of H-Maghnite0.25M were: a)1g b)0.5g

Time(mn)	60	150	330	420	500	900	1020	1440
Yield(%)(a)	13	21	35	56	67	75	78	79
Yield(%)(b)	3	7	10	12	16	44	55	56

compared to that of open-chain ether functions. This results in intermolecular chain transfer to polymer (reshuffling reaction), as well as intramolecular chain transfer (back-biting and end-bitting) at the origin of macrocyclic formation, consequently resulting in a decrease in the molecular weight.

Characterisation of products

An investigation was devoted to the analysis of the polyepichlorhydrinby ^{1}H NMR spectroscopy at 200MHz (Table 5 and Fig. 6).

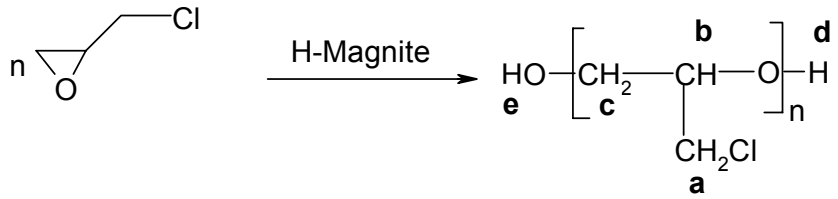


Table 5. Chemical shift of polymer protons

Proton type	(a)	(b)	(c)	(d)	(e)
δ(ppm)	3.60	3.70	3.70	2.14	1.22

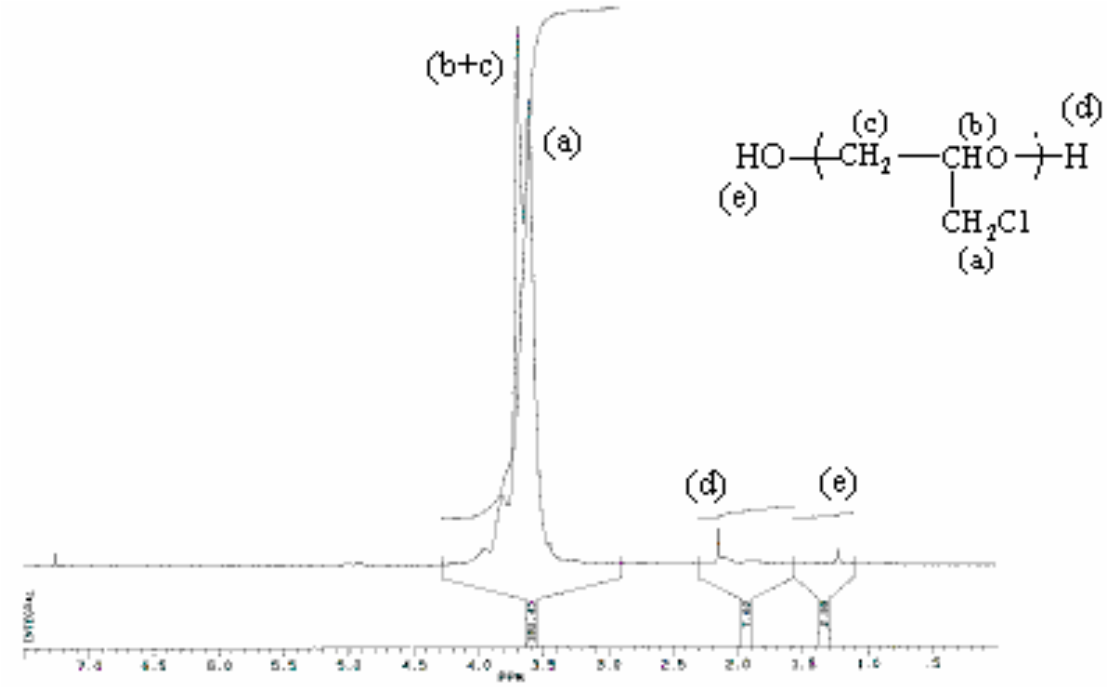


Figure 6. ^{1}H NMR (200 MHz) spectrum of polyepichlorhydrin in $CDCl_3$.

According to the work published by Schacht and al [26], ^{1}H NMR spectroscopy at 200 MHz (Solvent CDCl3) (Fig. 6) showed different peaks: (i) the methylene groups ($C\underline{H}_2Cl$) at 3.6ppm, and (ii) the methylene and methine groups ($C\underline{H}_2O$ and $C\underline{H}O$) at 3.7ppm. Besides these well-known resonances, analysis shows a characteristic resonance of the proton resulting from the double bond of the hydroxyl groups; the primary (CH_2-$O\underline{H}$) at 1.22 ppm and the proton of the secondary hydroxyl (CH-$O\underline{H}$) at 2.14 ppm .

Temperature effects

Using 10g ECH and 0.5 Maghnite0.25M, the polymerization was carried out at 20, 30, 50 and 70°C. In the absence of Maghnite0.025M no polymerization could be detected. In the presence of Maghnite0.25M, however, the polymerization was initiated. Figure 7 shows the temperature effect on the polymerization of ECH with Maghnite0.25M catalyst.

The effect of temperature on the degree of polymerization is more complex. In most polymerization reactions, an increase in temperature causes a decrease in the molecular polymer weight.

The intrinsic polymer viscosity (Fig 8) was found to decrease, depending on the polymerization temperature, in the following order: 20°C >30°C >50°C >70°C. Namely, the result indicates that the decrease in the intrinsic viscosity is enhanced by increasing the polymerisation temperature. This is because increasing the temperature causes an increase in the rate of chain transfer reaction of the growing polymer cation (inter and intramolecular) [27,28]. This is confirmed by the GPC curve (Fig 9) were one can see several peaks, at raised elution volumes, indicating the presence of macrocycles [29].

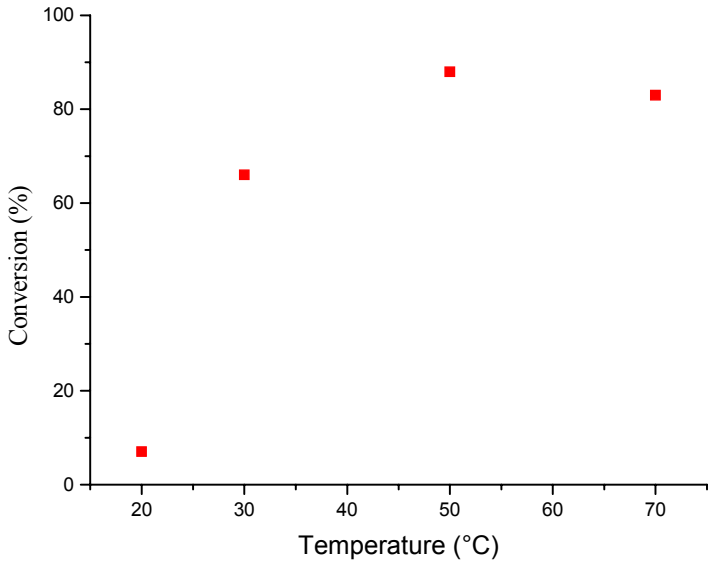


Figure 7. Effect of temperature on the conversion of Epichlorhydrin.

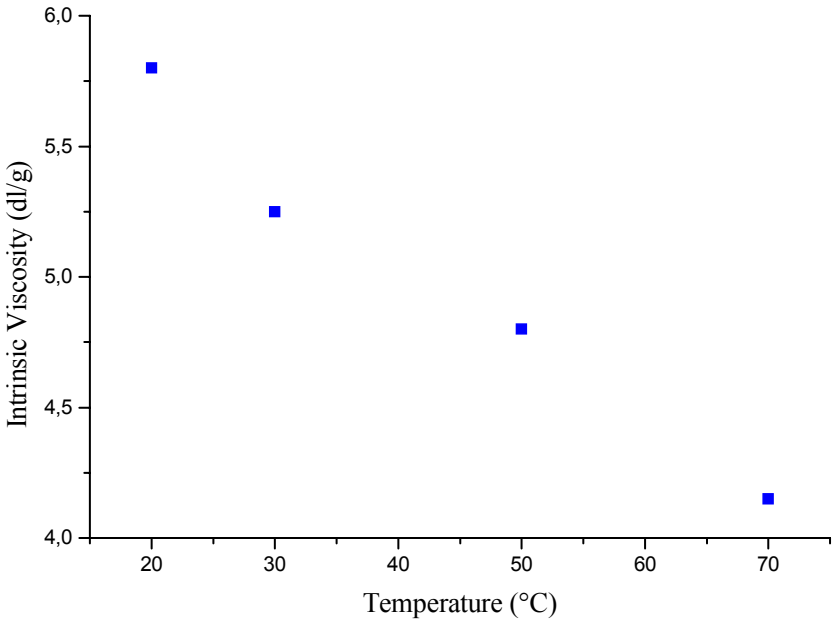


Figure 8. Effect of the temperature on the intrinsic viscosity of formed polymers.

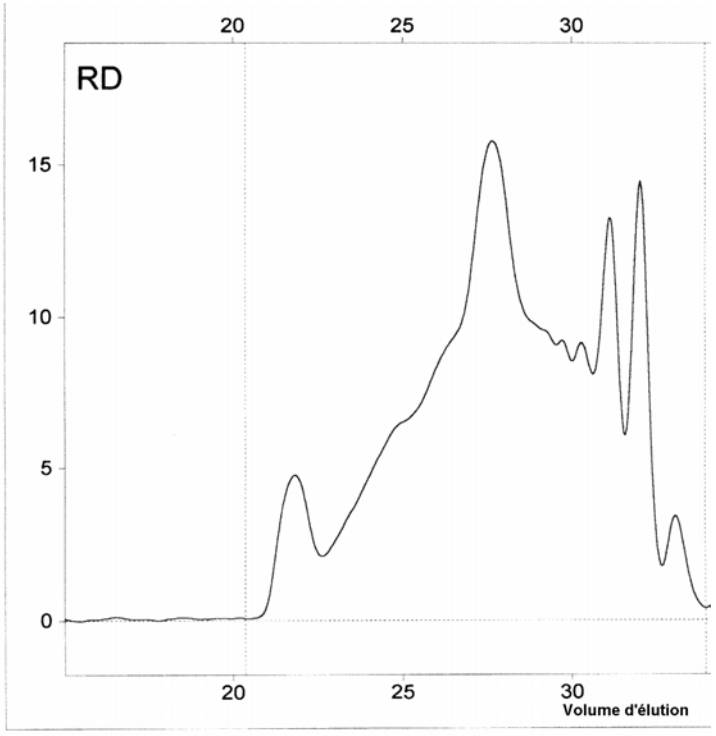
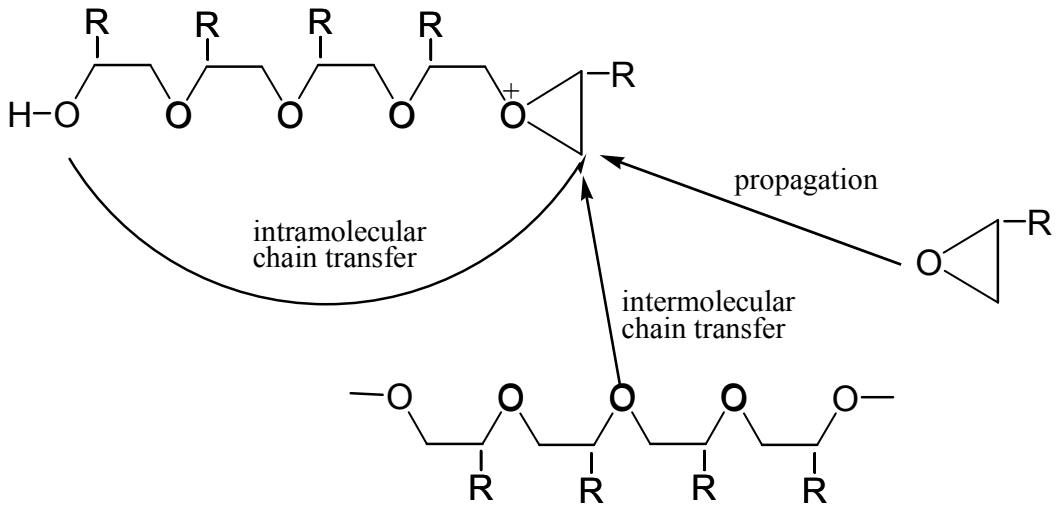


Figure 9. GPC curve of poly(ECH) prepared at 50 °C (5 % Maghnite0.25M, T = 2h 30 mn).

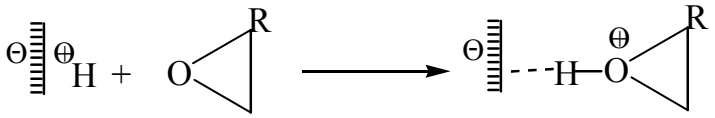
The global scheme can be described as:



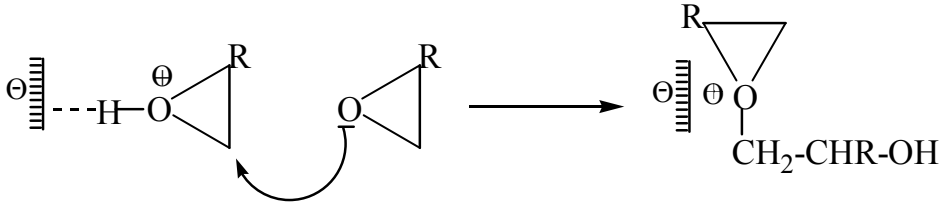
Polymerization mechanism

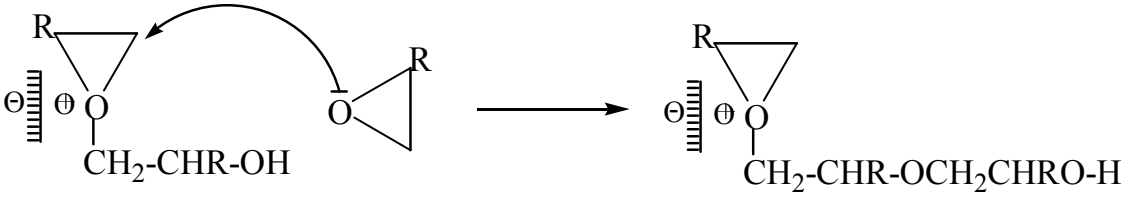
Epichlorhydrin is a monomer which is polymerizable only through a cationic path. According to the foregoing discussion and the results of products analysis, we may suggest a cationic mechanism for the resulting reaction of polymerization induced by "H-Maghnite0.25M". Protons carried by montmorillonite sheets of "H-Maghnite0.25M" induce the cationic polymerization. These montmorillonite sheets take place as counter-anions. Propagation and termination then take place by a conventional cationic mechanism. Termination by proton transfer to an initiator produces cyclization onto Polyepichlorhydrin chains.

Initiation:



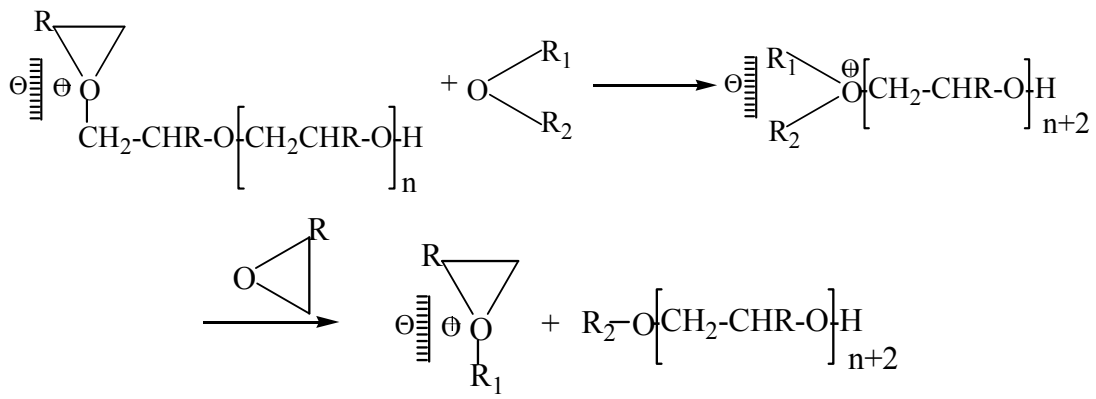
Propagation:



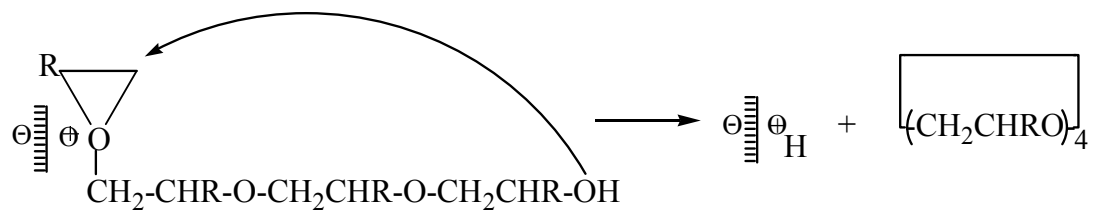


Transfer:

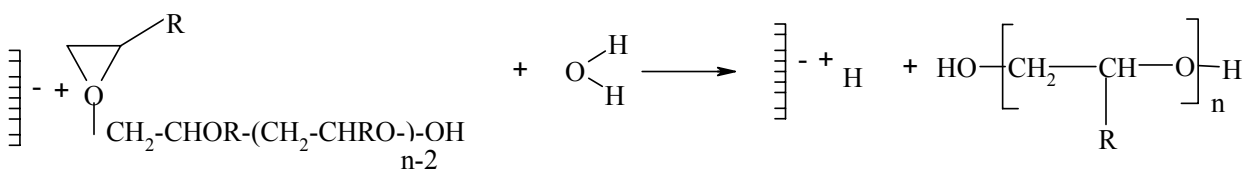
Transfer to polymer



Transfer to initiator



or



Conclusion

We have shown that Maghnite0.25M treated in an acid medium catalyses the polymerization of Epichlorhydrin. The catalytic activity as measured by the conversion rate and the molecular weight of formed polymers depend on the catalyst proportion in the reaction medium and the reaction temperature. Polyepichlorhydrins were produced by a very simple procedure. Through simple filtering the clay can be separated from the reaction mixtures. Moreover this acidic clay is inexpensive, stable and non corrosive.

Acknowledgements

The authors wish to thank Abdelhak Bensaoula Professor at Texas Center for Superconductivity at the University of Houston (TCSUH) for his support and encouragement.

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