Maghnite –Fe, a modified Montmorillonite clay "Algerian MMT" as an efficient and a New Solid Eco-Catalyst for the Cationic Polymerisation of Styrene

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Received: 10/2023, Published: 11/2023

Abstract

In this study, Fe-Montmorillonite "Fe-MMT" or "Magnite-Fe" was found and employed as a novel and efficient solid catalyst for the production of polystyrene (PS).

In this work, and in order to respect and implement the principles of green chemistry, a novel green approach was utilized for the first time to explore the cationic polymerization of styrene. This technique is to use Maghnite-Fe as an environmentally friendly catalyst in place of the harmful homogeneous catalysts.

It was discovered that the cationic polymerization of styrene caused by the maghnite-Fe takes happen under benign circumstances at low mass and temperature.

The term "Maghnite-Fe" refers to a montmorillonite sheet silicate clay from the city of Maghnia in western Algeria that has had the iron ions removed from it to act as a heterogeneous catalyst for the cationic polymerization of a number of monomers.

It is simple to regenerate and reuse the catalyst that has been removed from the reaction mixture by filtration. FTIR spectroscopy and X-ray diffraction were used to analyze the catalyst. By using FT-IR, ^{1}H-NMR, and ^{13}C-NMR analytical methods, the properties and structure of the resultant Schiff bases and poly(Styrene) were assessed. A possible mechanism for this cationic polymerization is proposed and discussed based on the NMR spectroscopy results of these model reactions. From studies of the reaction mechanism, it was found that the monomer was introduced into the growth chains.

Keywords: Catalyst; Magnite-Fe; Cationic polymerization; Clay; Fe-Montmorillonite; Styrene; poly Styrene; mechanism

Tob Regul Sci. ™ 2023 ;9(2): 900 - 918
DOI: doi.org/10.18001/TRS.9.2.55

1. Introduction

New environmental legislation calls for the reduction of waste generation and the use of more environmentally friendly alternative solvents and catalysts, which makes the current homogeneous polymerization system environmentally unacceptable [1]. Substitution of traditional homogeneous Lewis acid and Brönsted acid type catalysts for heterogeneous ones, for example, solid acid catalysts, can provide a more environmentally friendly alternative for the polymerization process. Compared to their homogeneous counterparts, these catalysts have a number of benefits, such as milder reaction conditions, no need for solvents, and the employment of less hazardous materials. (e.g. hydrocarbons), easy separation of the catalyst from the reaction mixture by filtration, and its possible regeneration and reuse, reducing the production of waste (not from the water-quenching step) and therefore harming the environment. Much work has been done about the polymerization of styrene and these derivatives.

Cationic polymerization is a widely used method for preparing hydrocarbon polymers [1]. Various examples of the cationic pathway polymerization of vinyl monomers with different Lewis acids such as $AlCl_3$ [2], BF_3 [3], $SnCl_4$ [4] and $TiCl_4$ [5] catalyst systems can be found in the literature.

When AYAT and colleagues [6–17] examined the cationic polymerization of -methylstyrene and other styrene derivatives with two distinct catalysts, "maghnite H+ and maghnite Na+," a few years ago, they showed that the polymers generated were successfully synthesized.

In this article, we want to carry on the same investigation with a minor modification. Cationic exchange is carried out within the sheets of the "Maghnite-Fe^{+2}" catalyst.

We would like to remind you that our lab uses two different catalysts, Maghnite-Na^+ [11] and Maghnite H^+ [12], to synthesize polystyrene. The main objective of this work is to use prior findings on the cationic polymerization of styrene in the presence of maghnite as a catalyst to create new, non-toxic solid catalyst Maghnite-Fe^{+2}. In this study, we report the synthesis of a new linear polymer made of styrene using an efficient ecocatalyst (Maghnite-Fe^{+2}). Maghnite-Fe^{+2} preparation is the first of two steps in the synthesis process. The second step is the cationic polymerization of styrene, which is catalyzed by maghnite-Fe^{+2}. Nuclear magnetic resonance techniques such as ^{1}H-NMR, ^{13}C-NMR, and FTIR are used to corroborate the acquired products' structural details.

2. The experimental part

2.1. Substances

Fractional distillation was used to purify the styrene (99%), which was acquired from Aldrich - Paris, France.

1,4 dioxane, 1,2 dichlorobenzene, 1,2 dichloromethane and Methanol, were dried on magnesium sulfate. Tetrahydrofuran (THF) and chloroform ($CHCl_3$) were used exactly as received from Aldrich Chemical. Aldrich was used to acquire all of the goods.

A business called "ENOF" (an Algerian manufacturer specializing in the production of nonferric products and valuable substances) supplied raw maghnite that was mined from a quarry in Maghnia, which is in the northwestern part of the country of Algeria.

2.2. Description of clays

2.2. 1. Catalyst structure

Several montmorillonite-type clay deposits are recognized throughout the world, the best known being those of Wyoming (USA) and Montmorillon (France). In our study, we were interested in Maghnite (Montmrillonite clay) which comes from the Hamam Boughrara deposit located in the Maghnia region in the far west.

The potential use of sodium-exchange montmorillonite clay, or "Maghnite-Na+," a novel nontoxic recyclable catalyst, to initiate the polymerization of styrene in bulk at room temperature is the primary objective of this research. **[6-17]**.

A company called ENOF Maghnia, which is situated in the western region of Algeria, produces the catalytic clay. Being a member of the phyllosilicate family, it is a montmorillonite clay. With an exceptional cation exchange property, it possesses an octahedral laminated sheet structure encased in tetrahedral silicate layers. **Fig 1** represents the cationic exchange inside the sheets. The chemical compositions of the raw-Maghnite and Maghnite-Fe^{2+} are reported in **Table 1**

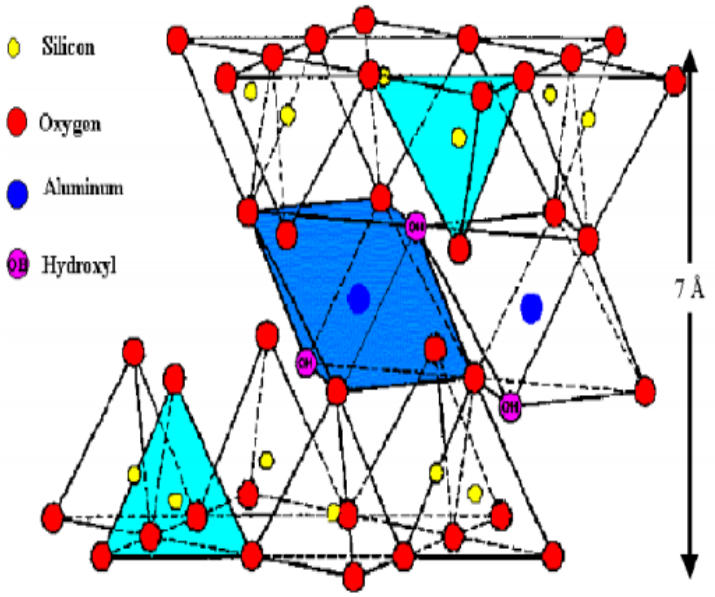


Fig. 1. The montmorillonite clay structure

Here, our main goal is to demonstrate the practicality of using Maghnite-Fe2+ clay as a solid catalyst and polymerization process initiator.

2.3. Modification of clays

Clays in their natural state have properties (specific surfaces, exchange absorption capacity, swelling, etc.). In order to improve its properties; several methods have been proposed.

2.4. Activation of clays:

Activation is a classic process that consists in improving the absorption properties of the clay by subjecting it to a physical (thermal) or chemical treatment (cationic exchange by: acid solution or saline solution).

Maghnia Bentonite is activated by a solution of sulfuric acid H_2SO_4 to give Maghnite-H^+ at a concentration of 0.25 M, as well as by a solution Hexametaphosphate $(NaPO_3)_6$ to give Maghnite-Na^+ at a concentration of 1 M **[6-17]**.

2.5. Catalyst preparation "preparation of the Maghnite Fe"

The following procedure was used to activate the maghnite: produce a 500 ml solution of distilled water containing 1M of iron sulfate, also known as "$FeSO_4$". 30 g of finely ground maghnite are added to a 1 liter flask holding 500 ml of distilled water, and the mixture is agitated for two hours.

The prior mixture is covered with the iron sulphate solution, which is then stirred for two days. After recovering the maghnite-Fe^{2+}, the maximum is cleaned five times to, get rid of the extra Fe^{2+} ions. Following filtration, drying, washing, and grinding.

- Maghnite-Fe^{2+} is ground and sieved after being dried for 24 hours at 105°C in an oven.

- Maghnite-Fe^{2+} must be kept in tightly sealed containers.

2.6. Polymerization procedure

To get rid of moisture that could easily be absorbed by the clay, enough Maghnite-Fe^{2+} used at the start of any reaction is placed in the kiln for thirty minutes.

2 g of styrene are added to well-dried flasks containing quantities of Maghnite-Fe^{2+} between 5 and 20% (catalyst effect), these flasks are stirred in a bath containing pieces of ice and the temperature must be constant 0°C. The reaction time is between 0.5 and 3 hours due to finding the best conditions to do the kinetic study for the remaining parameters. The catalyst is recovered by filtration on filter paper; the filtrate is then precipitated in cold methanol (a non-solvent).

A simple filtration makes it possible to recover the polymer which is then dried using a desiccator (device used to protect materials from humidity).

The yield of the polymers was calculated by dividing the final mass of the product by the initial mass of its monomer. The resulting product is a white color solid.

3. Results and discussion

This research focuses on cationic polymerization and investigates the ''Magnite-Fe^{2+}'' montmorillonite clay's catalytic activity through the linear polymerization of styrene. Previous works [6] have reported on the catalyst's structure and composition. XRF spectroscopy-based elemental analysis of maghnite-H^+ reveals a strong correlation between acid treatment and the catalytic activity of maghnite-Fe^{2+}. Raw magnite is treated with a ferrous sulfate solution to reduce the amount of octahedral aluminum oxide, which increases the proportion of silica [6–17]. The results showed that the best yield was obtained with Maghnite-crude treated with 1 M ferrous sulphate solution, in which the montmorillonite is completely saturable with iron cations without destroying the catalyst structure [6-17].

3.1. XRF: X-Ray Fluorescence Analysis of catalyst

XRF characterization: This analysis was performed to know the chemical compositions of the minerals that are present in maghnite and Mag-H^+. Alumina and silica oxide are present in significant amounts, as Table 1 illustrates. while other minerals are present in trace amounts and that maghnite clay contains mainly Al^{3+} with some Fe^{3+} and Mg^{2+} as octahedral cations and Ca^{2+},

K^+ and Na^+ as exchangeable interlayer cations. Results show, firstly, a dissolution (wt %) of cations, in particular Al^{3+}, there by resulting to a decrease of the Lewis

Table 1: Comparison of the chemical composition of Acid Maghnite, and Maghnite Ferric.

Samples	Compositions (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	PAF
Maghnite-H^+	93,75	14,70	2,57	5,10	3,25	1,25	0,63	0,04	11
Maghnite-Fe^{2+}	87,24	13,93	6,37	5,24	3,10	1,08	0,40	0,04	8

PAF : perte au feu (ignition loss)

XRF analysis shows a change in the chemical composition of the Maghnite-Fe^{2+} compared to the initial Maghnite-H^+ due to a reduction in silicon (Si), a reduction in alumina (Al), a reduction in sodium (Na), and a remarkable increase in the rate of iron. The ferric Fe^{3+} ions coming from the solution of $FeCl_3$ were exchanged in the Maghnite-H^+, giving ferric oxide, which was confirmed by the increase in the percentage of Fe_2O_3 from 2.57 to 6.37% for Maghnite-Fe^{2+}.

4. Characterization of catalysis

The chemical compositions of raw and iron activated maghnite were determined by XRF using a PW 2400 Philips Analytical wavelength-dispersive sequential XRF spectrometer with Super Q Panalytical software. X-ray powder diffraction spectra were performed on oriented samples with a Bruker AXS D8 Advance diffractometer equipped with LynxEye linear detector, with Co Kα1 radiation (λ = 1.54056 Å) and a scanning interval of 2θ = 0° to 70° and a scanning speed of 0.02°/s, at room temperature. The FTIR spectra were recorded on an Alpha FTIR Brucker spectrometer (4000-400 cm^{-1}).

4. 1. Analysis by IR spectroscopy

In Figures 2 and 3, respectively, the infrared spectra of raw maghnite and maghnite-Fe^{2+} are displayed. The infrared spectrum of maghnite-Fe^{2+} (Fig. 3) reveals bands associated with OH group vibrations between 3700 and 3400 cm^{-1}, angular deformation bands caused by absorbed water molecules between 1700 and 1600 cm^{-1}, a band at 1042 cm^{-1} associated with Si-O-Al elongations, and deformation bands associated with Si-O-M bonds with M=Al, Mg, Fe, and Li. A shift in the bands between 600 and 400 cm^{-1} is observed when compared to the IR spectrum of the raw maghnite (Fig. 2).

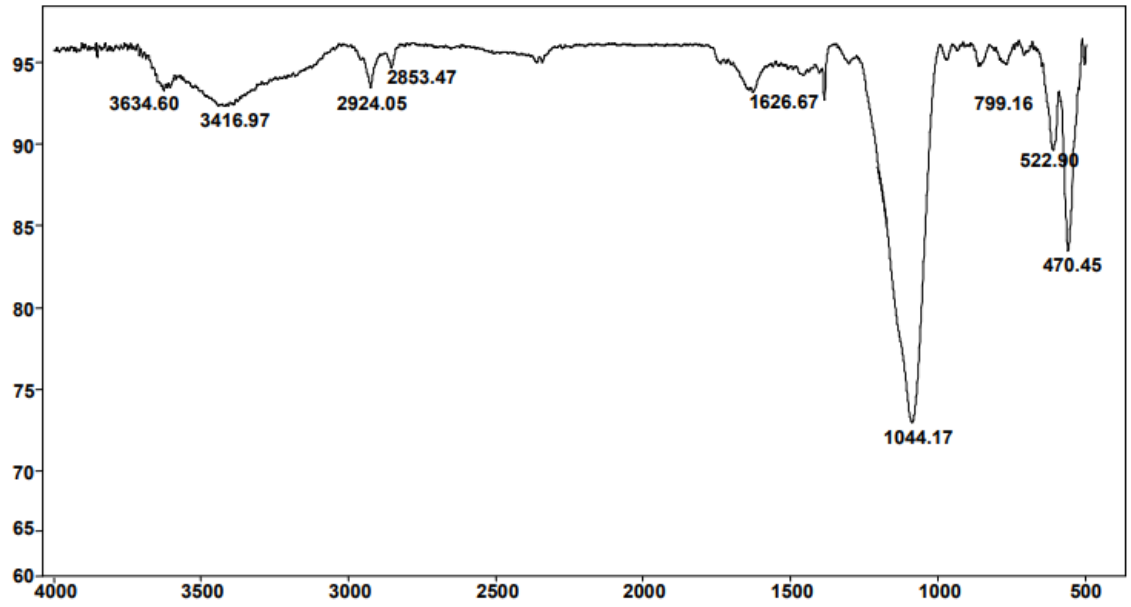


Fig.2. Infrared spectrum of Raw Maghnite

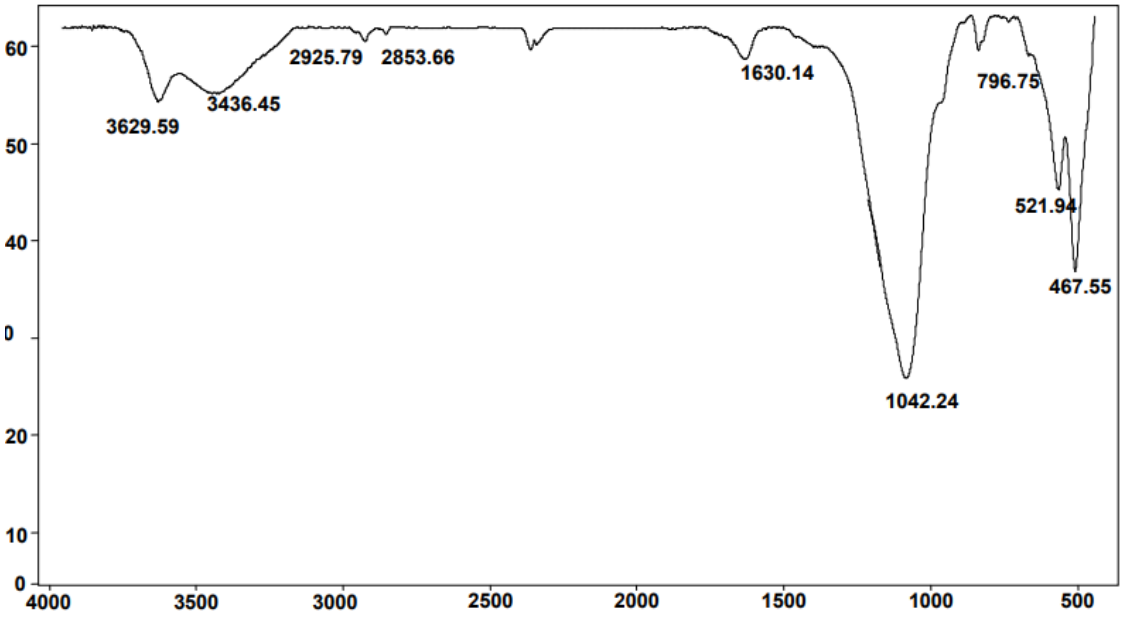


Fig.3. Infrared spectrum of Maghnite-Fe^{2+}

4. 2. Analysis by X-Ray Diffraction (XRD)

The X-ray diffraction patterns of Maghnite-H^+ and Maghnite-Fe (figs. 4 and 5) show the characteristic bands of the material with a difference in the small angles (from 5 to 10°), this indicates that there was a change when inserting the ferric ions into the Maghnite-H^+. The interfoliar distance (d001) calculated from the spectra and by applying Bragg's law $n\lambda=2d\sin\theta$, goes from d= 15 A° for Maghnite H^+ to d= 16.65 A° for Maghnite-Fe. These results are comparable to the literature **[18, 19]**.

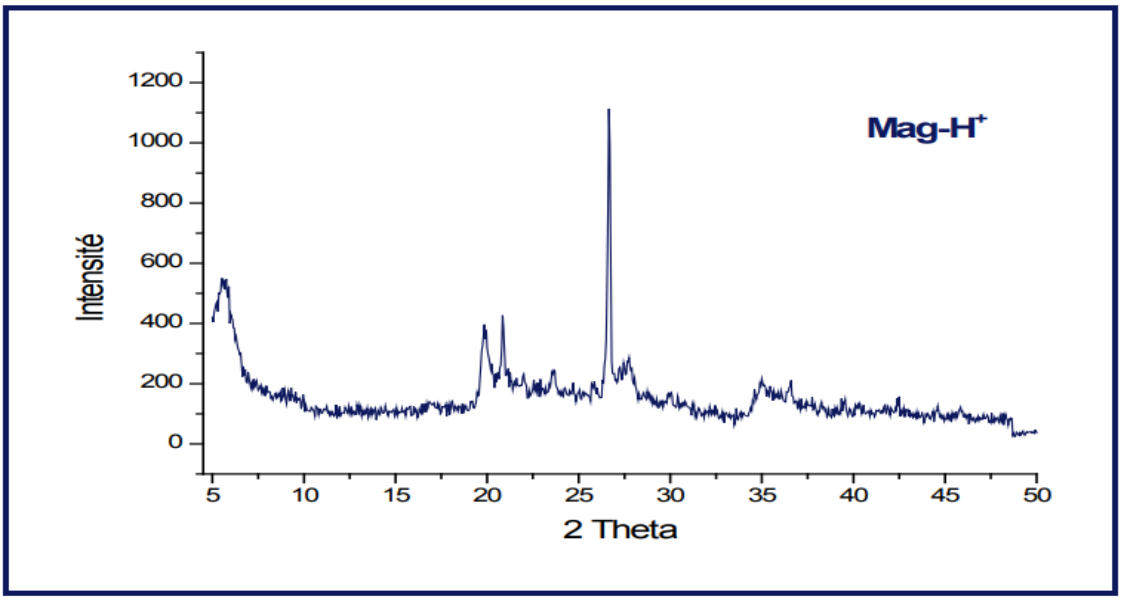


Fig.4: X-ray diffraction pattern of Maghnite H^+

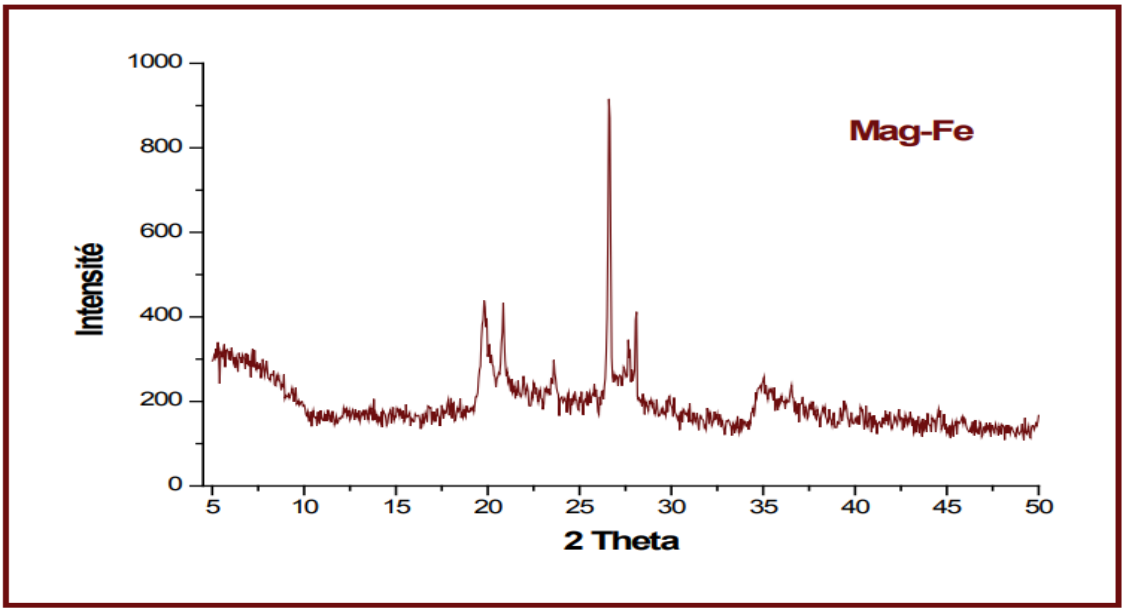


Fig.5: X-ray diffraction pattern of Maghnite Fe^{2+}

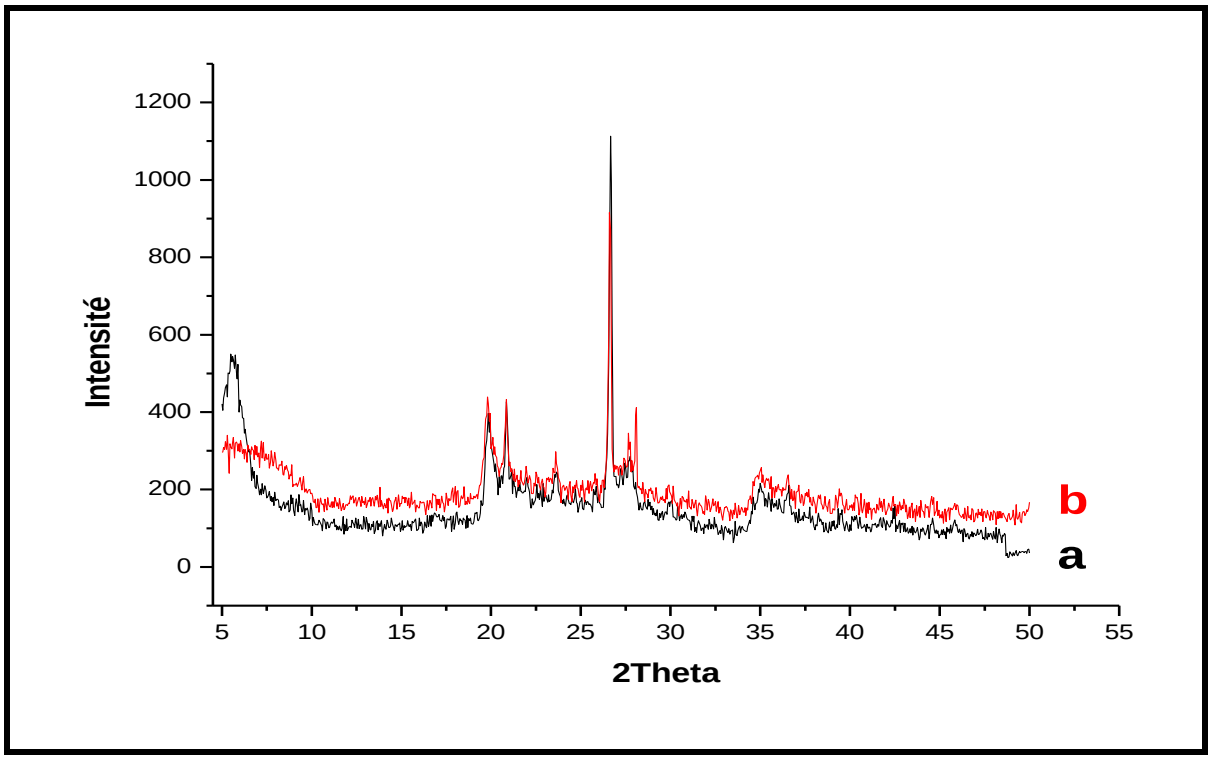


Fig.6. Maghnite-Fe (b) and maghnite H^+ (a) X-ray diffraction patterns

5. Characterization of polystyrene

The obtained polymers were characterized using a variety of methods, including IR, ^1H NMR, and ^{13}C NMR. Tetramethylsilane served as the internal standard and deuterated chloroform served as the solvent as ^1H NMR spectra were collected using a Bruker FT AM 300 spectrometer at room temperature. On an Alpha FTIR Brucker spectrometer (4000-400 cm^{-1}), the FTIR spectra were captured.

5.2. Structural identification of compounds

5.2 1. Characterization by IR of polystyrene catalyzed by Maghnite-H^+

Table.3 : Principales bandes caractéristiques of polystyrène by infrared. [12]

Groupings	Experimental frequency in cm^{-1}
aromatic C-H in Meta, in ortho, in para	657,30 (low), 697,92 (strong), 758,88 (broad)
aliphatic C-C, aromatic C-C	1029,23 (medium), 1084,59
aromatic C=C, -CH-aliphatic	1490.82 - 1598.63, 2847,60-2920,52

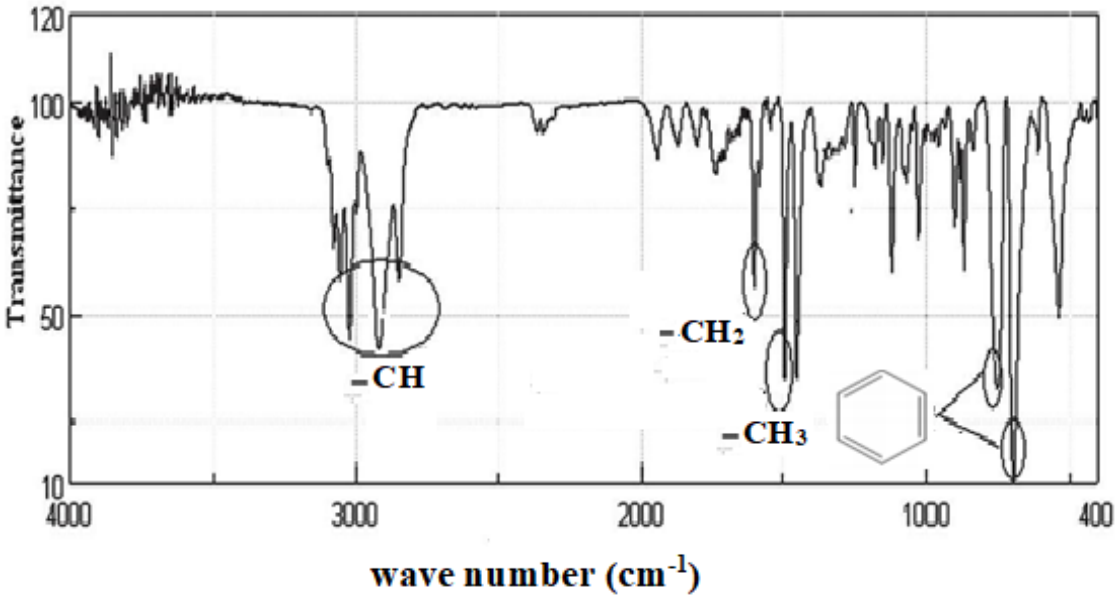


Fig.7: Infrared spectrum of polystyrene catalyzed by Maghnite- H^+ [12]

3.2 2.Characterization by IR of polystyrene catalyzed by Maghnite-Na^+

Table.2: The main characteristic bands of polystyrene [13]

Groupings	Experimental frequency in cm^{-1}
aromatic C-H in Meta	539,01
aromatic C-H in ortho	695,35
aromatic C-H in para	754,10
aliphatic C-C	1067,57
aromatic C-C	1369,86-1492
aromatic C=C	1600,14
-CH-aliphatic	2840-3020

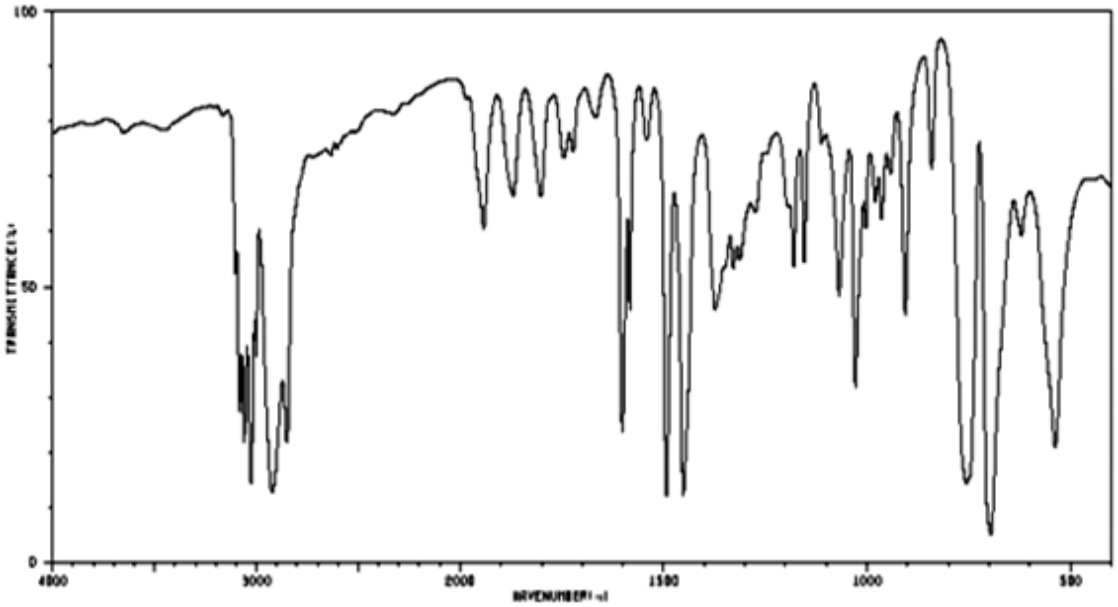


Fig.8: Infrared spectrum of polystyrene catalyzed by Maghnite- Na^+ [13]

3. 2 3. Characterization by IR of polystyrene catalyzed by Maghnite-Fe

Table.4: The main characteristic bands of polystyrene

Groupings	Experimental frequency in cm^{-1}
aromatic C-H in Meta	539,43
aromatic C-H in ortho	696,52-755, 09
aromatic C-H in para	907,64
aliphatic C-C	1068,18
aromatic C-C	1370, 60-1492,33
aromatic C=C	1600,60
-CH-aliphatic	2848,31-3059,05

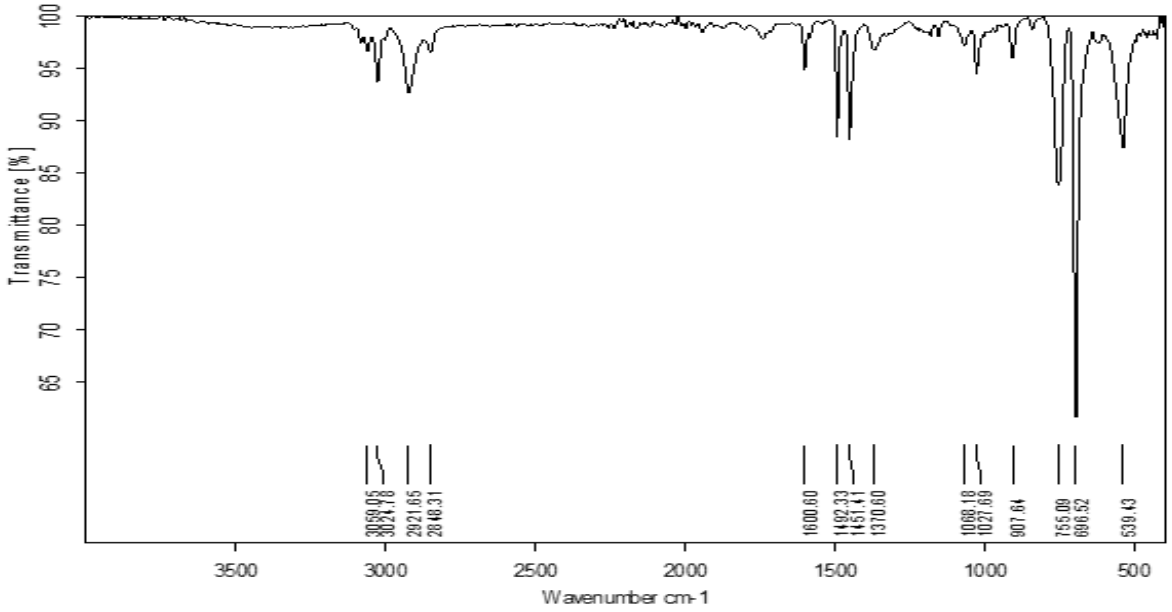


Fig.9. Infrared spectrum of polystyrene catalyzed by Maghnite-Fe

Note: the three figs. 7, 8 and 9 show the same displacements.

4. Characterization by NMR-H[1].

4.1. Characterization by H[1]-NMR of polystyrene using maghnite-H[+] as catalyst

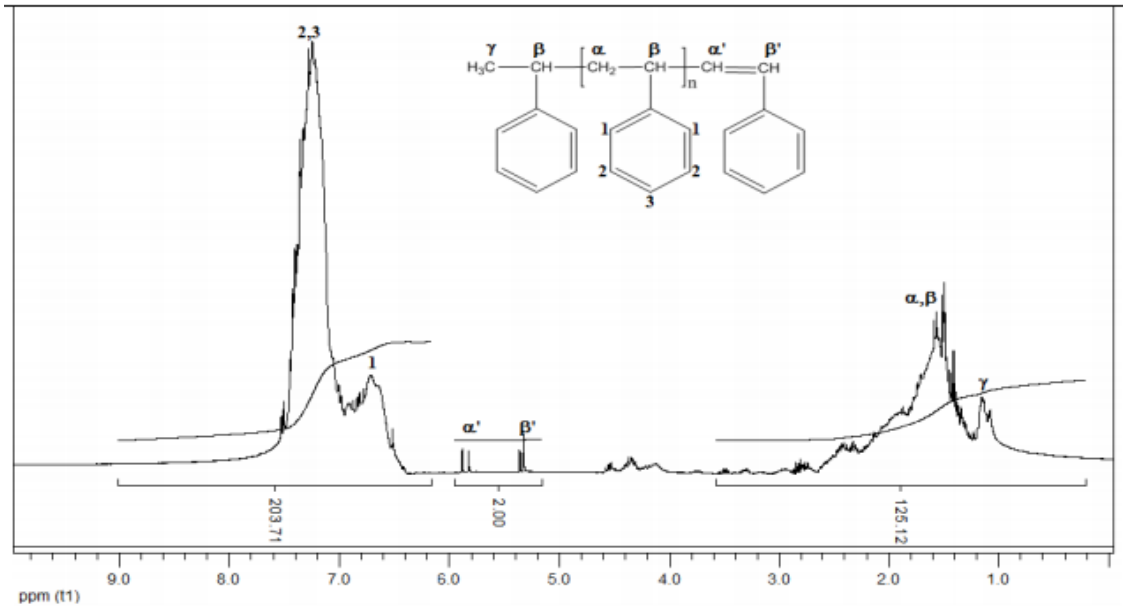


Fig.10: [1]H-NMR spectrum polystyrene catalyzed by maghnite-H[+] [13]

Table. 5: The main characteristic peaks of polystyrene (H^1-NMR) [13]

δ (ppm)	**Attribution**
6.9-7.25	$1H_4 + 2H_2$
6.3-6.8	$2H_2$
1.86	H_α
1.3-1.65	$2H_\beta$

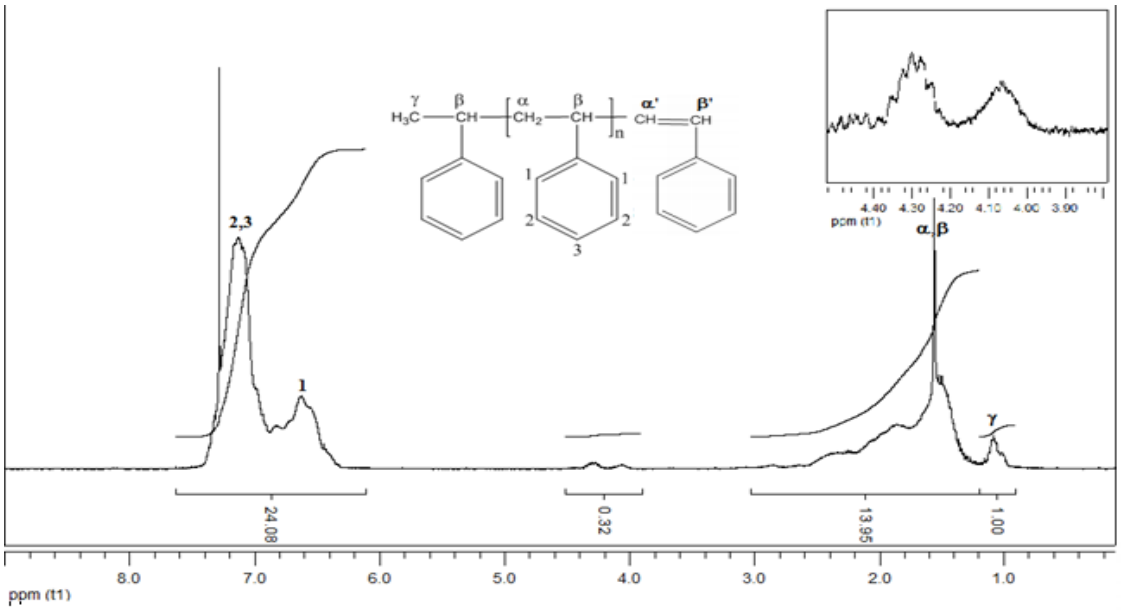


Fig. 11: ^{1}H-NMR spectrum of polystyrene. (Brucker AM 300MHz, solvent:$CDCl_3$)

Table 6: Chemical shifts in ^{1}H NMR of the various polystyrene protons

Attribution	**Quantity**	**Deplacement (*ppm*)**
¡ H γ (methyl)	doubled	0.9-1.1
¡ Hα (methylene),	Triple	1.2-2.4
¡ H β (methine)	multiple	
¡ H 1, 2, 3 (Aromatic)	multiple	6.3 - 7.3

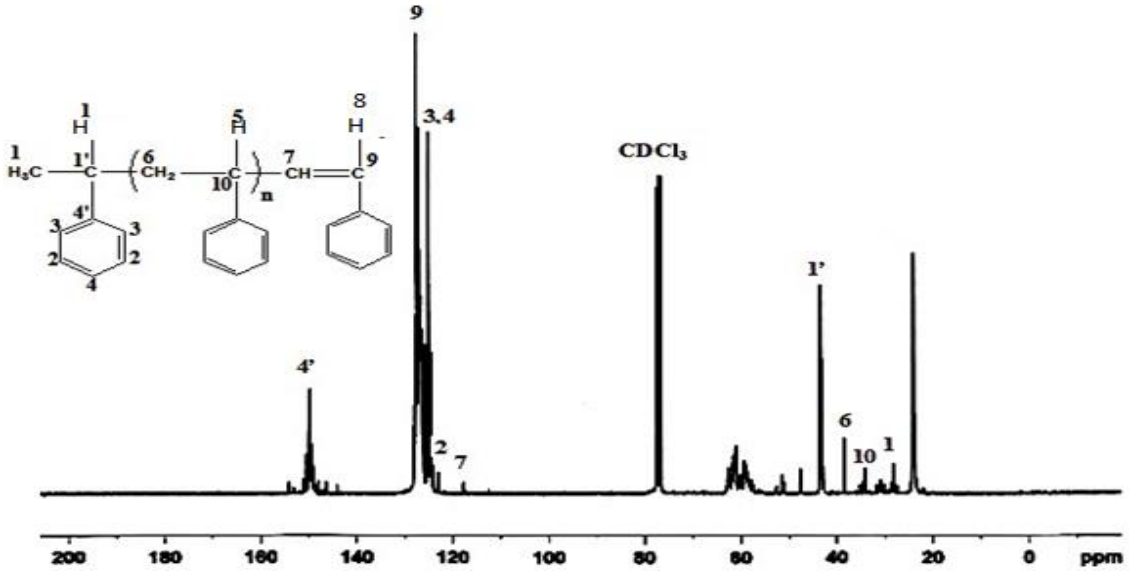


Fig.12: ^{13}C NMR spectrum of polystyrene catalyzed by maghnite-Fe^{2+}

Table. 7: The main characteristic bands of polystyrene (NMR^{13}C)

Number of carbon	C8	C1	C10	C6	C1'	C5	C7	C2	C3, C4	C9	C4'
į (ppm)	23.86	28.15	34.17	38.44	43.07	58- 62	118	123	125	130	150

Cation exchange of montmorillonite

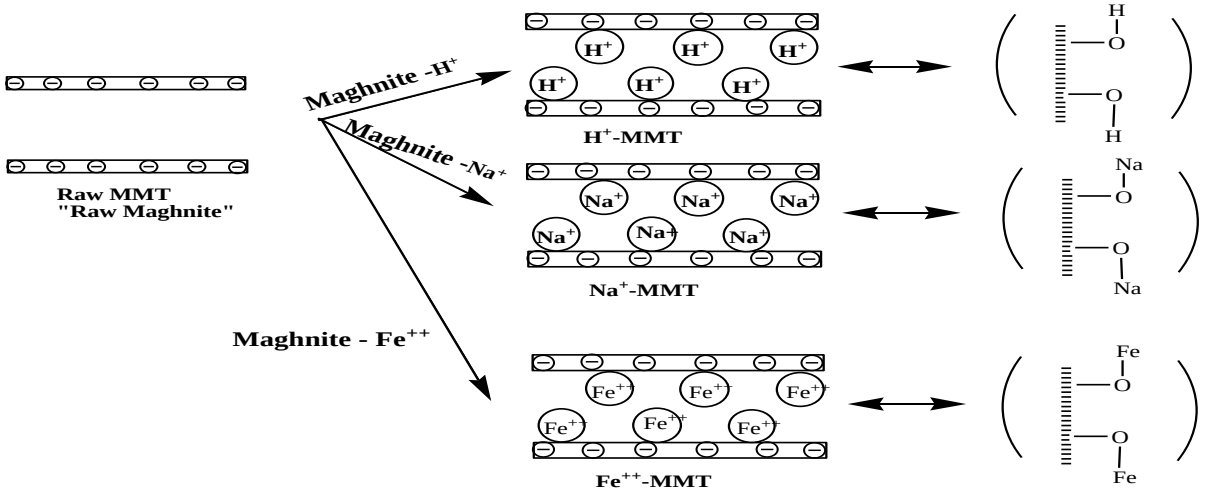
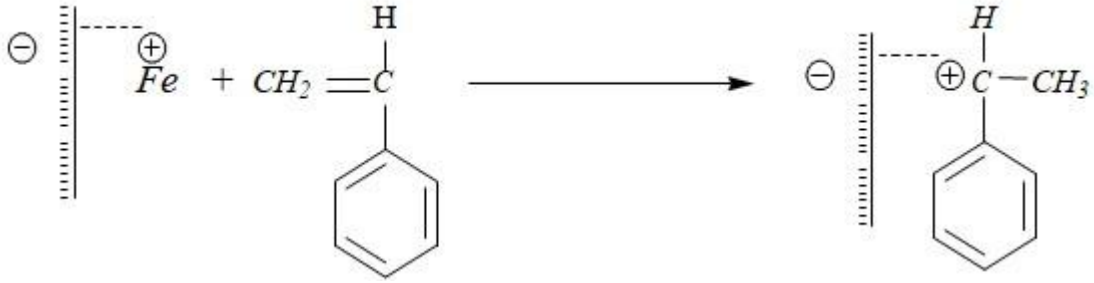


Fig. 13. Exchangeable Cations

III- Probable mechanism of the reaction

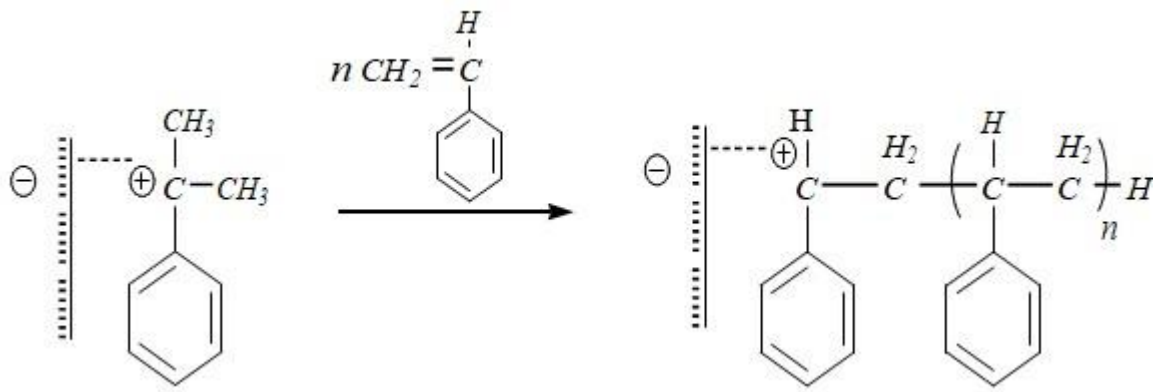
Initiation:

To create the active species, initiation is carried out between the initiator and the first styrene molecule.



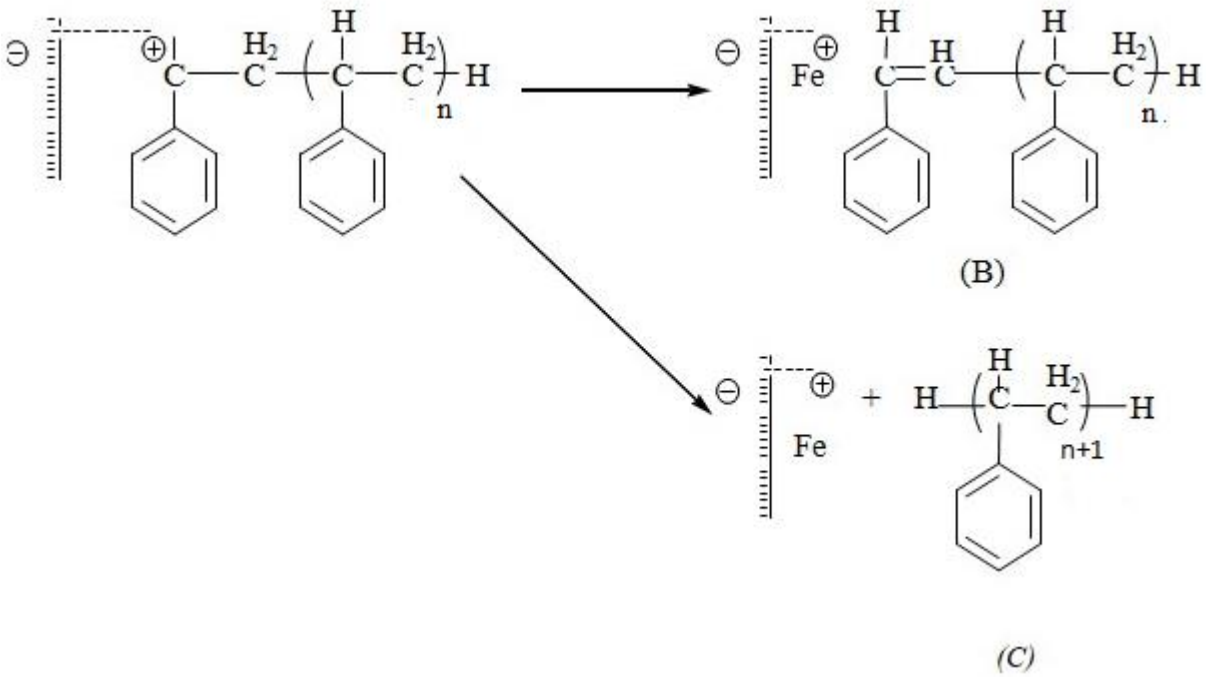
Propagation:

Styrene molecules are thought to be successively inserted between the active center and its counterion (sheet), causing the propagation to occur.



Termination:

At the end of the polystyrene chain, a double bond was formed through spontaneous transfer, as seen in Fig. 2.



Conclusion And Perspective

The problems raised by the environment: atmospheric pollution, (ozone layer, greenhouse gases) accidents due to chemical industries (Seveso, Bhopal) have led international institutions to rethink the future of the planet. Chemistry is called upon to question itself and above all to remedy the errors of old Chemistry. It must create clean chemical engineering that respects the environment in all its forms; This is why research is currently moving towards the new name: “Green Chemistry” or Green Chemistry.

In order to apply the principles of green chemistry and In order to preserve the environment and the health of human beings, it is recommended to reduce the use of homogeneous catalysts, which have a very negative impact, especially in chemistry. industrial. Wherein an acid catalyst such as Brönsted acids (HCl, H2SO4, H3PO4) is employed. The total elimination of the counter ion of the acid used is practically impossible, which consequently poses problems of contamination of the product. Moreover, they are non-recyclable initiators, which therefore generates ecological and economic problems.

Finally, all these disadvantages could be avoided by applying the principles of Green Chemistry and the use of a Heterogeneous catalyst, is a natural Algerian clay of the Montmorillonite type called Maghnite Fe^{2+}. It is a solid, ecological, recyclable and reusable catalyst. This catalyst is of lamellar structure, less expensive natural, which showed a great efficiency for the preparation of several polymers. The operating conditions will be chosen, with respect for the environment (ambient temperature, minimal concentrations, reduced reaction times, etc.).

The use of this catalyst has given rise to several publications such as Styrene-based polymers and these derivatives **[6-17].**

The use of PS polymer is not limited to one industry because it has so many advantages in so many other fields. A good polymer's appealing qualities include being lightweight, portable, resistant to moisture, easily affordable, recyclable, and visually appealing.

Although PS has a certain degree of brittleness and mechanical stability due to the nature of its plasticity, it has been observed that its physical properties are significantly improved upon integration with other materials, which leads us to consider the future research on its polymerization with other monomers to increase its physical and chemical properties.

Because of its excellent physical properties and affordable price, polystyrene is one of the most important materials in the contemporary plastics industry and one of the most extensively used synthetic polymers. For a greener environment and to lessen the disposal of plastic waste, petroleum-based materials must be swapped out for biodegradable, recyclable, and renewable polymers. Recycling plastic waste will improve sustainability and lessen global warming.

In conclusion, we have looked at the synthesis, processing, significance, and industrial uses of PS. The chemistry relating to the structure of PS is playing a major role in its ability to be used for the majority of applications by continuing to be distinct from many other polymers at various conditions of temperature and other atmospheric conditions.

Conflicts of interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1]Sigwalt P. "Recent Results in Proton-Initiated and non Proton-Initiated Cationic Polymerizations". *Polym. J.* 17 (1), pp.57-71, January 1985.

[2] Ribeiro, R.M., Portela, M.F., Deffieux, A., Cramail, H., Rocha, M. "Isoespecific homo and copolymerization of styrene with ethylene in the presence of VCl_3, $AlCl_3$ as catalyst". *Macromol. Rapid. Commun.* 17 (7), pp. 461-469, July 1996.

[3]. Satoh K., Nakashima J., Kamigaito I., Sawamoto M. "Novel BF_3OEt_2/R-OH initiating system for controlled cationic polymerization of styrene in the presence of water". *Macromolecules*, 34 (3), pp. 396-401, January 2001.

[4]. Higashimura T., Ishihama Y., Sawamoto M. "Living cationic polymerization of styrene: new initiating systems based on added halide salts and the nature of the growing species". *Macromolecules,* 26 (4), pp. 744-751, February 1993.

[5]. Hasebe T., Kamigaito M., Sawamoto M. "Living cationic polymerization of Styrene with $TiCl_3$ (OiPR) as a lewis-acid Activator". *Macromolecules,* 29 (19), pp. 6100-6103, September 1996.

[6]. Belbachir M, Bensaoula A. *US Patent* N°. 0069446 A1, 2006.

[7]. Ayat M, Harrane A, Belbachir M. Maghnite-H^+, "A solid catalyst for the cationic polymerization of a-methylstyrene". *J. Appl. Polym. Sci.* 109 (3), pp. 1476–1479, April 2008.

[8]. Ayat M, Bensaada N, Belbachir M, Harrane A, Meghabar R. "Synthesis and characterization of Poly (α-methylstyrene) by cationic polymerization using a new solid ecological catalyst". *Orient. J. Chem.* 31 (4), pp. 2115–2123, December 2015.

[9] Ayat M, Rahmouni A, Belbachir M. "Selective synthesis, characterization, and kinetics studies of poly(a-methyl styrene) induced by Maghnite-Na^+ Clay (Algerian MMT)". *Bull. Chem. React. Eng. Catal.*, 11 (3), pp. 376–388, December2016.

[10]. Ayat M, Rahmouni A, Belbachir M. "Methyl methacrylate and alpha-methylstyrene: new strategy for synthesis of bloc copolymers for use in potential biomedical applications generated by an ecologic catalyst called maghnite (Algerian MMT)". *Bull. Chem. React. Eng. Catal.,* 11 (3), pp. 316–329, December 2016.

[11].Bensaada N, Ayat M, Meghabar R, Belbachir M. "The synthesis of polystyrene with a new chemical approach". *Current Chemistry Letters* 4 (2):pp. 55–60, March 2015.

[12] Baghdadli M. C, Meghabar R, Belbachir M Acid-activated Algerian montmorillonite as heterogeneous catalysts for cationic polymerization of styrene. *Asian J Chem.*, 28 (6): pp. 1197–1204, February 2016.

[13] M. Ayat, M. Belbachir, A. Rahmouni, Synthesis of block copolymers consists on vinylidene chloride and a- Methylstyrene by cationic polymerization using an acid exchanged motmorillonite clay as heterogeneous catalyst (Algerian MMT). *Journal of Molecular Structure,* 1139: pp. 381-389, July 2017.

[14] M. Ayat, A. Rahmouni, M. Belbachir. Polym. Bull. Cationic polymerization of poly (α-methylstyrene-block- isobutyl vinyl ether) using Maghnite-H^+ clay (Algerian MMT) as catalyst. *Polymer Bulletin.*, 75, pp. 5355-5371, April 2018.

[15] M. Ayat, A. Rahmouni, M. Belbachir, N. Bensaada, M. C. Baghdadli, R. Meghabar Thermoplastic block copolymer: α-MethylStyrene and vinyl acetate catalyzed by clay layered called Maghnite-Na^+ (Algerian MMT). *Journal of Polymer Research* 26: 230, August 2019.

[16] Derkaoui. S, Belbachir. M, Haoue. S., Zeggai. F. Z. Rahmouni. A, Ayat M Homopolymerization of methacrylamide by anionic process under effect of Maghnite-Na^+ (Algerian MMT). *Journal of Organometallic Chemistry*, 893:pp. 52-60, August 2019.

[17] A. Rahmouni, M. Belbachir, M. Ayat, Structural Investigation: Anionic Polymerization of Acrylamide under Microwave Irradiation using Maghnite-Na^+ Clay (Algerien MMT) as Initiator. *Bull. Chem. React. Eng. Cat.*, 13 (2), pp. 262-274, June 2018.

[18] T.Mishra, K.M.Parida and S.B.Rao. Transition Metal Oxide Pillared Clay: 1. A Comparative Study of Textural and Acidic Properties of Fe(III) Pillared Montmorillonite and Pillared Acid Activated Montmorillonite . *Journal of Colloid and Interface science*, 183 (1), pp. 176-183, October 1996.

[19] Fu-Chuang Huang, Jiun-Fwu Lee, Chung-Kung Lee, Huang-Ping Chao, Colloids and Surfaces A: *Physicochem.Eng.Aspects.*, 239 (1-3), pp. 41-47, May 2004.