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MONTMORILLONITE MAGHNITE-Na$^+$, A GREEN CATALYST FOR SYNTHESIS OF POLY (STYRENE-CO-1,3,5-TRIOXANE)

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In the present work the copolymerization of 1,3,5-Trioxane (TOX) with Styrene (ST) was done. The Maghnite-Na+ is a Na+ exchanged montmorillonite clay initiator. This solid catalyst has many advantages. Among them, process easy to use, ecological and there are no traces of initiator in the product obtained. We have studied the kinetic of the reaction by the effect of the amount of Maghnite-Na$^+$. The copolymer obtained was characterized by 1H-NMR, DSC and IR spectroscopy and the catalyst analysis by XRD technique.Keywords: green catalyst; ε-caprolactone; 1,3-dioxolane; Maghnite -H$^+$; poly (ε-caprolactone-co-1,3-dioxolane).

INTRODUCTION

Given the importance of polystyrene to industry, researchers around the world are seeking to minimize the cost of producing polystyrene by using inexpensive, recyclable and non-toxic catalysts. As an example, heterogeneous catalysts based on clay, such as acid activated montmorillonite which are the subject of special attention in different chemical processes due to their environmental compatibility, low cost, selectivity, thermal stability and recyclability[1]. They are used as a catalyst[2,3]. or as a catalytic support[4,5]. Indeed, the acid-treated montmorillonite is one of the acid catalysts widely studied in many organic transformations such as isomerization [6]. alkylation[4,5,7], acylation[8] and polymerization[9].

The acid property of montmorillonite can be easily altered by replacing of the crystalline structure[9,10]. It has been reported that aluminium, iron and tin ion-exchanged montmorillonites are strongly acidic and efficient for several acid-catalyzed organic reactions, such as aldol and Michael reactions[11,12]. Almost all of their clay catalysts have been either (a) acid-treated clays such as K-10, or ion-exchanged clays such as Al^{3+}, Cr^{3+} or H$^+$ exchanged Wyoming or Texas bentonites[13].

Many catalysts can catalyze the ring-opening polymerization reaction of epoxides and aromatic. By giving some examples of these catalysis, boron trifluoride[14], 12-tungstophosphoric ($H_3PW_{12}O_{40}$) acid[15], Boron trifluoride-ether complexes[16], sulfonic super acids (CF_3SO_3H, FSO_3H, and $ClSO_3H$), methanesulfonic acid (CH_3SO_3H)[8,17], Pd(II) and Ni(II) α-diimine catalysts[18], Metal alkyls $TiCl_3–Al(C_2H_5)_3$, $VCl_3–Al(C_2H_5)_3$[19], Heteropolyacid, 12-1phosphotungstic acid (PW12)[20], Metal Complexes[21], $AlCl_3/SbCl_3$[22] and 2-iodoimidazolium salts[23].

Recently, an Algerian proton exchanged montmorillonite clay called Maghnite-Na+, a new nontoxic cationic initiator, was used as a catalyst for cationic polymerization of a number of vinylic and heterocyclic monomers[24-25], which is environmentally friendly, strong and can be recovered by simple filtration[26].

In this work we are interested in the copolymerization of 1,3-dioxolane with styrene catalyzed by a clay-based catalyst. called Maghnite Na$^+$, which is environmentally friendly, strong and can be recovered by simple filtration.

Maghnite has already been used, for refining sugars from oils and other chemicals, so this work was also done with the aim of upgrading this catalyst.

For example T. Higashimura[27], carried out copolymerization reactions of cyclic ethers among them, ethylene oxide and propylene oxide with styrene, using ($BF_3.OEt_2$) at 30°C as a catalyst.

In this work we have taken this reaction and we are going to replace this toxic catalyst with a clay-based catalyst called Maghnite H^+. Techniques such as Infra Red (IR), Differential Scanning Calorimetry (DSC), Hydrogen and Proton Nuclear Magnetic Resonance (1H-NMR), were used to characterize the products of the reaction. The effects of the amounts of the Maghnite-H+ on the synthesis of poly (ST-co-TOX) are also discussed.

EXPERIMENTAL

PREPARATION OF MAGHNITE-Na^+

Maghnite-Na+ was prepared according to the process reported in our previous study [28]. The raw maghnite was put in an Erlenmeyer flask with 500 mL of 1 M NaCl solution. The mixture was stirred with a magnetic stirrer until saturation in 24 h at room temperature.

The maghnite-Na+ was then washed with water to be free of chloride ions, dried at 105°C .

COPOLYMERIZATION AND PRODUCTS CHARACTERIZATION

In a 50 ml beaker, 1,3,5-Trioxane (TOX) (0.3 mol) and Styrene (ST) (0.3 mol) induced by Maghnite-Na+ (0.25M) were a chosen amount of Maghnite-Na+ was added at room temperature 40 ° C and $CHCl_3$ as solvent (Fig. 1). The weight ratio was kept constant in all flasks. After the required time was reached, an aliquot of the reaction mixture was then removed in such a manner as to exclude any clay mineral, and then dried by evaporation to remove solvent and remaining monomer (Table1).

CHARACTERIZATION

Measurements of 1H-NMR spectra were conducted in $CDCl_3$ solution, under ambient temperature on an AM 300 FT Bruker spectrometer. IR absorption spectrum was recorded on an Bruker FT-IR instrument alpha. X-ray diffraction (XRD) for Maghnite-Na^+, obtained on D8 Advance Bruker AXS X-ray diffractometer.

MECHANISM OF POLYMERIZATION

Maghnite-Na^+ is ion-exchanged montmorillonite sheet silicate clay. The montmorillonite lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet[29,30].The sodium ion Na+ carried by Maghnite-Na^+ in the interlayer space induce cationic polymerization, and the montmorillonite sheets play the role of counter-anions (Fig. 2).

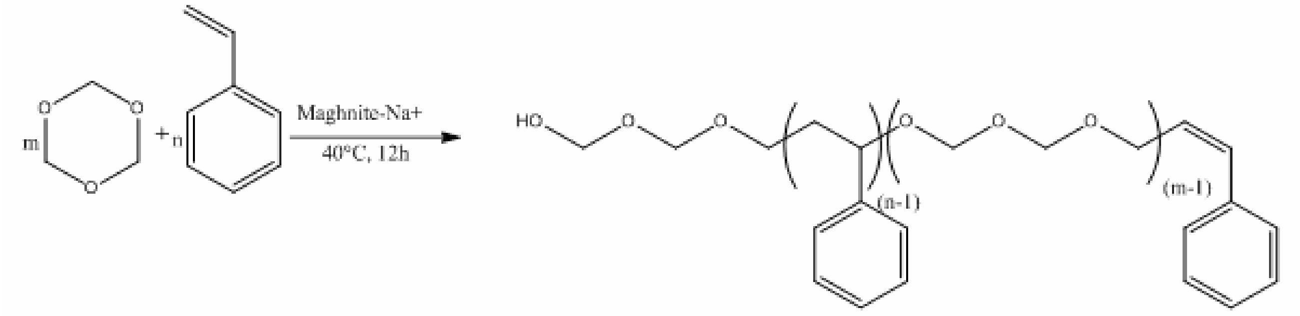

Figure 1. Styrene (ST) polymerization reaction with 1,3,5-Trioxane (TOX).

Table 1

Experimental conditions for the copolymerization of (TOX) with (ST), in the presence of Maghnite-Na + and $CHCl_3$ (0.25M)

ST (mol)	**TOX (mol)**	**Reaction time (h)**
0.3 mol	0.3 mol	12

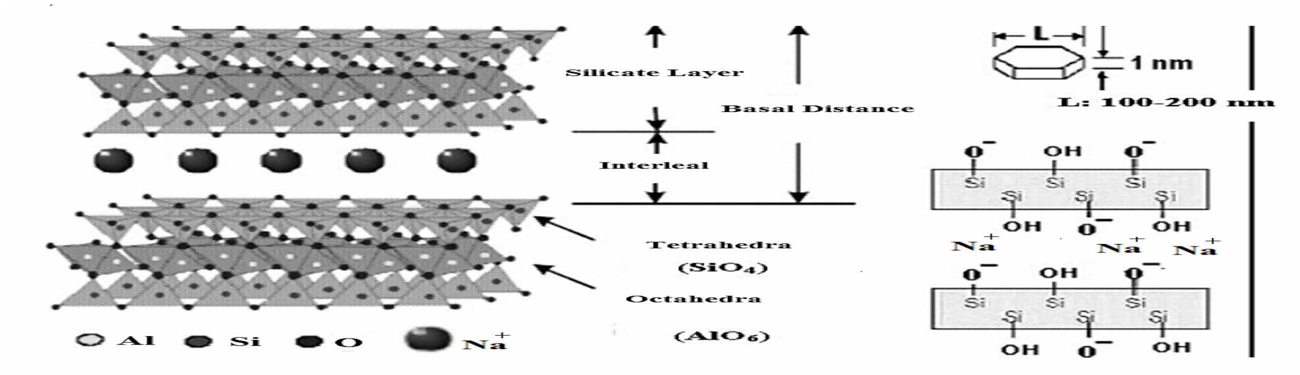

Figure 2. Schematic representation of Maghnite-Na^+.

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE CATALYST (XRD)

The increase in basal spacing from d=11.45 Å in "raw-Maghnite" (Fig. 3), characteristic of a single water layer between the sheets, to a d=16.06 Å value in Maghnite-Na^+ (Fig. 3) for two interlamellar water layers reflects the changes in interlayer cation and its associated hydration state as a result of the treatment[30, 31].

The elementary analysis of Maghnite-Na+ show that there is an excellent correlation between the salt treatment and the catalytic activity of Maghnite-Na^{+}[32]. We suppose that sodium exchange of "raw-Maghnite" reduces the octahedral content (Al_2O_3) which causes an increase in the proportion of silica (SiO_2)[33,34].

EFFECT OF THE AMOUNT OF MAGHNITE-Na^+ ON THE COPOLYMERIZATION

We can see from (Fig. 4) that the yield increases as the proportion of Maghnite-Na^+ 0.25 M increases (experiments 1, 2, 3). Shows the effect of the amount of Maghnite-Na^+ on the polymerization yield. Indeed, using various amounts: 2.5%, 5% and 10% by weight, the copolymerization was carried out in bulk at 40 °C. The copolymerization rate increased with the amount of Maghnite-Na^+, in which the effect of catalyst as a cationic catalyst of TOX and ST is clearly shown. This phenomenon is probably the result of an increase in the number of "initiating active sites" responsible of inducing polymerization, a number that is pro rata to the amount of catalyst used in reaction[35].

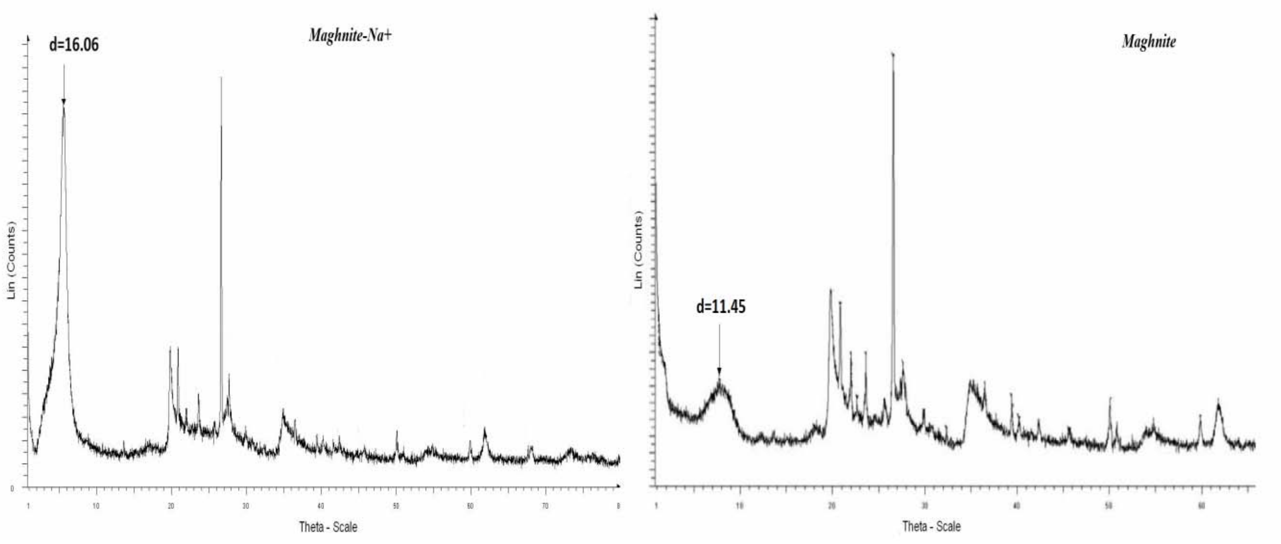

Figure 3. XRD diffraction of Maghnite-Na+ and XRD diffraction of raw Maghnite.

Table 2

Mass yield values as a function of the percentage of Maghnite-Na$^+$

Catalyst %	Yield%
2,5	26
5	41
10	46

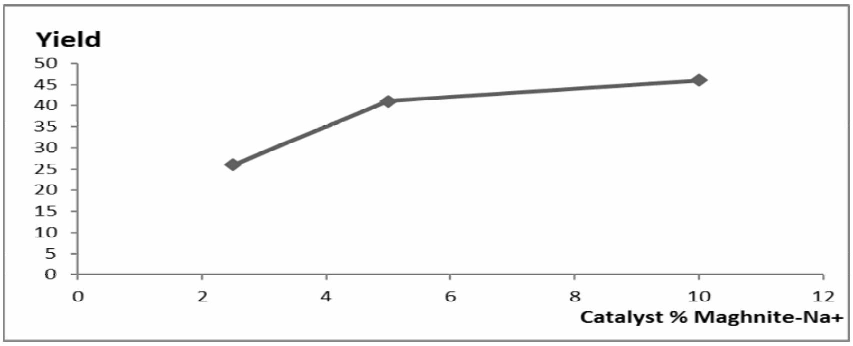

Figure 4. Effect of Maghnite-H$^+$ amount on the copolymerization of ST with TOX.

CHARACTERIZATION OF PRODUCTS

1H NMR ANALYSIS

1H NMR spectra of polymer was recorded in $CDCl_3$ using a Brucker AM 300 MHz apparatusat 25°C and gives the following informations. On the 1H NMR spectrum of polymer in (Fig. 5), several peaks appear.

INTERPRETATION OF INFRARED ANALYSIS

Product obtaine from copolymerization of TOX with ST was analyzed after purification by IR, and he gave the spectrum in Figure 6, which shows the existence of :

1. Phenyl in styrene occurs in three absorption bands, one at the approximately 1493.37 cm^{-1} for the (C = C), another at 3027.39cm^{-1} and 3060.95 cm^{-1} for (C-H) and the last at 697.56 cm^{-1} and 750.92 cm^{-1} for the in-plane strain of (C-H).
2. A strong absorption band around 1026.77 cm^{-1} corresponds to the ether function (C-O-C).
3. Medium intensity bands located between 2856.40 cm^{-1} and 2925.16 cm^{-1}, which correspond to the asymmetric vibration (C-H) of the methylene group.
4. Double olefin bonds-CH=CH- appear at 1601.67cm^{-1}.

The alcohol -OH function characterized by a weak band which appears at 3466.32 cm^{-1}.

DSC ANALYSIS

The study of polymers degradation (Fig. 7) can most often intervene on the factors which improve their thermal stability and also which allow to situate better their own domain of application. DSC analysis of the polymer to give a glass transition temperature obtained at 113,4 °C, it proves that we have a single compound.

Table 3

Results obtained by 1H-NMR

Index	Nature of proton	Monom	δ (ppm)
A	Ph-CH-CH2-	ST	1.9
B	Ph-CH-	ST	1.3
C	-O-CH2-O-	TRO	5,2
D	-CH=CH-Ph	ST	5,3
E,	=CH-Ph	ST	5,8
F	2H (ortho to phenyl)	ST	6,9
G,H	H (in meta and in para of phenyl)	ST	7.1
I	OH	TRO	3,7

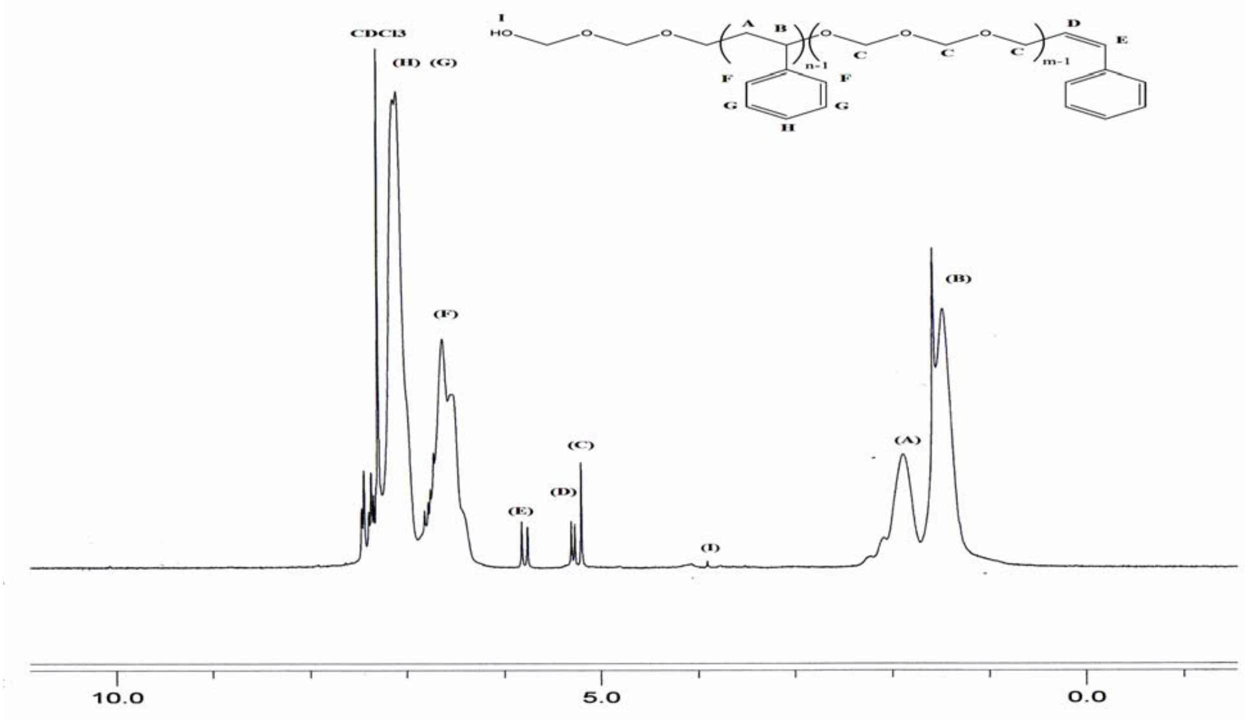

Figure 5. 1H- NMR spectrum of poly (TOX-co-ST) in $CDCl_3$.

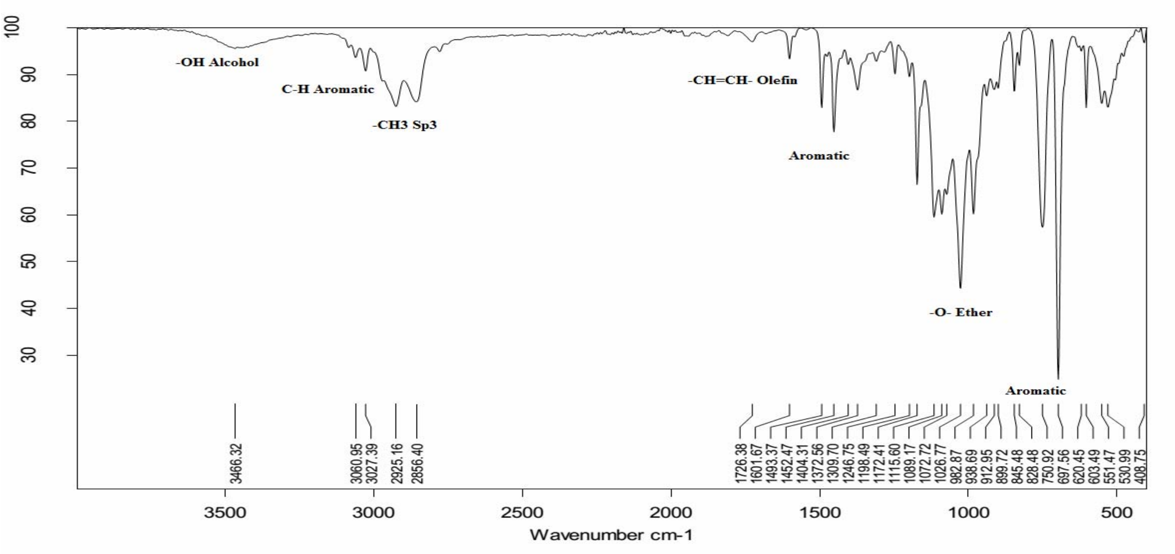

Figure 6. IR spectrum of poly (TOX-co-ST) in $CDCl_3$.

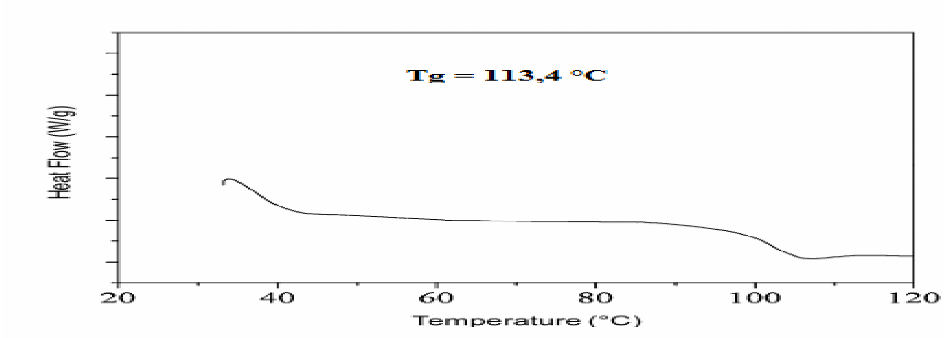

Figure 7. DSC thermogram of poly (TOX -co- ST).

CONCLUSIONS

The present work shows that:

– Maghnite-Na$^+$, a proton exchanged montmorillonite clay, is an effective initiator for the polymerization of Copolymerization of 1,3,5-Trioxane with Styrene.

– This copolymerization was found to be initiated by Maghnite-Na$^+$ powder in heterogeneous phase.

– In the polymerization, the solid catalyst was thought to act as an acid to generate cation species.

– The copolymerization rate increased with the amount of Maghnite-Na$^+$.

– The polymerization proceeds smoothly by a very simple procedure, and a simple filtration is sufficient to recover the catalyst.

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