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СИНТЕЗ ПОЛИ (СТИРОЛ-СО-1,3,5-ТРИОКСАНА) ЭКОЛОГИЧЕСКИМ КАТАЛИЗАТОРОМ МОНТМОРИЛЛОНИТ МАГНИТ-NA$^+$ КАТАЛИЗАТОР

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В данной работе обсуждается экологический подход к синтезу сополимеров (1,3,5-триоксан-со-стирол), полученных сополимеризацией 1,3,5-триоксана (TOX) со стиролом (ST) в присутствии Магнит-Na+ в растворе. Магнит-Na+ представляет собой инициатор из монтмориллонитовой глины с обменом Na+. Этот твердый катализатор имеет много преимуществ. Среди них: процесс прост в использовании, экологичен и в конечном продукте нет следов инициатора. Мы изучали кинетику реакции по влиянию количества магнита - Na +. Полученный сополимер охарактеризовали с помощью ^{1}H ЯМР, ДСК и ИК-спектроскопии и анализа катализатора с помощью XRD. После проведения этих кинетических исследований и анализов в конце можно предложить механизм реакции сополимеризации.

Ключевые слова: экологический катализатор, стирол, 1,3,5-триоксан, магнит-Na$^+$, поли (1,3,5-триоксан-со-стирол)

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

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This study discusses an ecological approach to the synthesis of copolymers (1,3,5-trioxane-co-styrene) obtained by copolymerization of 1,3,5-trioxane (TOX) with styrene (ST) in the presence of Maghnite -Na + in solution. Maghnite -Na $^+$ is a montmorillonite clay initiator with Na+ exchange. This solid catalyst has many advantages. Among them, the process is easy to use, environmentally friendly and there are no traces of initiator in the resulting product. We studied the kinetics of the reaction by the influence of the amount of Maghnite -Na+. The resulting copolymer was characterized by ^{1}H NMR, DSC and IR spectroscopy and analysis of the catalyst by XRD. After these kinetic studies and analyzes have been carried out, a copolymerization reaction mechanism can be proposed at the end.

Key words: ecologic catalyst, Styrene, 1,3,5-Trioxane, Maghnite-Na$^+$, poly(1,3,5-Trioxane-co-styrene)

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INTRODUCTION

Attempts are being made to improve the properties of polystyrene by adding other monomers such as 1,3,5-trioxane, styrene-based polymers such as styrene-acrylic polymers, which are used in the production of coatings on textiles, and some other styrene-based monomers, copolymers which have been studied and developed [1]. Researchers around the world are striving to minimize the cost of polystyrene production through the use of inexpensive, recyclable and non-toxic catalysts. One of these acid-activated catalysts is montmorillonite, which is the subject of particular attention in various chemical processes because of its environmental compatibility, low cost, selectivity, thermal stability, and reusability [2]. Montmorillonite is used as a catalyst [3-4] or as a catalytic carrier [5-6]. Indeed, acid-treated montmorillonite is one of the acid catalysts widely studied in many organic transformations, such as isomerization [7], alkylation [5-6-7], acylation [9], and polymerization [10].

The acid property of montmorillonite can be easily altered by replacing of the crystalline structure [10-11]. 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 [12-13]. 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+}, Mg^{2+} or H^+ exchanged Wyoming or Texas bentonites [14].

Many catalysts can catalyze the ring opening polymerization reaction of epoxy resins and aromatics. Here are some examples of these catalysts: boron trifluoride [15], 12-tungstophosphoric acid [16], trifluoride-boron ether complexes [17], sulfonic superacids [9-18], Pd (II) and Ni (II) α-diimine [19], metal alkyls [19] [20], heteropoly acid [21], metal complexes [22-23] and 2-iodimidazolium salts [24].

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 [25-26], which is environmentally friendly, strong and can be recovered by simple filtration [27]. In this work we are interested in the copolymerization of 1,3-dioxolane with styrene catalyzed by a clay-based catalyst. called Maghnite Na$^+$.

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 [28], 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-Na$^+$. 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-Na$^+$ 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 [29]. 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, and it was 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$^+$ (0.25 M) 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 (Table 1).

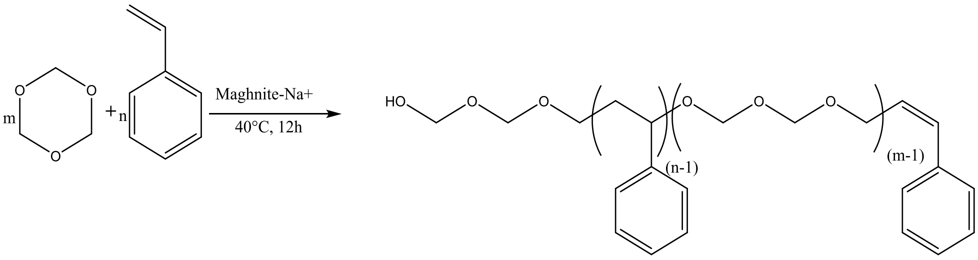

Fig. 1. Styrene (ST) polymerization reaction with 1,3,5-Trioxane (TOX)
Рис. 1. Реакция полимеризации стирола с 1,3,5-триоксаном

Table 1
Experimental conditions for the copolymerization of (TOX) with (ST), in the presence of Maghnite-Na$^+$ and CHCl$_3$ (0.25M)
***Таблица 1*. Экспериментальные условия сополимеризации 1,3,5-триоксана со стиролом в присутствии Maghnite-Na$^+$ и CHCl$_3$ (0,25 M)**

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

Characterization

Measurements of ^{1}H NMR spectra were conducted in CDCl$_3$ solution, under ambient temperature on an AM 300 FT Bruker spectrometer. IR absorption spectrum was recorded on Bruker FT-IR instrument alpha. X-ray diffraction (XRD) for Maghnite-Na$^+$, obtained on D8 Advance Bruker AXS X-ray diffractometer.

Mechanism of Polymerization

Natural montmorillonite has the potential for efficient electrolytic modification of 2D layered nanomaterials [30], the 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 [31-32]. 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).

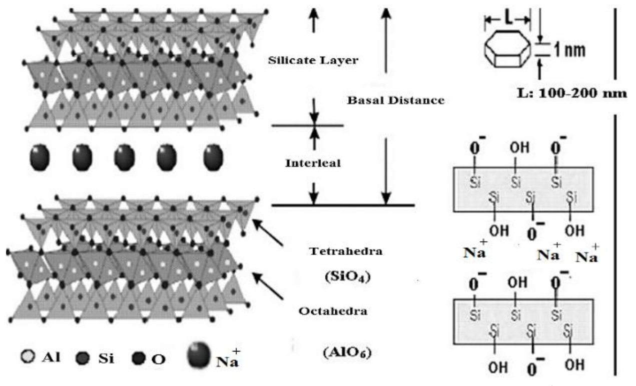

Fig. 2. Schematic representation of Maghnite-Na$^+$
Рис. 2. Схематичный вид Maghnite-Na$^+$

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 [32-33].

The elementary analysis of Maghnite-Na+ shows that there is an excellent correlation between the salt treatment and the catalytic activity of Maghnite-Na$^+$ [34], We suppose that sodium exchange of "raw-Maghnite" reduces the octahedral content (Al$_2$O$_3$) which causes an increase in the proportion of silica (SiO$_2$) [35-36].

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). 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 for inducing polymerization, a number that is pro rata to the amount of catalyst used in reaction [37].

Characterization of products

^{1}H NMR Analysis

^{1}H NMR spectra of polymer was recorded in CDCl$_3$ using a Brucker AM 300 MHz apparatus at 25 °C and gives the following information. On the ^{1}H NMR spectrum of polymer in (Fig. 5), several peaks appear:

Interpretation of Infrared analysis

The product obtained from copolymerization of TOX with ST was analyzed after purification by IR, and gave the spectrum in Fig. 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 3027.39 cm^{-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} correspond to the asymmetric vibration (C-H) of the methylene group.

4. Double olefin bonds-CH=CH- appear at 1601.67cm^{-1}.

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

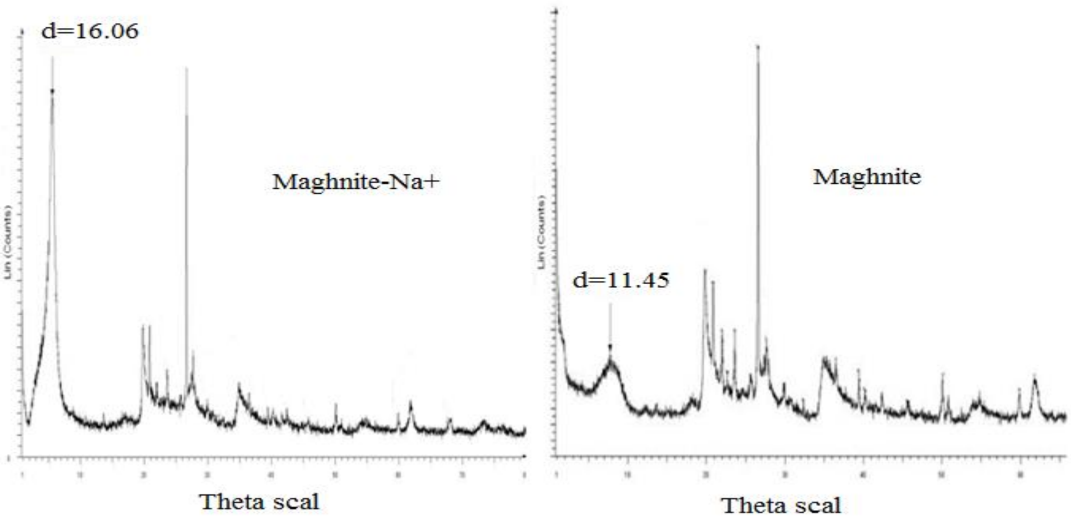

Fig. 3. XRD diffraction of Maghnite-Na^+ and XRD diffraction of raw Maghnite
Рис. 3. Рентгенограмма Maghnite-Na^+ и необработанного Maghnite

Table 2

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

***Таблица 2.* Массовый выход как функция процентного содержания Maghnite-Na^+**

Catalyst %	Yield%
2.5	26
5	41
10	46

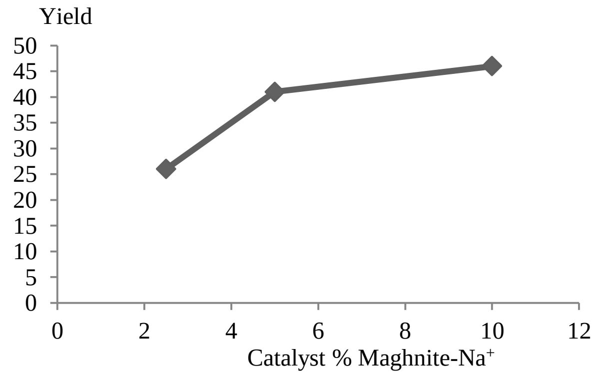

Fig. 4. Effect of Maghnite-Na^+ amount on the copolymerization of ST with TOX
Рис. 4. Влияние количества Maghnite-Na^+ на сополимеризацию стирола с 1,3,5-триоксаном

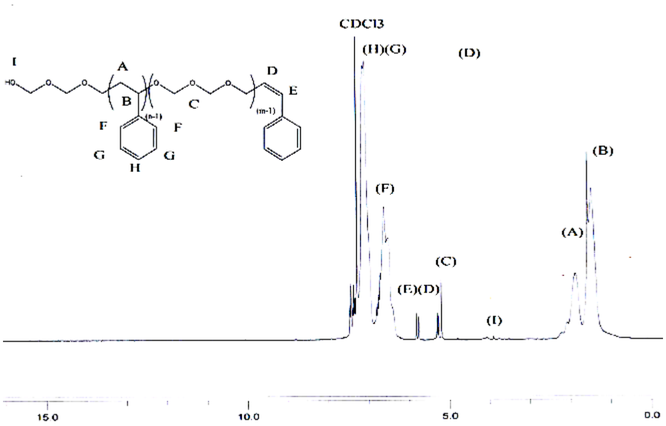

Fig. 5. ^1H- NMR spectrum of poly (TOX-co-ST) in $CDCl_3$
Рис. 5. ^1H ЯМР спектр сополимера стирола с 1,3,5-триоксаном в $CDCl_3$

Table 3

Results obtained by ^1H NMR

***Таблица 3.* Результаты ^1H ЯМР**

Index	Nature of proton	Monom	δ (ppm)
A	Ph-CH-CH_2-	ST	1.9
B	Ph-CH-	ST	1.3
C	-O-CH_2-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

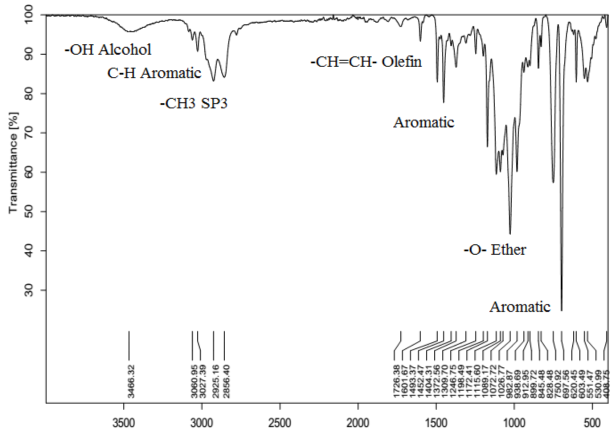

Fig. 6. IR spectrum of poly (TOX-co-ST)
Рис. 6. ИК спектр сополимера стирола с 1,3,5-триоксаном

DSC Analysis

The study of the degradation of polymers (Fig. 7) can most often influence the factors that improve their thermal stability, and also make it possible to better determine the area of their application. DSC analysis of the polymer gives a glass transition temperature of 113.4 °C, which proves that we have one compound.

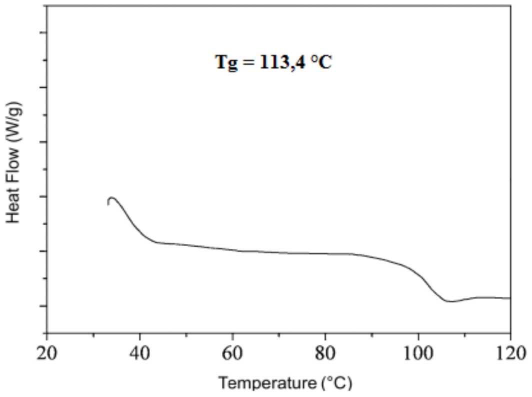

Fig. 7. DSC thermogram of poly (TOX-co-ST)
Рис. 7. ДСК кривая сополимера стирола с 1,3,5-триоксаном

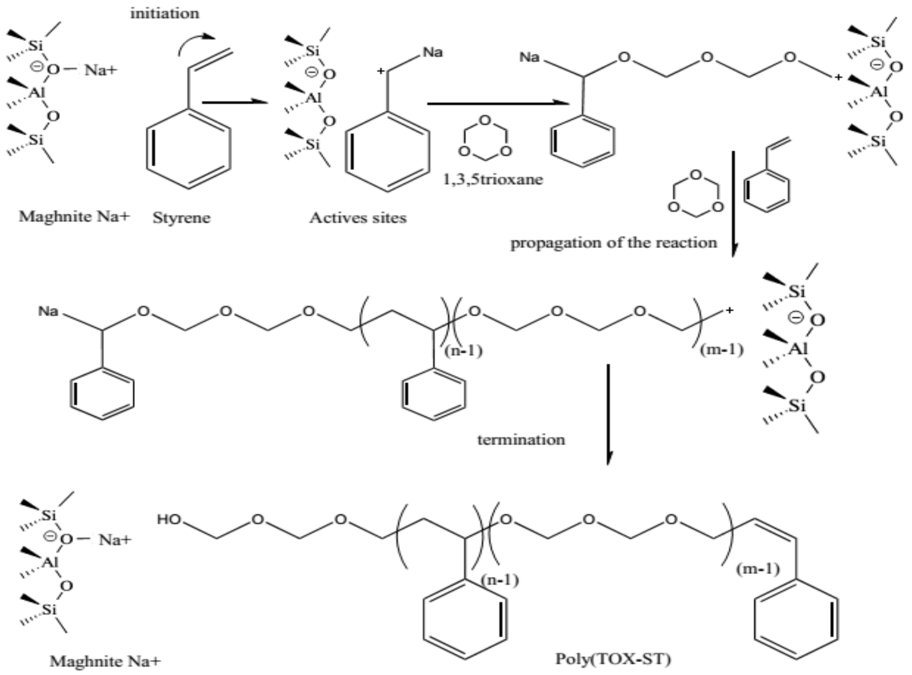

Fig.8. Reaction mechanism of poly (TOX-co-ST)
Рис. 8. Механизм образования сополимера стирола с 1,3,5-триоксаном

CONCLUSIONS

The present work shows that:

the Maghnite was modified using an ion exchange process to obtain Maghnite-Na$^+$ (sodium exchange process) that is a non-toxic catalyst. XRD proved that this clay belonged to the montmorillonite family, this copolymerization was found to be initiated by Maghnite-Na$^+$ powder in heterogeneous phase. The structure of the monomer and the polymer are confirmed by FT-IR, ^{1}H NMR. Maghnite-Na$^+$, a proton exchanged montmorillonite clay, is an effective initiator for the copolymerization of 1,3,5-Trioxane with Styrene. Studies carried out on the effect of the amount of catalyst on the synthesis of poly (TOX-co-ST) proved the effectiveness of Maghnite and 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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