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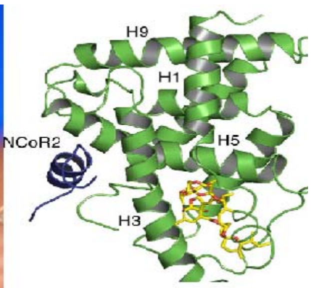

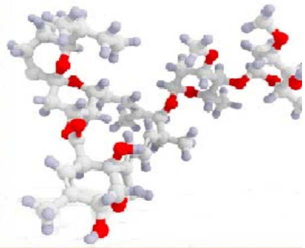

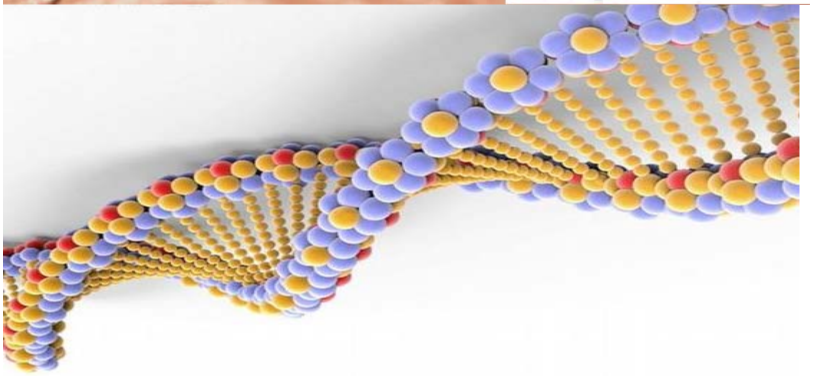

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Protonated Montmorillonite Maghnite-H^+ Clay Used as Green Non-toxic Catalyst for the Synthesis of Biocompatible poly (DXL -co- Styrene).

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Abstract *Copolymerization of 1,3-Dioxolane (DXL) with Styrene (St) catalyzed by Maghnite-H^+ a montmorillonite sheet silicate clay exchanged with protons, was investigated. The cationic ring opening polymerization was initiated by Maghnite-H^+ in bulk. The copolymer obtained was characterized by ^{1}H-NMR, DSC and IR spectroscopy. The studies done, such as the effect of the amount of Maghnite-H^+ on the syntheses of poly (DXL -co- Styrene).*

Key Words: *1,3-Dioxolane, Styrene, Maghnite-H^+, Montmorillonite, Copolymerization*

Introduction

The presence of toxic initiators presents problems in the manufacture of polymers used especially in medical and veterinary procedures. There is still a great demand for heterogeneous catalysis under mild conditions and in environmentally friendly processes[1].The reactions catalyzed by montmorillonite are usually carried out under mild conditions with high yields and high selectivities, 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[2].Clay minerals, a large family of alumino-silicate structures with a range of chemical composition, structure and surface properties, are very reactive materials due to their small grain size large surface area, adsorption properties and chemical variability [3] ,Montmorillonites have both brönsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly-active catalysts initiators for acid-catalysed reactions[4] .These exchanged montmorillonites initiators have been successfully used as catalysts in polymerization reactions[5],for example, polystyrene (PS) [6-7], and polystyrene-block-polyisoprene-block-polystyrene[8].Clay montmorillonite is a layered silicate possessing ion-exchange ability. The acid property of montmorillonite can be easily altered by replacing of the crystalline structure [9]. 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 [10-11]. 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 [12]. Recently, an Algerian proton exchanged montmorillonite clay called Maghnite-H+, a new nontoxic cationic initiator, was used as a catalyst for cationic polymerization of a number of vinylic and heterocyclic monomers [13-14], the purpose of this paper is to study the copolymerization of DXL with Styrene, catalyzed by Maghnite-H+ a proton exchanged Montmorillonite clay. 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 (DXL-co-Styrene) are also discussed.

2. Experimental section

2.1. Materials

Styrene (grade 99%) was used as purchased from Aldrich. 1,3-Dioxolane (DXL) was distilled over the blue benzophenone–Na complex.Chloroform was dried on CaH_2 anhydrous and distilled before use. Raw-Maghnite: Algerian Montmorillonite clay was procured from BENTAL (Algerian Society of Bentonite).

2.2. Preparation of "Maghnite-H^+ 0.25M"

Maghnite-H^+ was prepared according to the process reported in our previous study[13]. Raw-Maghnite (20 g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 hours at 105 °C the Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until saturation was achieved over 2 days at room temperature, the mineral was then washed with distilled water to became sulfate free and then dried at 105 °C, a test of the barium nitrate of the residue of rinsing water is needed to ensure that the sulfate is eliminated.

2.3.Copolymerization and products characterization

In a 50 ml beaker, DXL (11.7 mol/l) and Styrene (6.3 mol/l) were dissolved in 20 ml of Chloroform and a chosen amount of Maghnite-H^+ was added at 40 °C. 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.

3. Results and discussion

The results of experiments of DXL with Styrene Copolymerization induced by Maghnite-H^+ 0.25M proceed in bulk are reported in (Table 1). For all these experiments the temperature was kept constant at 40 °C for 12 hours.

Table 1: Copolymerizations of 1,3-Dioxolane with styrene using different amount of Maghnite-H^+

Experiment	Maghnite-H^+ (0.25% M)	Yield %
1	10	39.56
2	5.0	19.23
3	2.5	10.13

Figure 1 shows the effect of the amount of Maghnite-H^+ on the synthesis yield of poly (ε-caprolactone-co-THF)

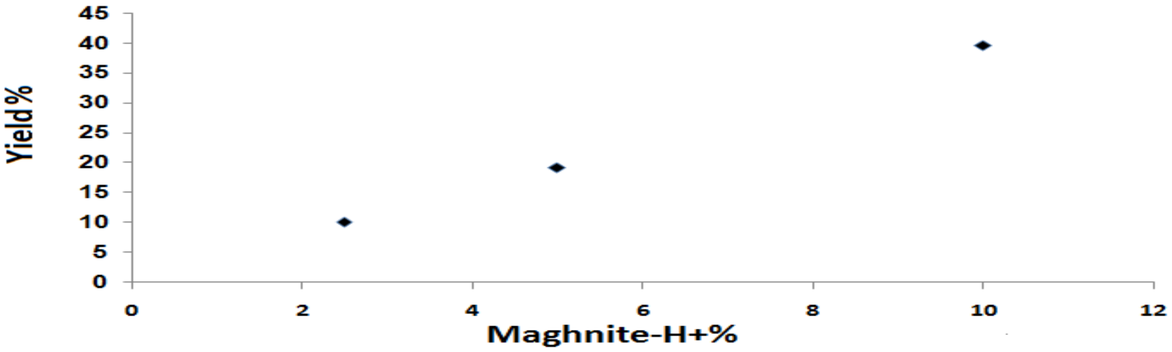

Figure 1: Effect of Maghnite-H+ amount on the copolymerization yield of ,3-Dioxolane with Styrene

3.1. Effect of the amount of Maghnite-H+ on the copolymerization

We can see from (Figure 1) that the yield increases as the proportion of Maghnite-H^+ 0.25 M increases (experiments 1, 2, 3). Shows the effect of the amount of Maghnite-H^+ on the polymerization yield. Indeed, using various amounts: 2.5, 5 and 10% by weight, the polymerization was carried out in bulk at 40 °C. The copolymerization rate increased with the amount of Maghnite-H^+, in which the effect of catalyst as a cationic catalyst of 1,3-Dioxolane and Styrene 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.

3.2. Characterization of products

The reaction taking place is shown in the following (Figure 2)

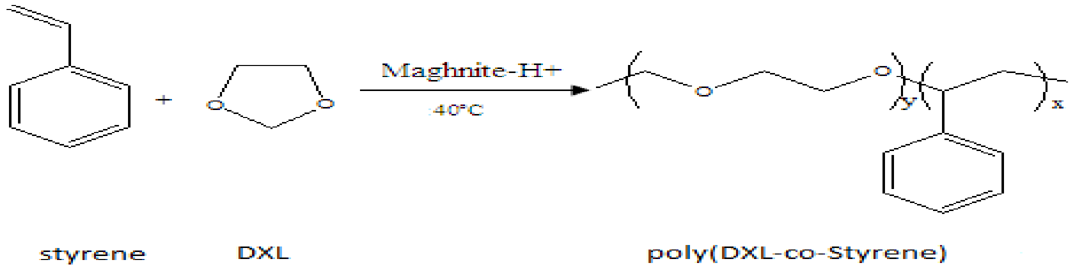

Figure 2: Synthesis of poly (DXL -co- Styrene) by Maghnite-H^+ catalyst

According to the work published by Masahiko Okada[14] the polymer obtained was characterized by 300 MHz ^{1}H-NMR in CDCl3 [15]. (Figure 3) shows the chemical shifts at 7.23 ppm and 7.33 ppm for the protons of benzene ring, that at 3.74 ppm for the protons of methylene groups and that at 4.8 ppm for the protons of ethylene group of Poly DXL and those at 1.26 ppm and 1.74 ppm for the methylene and methine groups of Poly St.

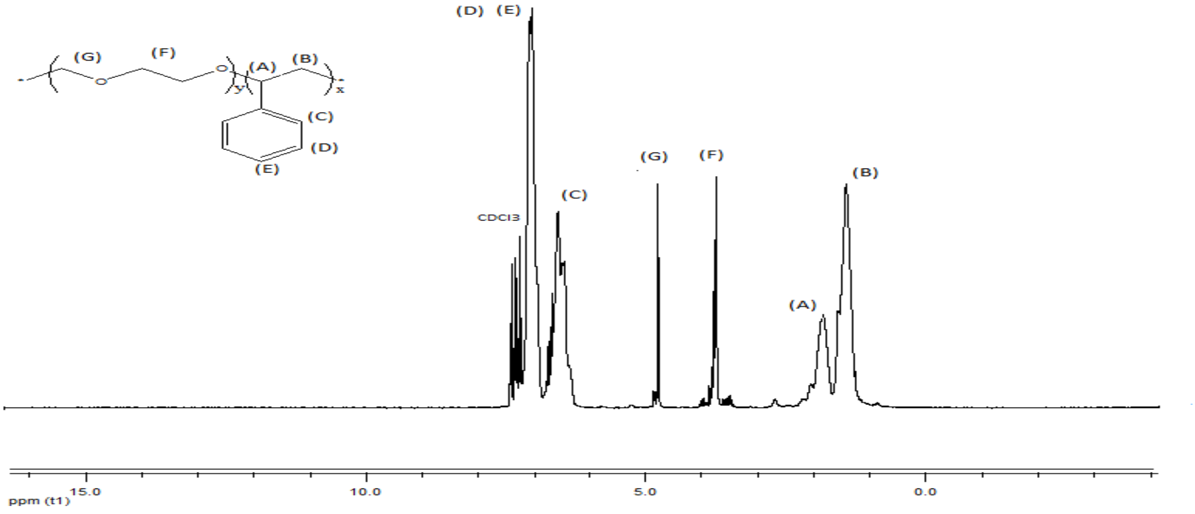

Figure 3: ^{1}H NMR spectrum of poly (DXL-co- Styrene) in $CDCl_3$

IR spectroscopy (Figure 4) allows us to confirm the nature of the polymer by identifying, The phenyl of St appears in three absorption bands: one at 1645.77 cm^{-1} for the (C = C), another at 3157.29 cm^{-1} for (CH) and the last at 781.10 cm^{-1} for the deformation in the plan of (CH).The ether function appears clearly at 1051.42 cm^{-1} .The large band at 3473.29 cm^{-1} is attributed to the connection (OH), which is probably due to a bad drying of KBr used for this analysis.

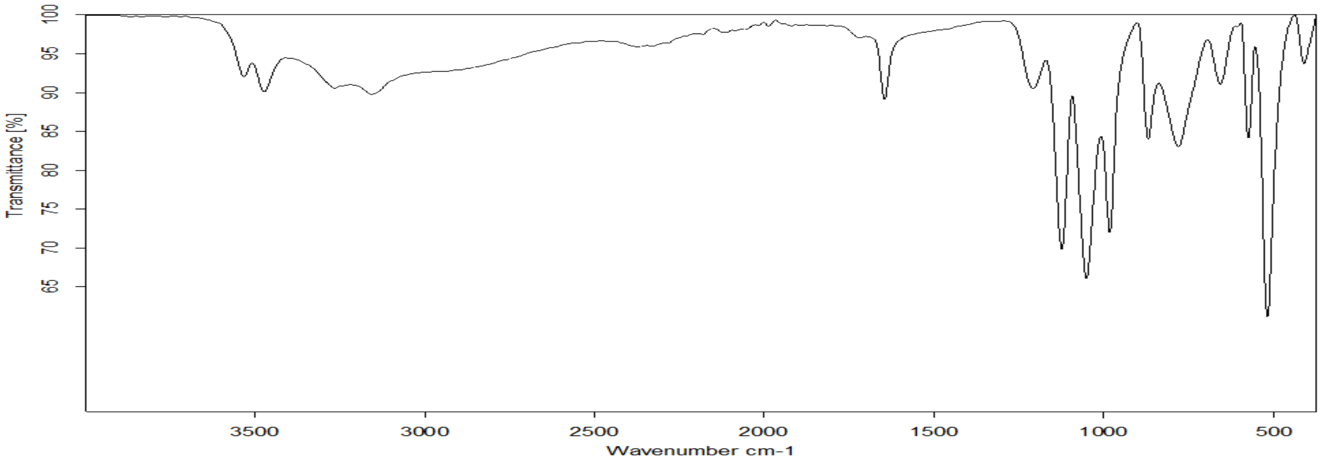

Figure 4: IR spectrum of poly (DXL-co- Styrene)

The study of polymers degradation (Figure 5) 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 55.7 °C and a melting temperature at 141.1 °C, the presence of both the transition temperature and the melting temperature, shows that the polymer is semi crystalline.

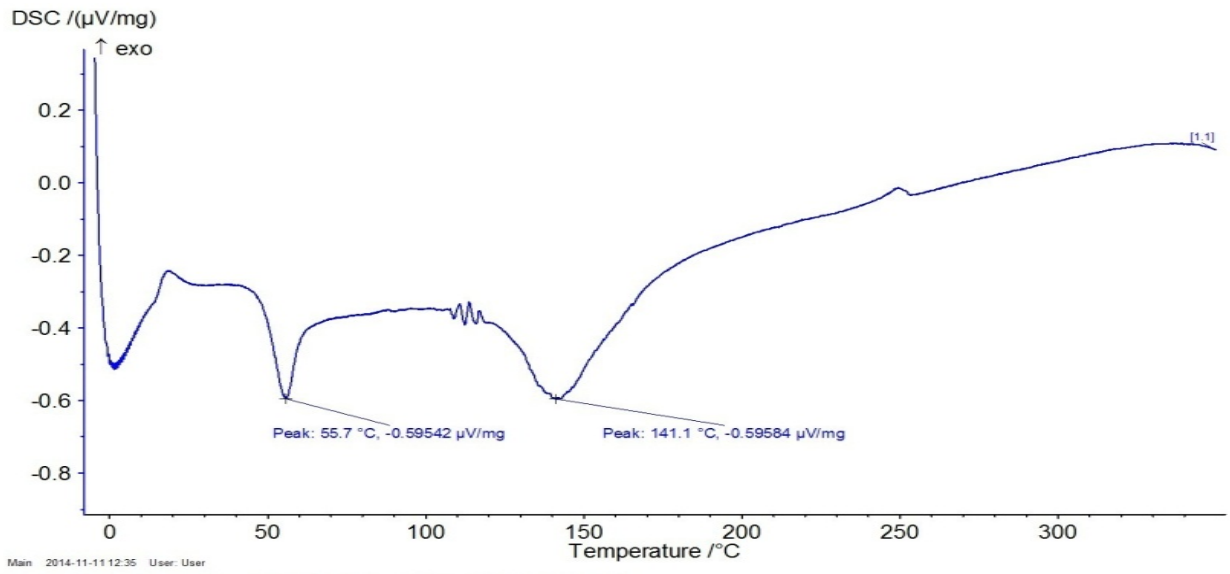

Figure 5: DSC thermogram of poly (DXL-co- Styrene)

Conclusion

The present work shows that:
- Maghnite-H$^+$, a proton exchanged montmorillonite clay, is an effective initiator for the polymerization
of Copolymerization of 1,3-Dioxolane with Styrene.
-This copolymerization was found to be initiated by Maghnite-H$^+$ 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-H$^+$.
-The polymerization proceeds smoothly by a very simple procedure, and a simple filtration is sufficient to recover the catalyst.

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