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Copolymerization of ε-Caprolactone WithTetrahydrofuran by a solid acid, in the Presence of Acetic Anhydride

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Abstract

Maghnite is a montmorillonite sheet silicate clay that is exchanged with protons to produce Maghnite-H^+ (Mag-H^+). This non-toxic and cheaper cationic catalyst was used for the copolymerization of ε-caprolactone (CL) with tetrahydrofuran (THF), in presence of acetic anhydride (AA). The effects of the amounts of Mag-H^+, acetic anhydride and the temperature on the synthesis of poly (ε-caprolactone-co-tetrahydrofuran) were studied. The copolymer obtained was characterized by ^{1}H-NMR and IR spectroscopy.

Keywords: Maghnite; Montmorillonite; Tetrahydrofuran; epsilon-caprolacton; Ring opening polymerization

Introduction

The use of acid treated clays as a solid source of protons in a number of industrially significant reactions continues to be of interest because they constitute a widely available and inexpensive solid source of protons. Montmorillonites have both Brönsted and Lewis acid sites and when exchanged with cations having a high charge density, such as protons, they produce highly-active catalysts for acid-catalysed reactions [1].

Polycaprolactone (PCL) is one of the most important biodegradable polymers due to its biodegradability, biocompatibility, non-toxicity and good permeability to drug [2–4]. Many copolymers of ε-caprolactone (CL) with other monomers such as lactide (LA) [5,6], 5-methyl-5-benzyloxycarbonyl-1,3-dioxane-2-one (MBC) [7,8], 1,3-dioxane-2-one (TMC) [9–11], glycolide (GA) [12, 13], tetrahydrofuran (THF) [14] and poly (ethylene glycol) (PEG) [15,16] have been extensively investigated in order to expand applications of PCL, but most of the cationic initiators used in the synthesis of these copolymers are expensive. They may be poisoned by products of the reaction or impurities present in the monomer feed, and contain heavy metals, such as chromium, mercury, antimony, etc, that presents environmental disposal problems for the user. Frequently, these initiators require the use of very high or very low temperature and high pressures during the polymerization reaction. The separation of the initiators from the polymer is not always possible. Therefore, 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. Montmorillonite, a class of inexpensive and noncorrosive solid acids, have been used as efficient catalysts for a variety of organic reactions. The reactions catalyzed by montmorillonite are usually carried out under mild conditions with high yields and high selectivity, 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 [17, 18].

The purpose of this paper is to study the copolymerization of ε-caprolactone with Tetrahydrofuran, catalyzed by Maghnite-H+ [19], a proton exchanged Montmorillonite clay in the presence of aceticanhydride. This new non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers [20, 21]. The effects of the amounts of the Maghnite-H+, acetic anhydride and the temperature on the synthesis of poly (ε-caprolactone-co-tetrahydrofuran) are also discussed.

2. Materials and methods.

2.1. General

The ^{1}H-NMR spectra were recorded on Bruker Avance-300 spectrometer in deuterochloroform. Chemical shifts are shown in δ values. The IR absorption spectra were recorded in the region 400-4000 cm^{-1} on alpha BurkerSpectrometre.

2.2 Materials

ε-caprolactone (grade 99%) was used as purchased from Aldrich. Tetrahydrofuran (THF) was distilled over the blue benzophenone–Na complex. Chloroform was dried on CaH_2 anhydrous and distilled before use. The acetic anhydride is distilled with the anhydrous sodium acetate under a pressure reduced to eliminate the halogenous compounds and metals. Raw-Maghnite: Algerian Montmorillonite clay was procured from BENTAL (Algerian Society of Bentonite).

2.3. Preparation of ''Maghnite-H+ 0.25M

Maghnite-H$^+$was prepared according to the process similar to that described by Belbachir and al [20]. 20 gram of raw-Maghnite 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 200 ml of sulfuric acid 0.25M, 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.

2.4. Copolymerization and products characterization

Copolymerizations were carried out in stirred flasks at 25 °C. The catalyst was dried in a muffle furnace at 120 °C overnight and then transferred to a vacuum desiccator containing P_2O_5. After cooling to room temperature under vacuum, the mineral was added to the ε -caprolactone (0.03 mol/L), THF (0.03 mol/L), and Acetic anhydride (1% in weight) mixtures previously kept in the stirred flask at 25 °C. After the required time (24hours) 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

3.1. Copolymerization and products characterization

The result of bulk copolymerization experiment of ε - caprolactone (0.03mol), with THF (0.03mol) and Acetic anhydride (1% in weight) induced by "Maghnite-H$^+$ 0.25M" is reported in Table 1. For all these experiments the temperature was kept constant at 25°C for 24 hours.

Table 1: Copolymerization of ε - caprolactone with THF induced by "Maghnite-H+0.25M" in the presence of acetic anhydride

Experiment	Mag-H+0.25M (%)	AA (%)	Yield (%)
1	10	1	62.84
2	5	1	45.17

3.2. The effect of the temperature on the synthesis

The effect of temperature on the synthesis of poly (ε-caprolactone-co-THF) in presence of acetic anhydride initiated by Maghnite-H+ is shown in Fig. 1. The copolymerization yield reaches maximum value around 65–85°C. On the other hand, with the increase in the reaction temperature above 60°C, the molecular weight of the obtained copolymer decreases progressively, suggesting the possible occurrence of thermal degradation. On the basis of these results, subsequent copolymerizations were carried out at 65°C.

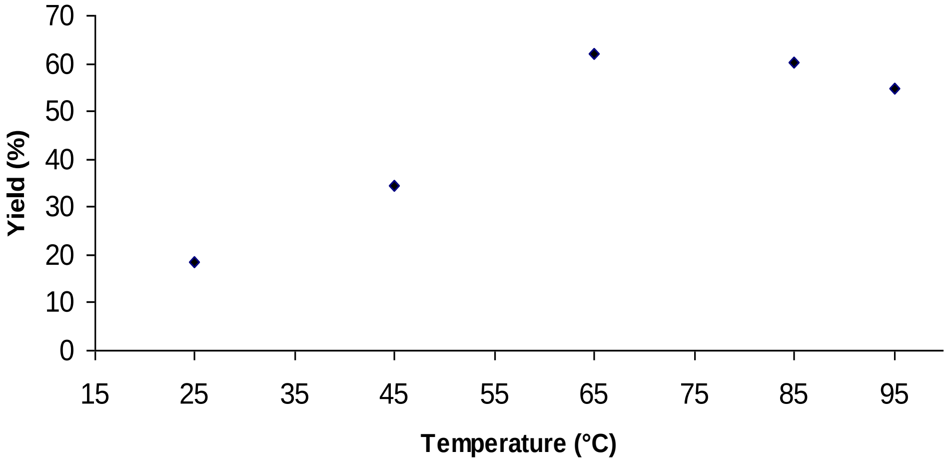


Figure 1: Effect of temperature on the copolymerization yield of ε-caprolactone with THF, in presence of acetic anhydride, catalyzed by Mag-H^+.

3.3. Effect of the amount of Maghnite-H^+ on the copolymerization

Fig. 2 shows the effect of the amount of Maghnite-H^+ on the synthesis yield of poly (ε-caprolactone-co-THF) in presence of acetic anhydride. Indeed, using various amounts of Maghnite-H^+, 1, 2, 3, 5, 7.5, and 10% by weight, this copolymerization was carried in bulk at 65°C. The copolymerization yield increased with the amount of Maghnite-H^+, thus clearly showing the effect of Maghnite-H^+ as a catalyst. This phenomenon is probably the result of an increase in the number of "initiating active sites" responsible of inducing polymerization,So, a large number of active site provides a large number of polymer chain.

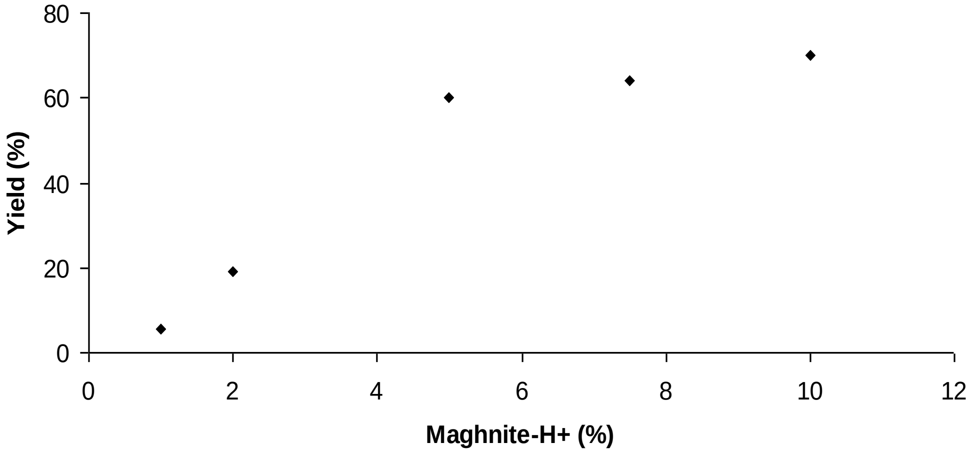


Figure 2: Effect of Maghnite-H+ amount on the copolymerization yield of ε-caprolactone with THF, in presence of acetic anhydride.

3.4. Effect of the amount of acetic anhydride on the copolymerization

In this study we carried out experiments under fixed experimental conditions (ε-caprolactone (0.03mol), with THF (0.03mol), (5% in weight) of Maghnite H^+, temperature of reaction T=65°C, and reaction time t=5h) with a change of the percentage in weight of the acetic anhydride in each experiment.

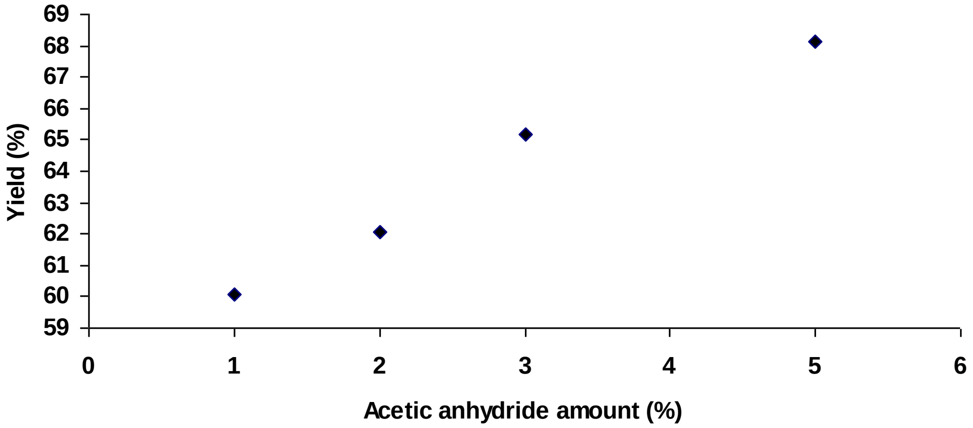
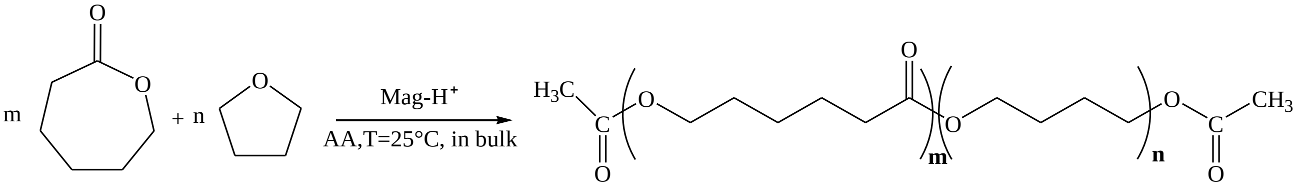


Figure 3: Effect of acetic anhydride amount on the copolymerization yield of ε-caprolactone with THF.

We observe that the yield of the copolymerization of epsilon caprolactone with tetrahydrofuran catalyzed by Maghnite-H^+ increases with elevation of the amount of acetic anhydride, this may be explained by the multiplication of active centers.

3.5. Characterization of products.

The formation of the copolymer was confirmed by ^1H NMR spectroscopy at 300 MHz (Figure 4). The reaction taking place is shown in the following scheme1

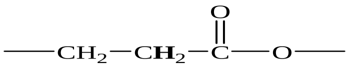
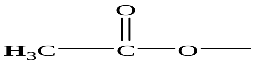


CL THF poly (ε- caprolactone-co-THF)

Scheme.1 : The reaction scheme of the synthesis of poly (tetrahydrofuran-co-caprolactone) in the presence of acetic anhydride catalyzed by Maghnite-H^+

The various signals observed and their chemical shifts of the poly (ε- caprolactone-co-THF) synthesized in the presence of the AA are carried in the table 2.

Table 2: Signals and chemical shifts of the various protons present in the poly (ε-caprolactone-co-THF) synthesized in the presence of AA

Nature of the proton	δ (ppm) Theortical[21]	δ (ppm) Experimental
-CH2—C**H**2—O—	3.5 - 4.3	4.07
—C**H**2–C**H**2– C**H**2—CH2—O–	1.2 - 1.8	1.38-1.66
 $—CH_2—\mathbf{CH_2}—\overset{O}{\overset{\Vert}{C}}—O—$	1.8 - 2.6	2.31
 $\mathbf{H_3}C—\overset{O}{\overset{\Vert}{C}}—O—$	1.8 – 2.6	2.05

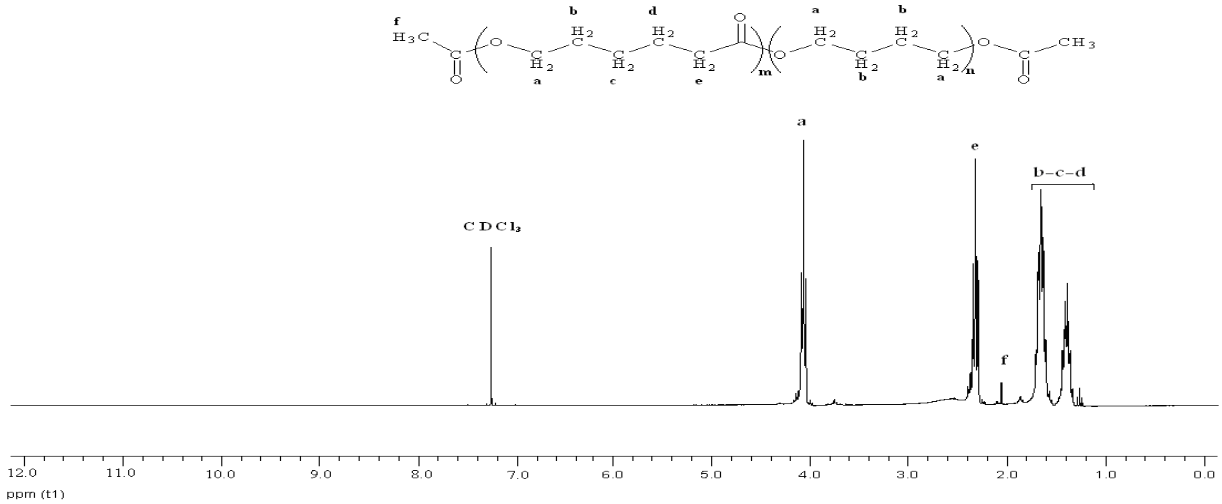


Figure 3: ^{1}H NMR spectrum of poly (ε-caprolactone-co-THF) synthesized in presence of acetic anhydride catalyzed by Maghnite-H$^+$ in $CDCl_3$

The analysis of thepurified copolymer by IR (Figure 4) gave the following results:
The function ester present in the reason for the ε-caprolactone appears in two areas: to1720 cm^{-1} for carbonyl (C=O), and to1167cm^{-1} for (C-O).
The function ether (CO) of the THF is schematized at 1102cm^{-1}.
The asymmetrical vibration (CH) of methylene is located at 2942cm^{-1} and the symmetrical one to 2865 cm^{-1}.

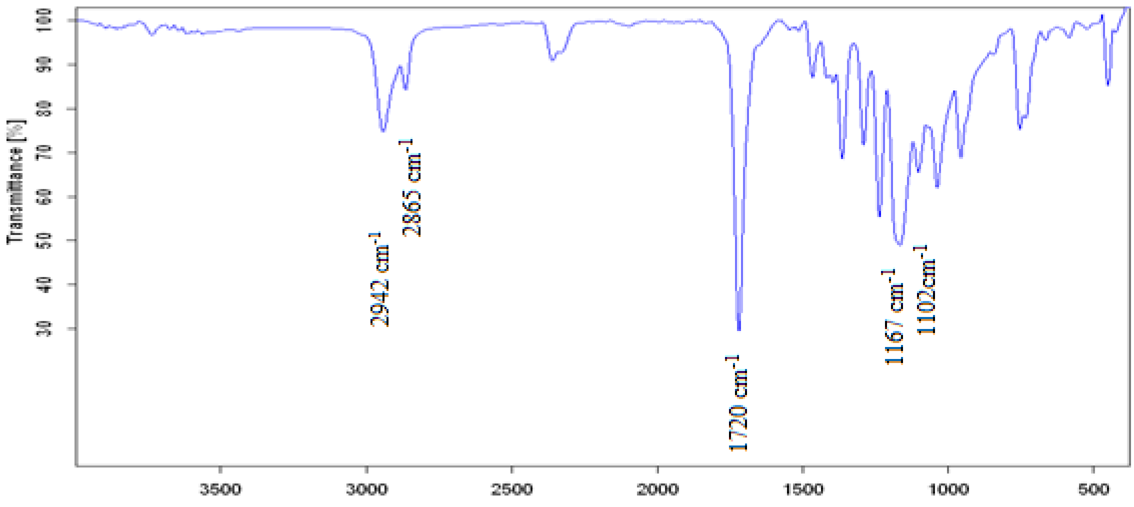


Figure 4: IR spectrum of poly (ε-caprolactone-co-THF) synthesized in presence of acetic anhydride catalyzed by Mag-H$^+$

Conclusion

During this study we showed that:

-The bulk copolymerization of the ε-caprolactone with THF in presence of acetic anhydride is possible by the heterogeneous catalyst Maghnite-H$^+$.

-The balance of copolymerization moves towards the formation of copolymer with the rise in the temperature and the increase in the quantity of catalyst and the quantity of anhydride acetic.

-Thegood yieldof the synthesis of poly (ε-caprolactone-co-THF) in the presence of acetic anhydrideis achieved at a temperature between65°C and 75°C.

-The copolymerization proceeds smoothly, and a simple filtration is sufficient to recover the catalyst.

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