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Maghnite, a green catalyst for synthesis of poly(ε-caprolactone-co-tetrahydrofuran)

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ABSTRACT

In the present work the copolymerization of ε-caprolactone with tetrahydrofuran using a proton exchanged Montmorillonite clay as initiator is reported. The effects of the amounts of Maghnite-H^+ (Mag-H) 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, ε-caprolactone*

1. Introduction

Polycaprolactone (PCL) is one of the most important biodegradable polymers due to its biodegradability, biocompatibility, non-toxicity and good permeability to drug [1–3]. Many copolymers of CL with other monomers such as lactide (LA) [4, 5], 5-methyl-5 benzyloxycarbonyl-1,3-dioxane-2-one (MBC) [6,7], 1,3-dioxane-2-one (TMC) [8–10], glycolide (GA) [11, 12],tetrahydrofuran(THF)[13] and poly (ethylene glycol) (PEG) [14, 15] 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 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 [16, 17]. The purpose of this paper is to study the copolymerization of ε-caprolactone with

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tetrahydrofuran, catalyzed by Maghnite-H+ [18], a proton exchanged Montmorillonite clay. This new non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers [19, 20]. The effects of the amounts of the Maghnite-H+ and the temperature on the synthesis of poly (ε-caprolactone-co-tetrahydrofuran) are also discussed.

2. Experimental section

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 Burker Spectrometre.

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

2.3. Preparation of "Maghnite-H$^+$ 0.25M". Maghnite-H$^+$ was prepared according to the process similar to that described by Belbachir et al. [20]. 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.

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 (0.03mol/L), THF (0.03mol/L) mixtures previously kept in the stirred flask at 25°C. 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 section

3.1. Copolymerization and products characterization. The result of bulk copolymerization experiment of ε - caprolactone (0.03mol), with THF (0.03mol) 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. Copolymerizations of ε - caprolactone with THF induced by "Maghnite-H$^+$0.25M"

Experiment	Mag-H$^+$ 0.25M (%)	Yield %	Mn*	Mw**	Mw/Mn***
1	10	58.21	545	3513	6.44
2	5	42.60	696	4620	6.64

* the Number Average Molecular Weight. **the Weight Average Molecular Weight.

***polydispersity index (PDI).

3.2. Effect of temperature on copolymerization. The effect of temperature on the copolymerization of ε-caprolactone with THF initiated by Maghnite-H^+ is shown in Fig. 1. The copolymerization yield reaches maximum value around 60–70°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 60°C.

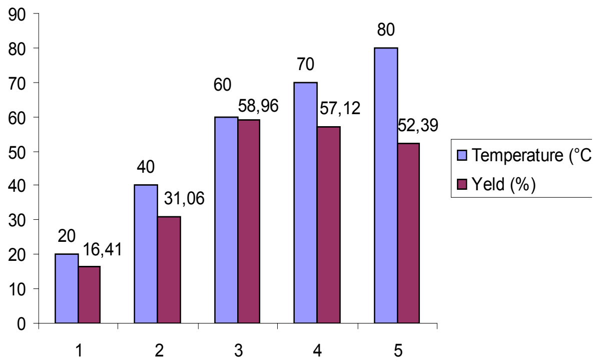


Figure 1: Effect of temperature on copolymerization of ε - caprolactone (0.03mol), with THF(0.03mol).

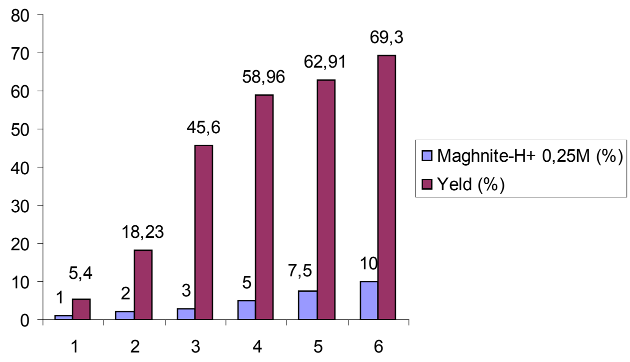
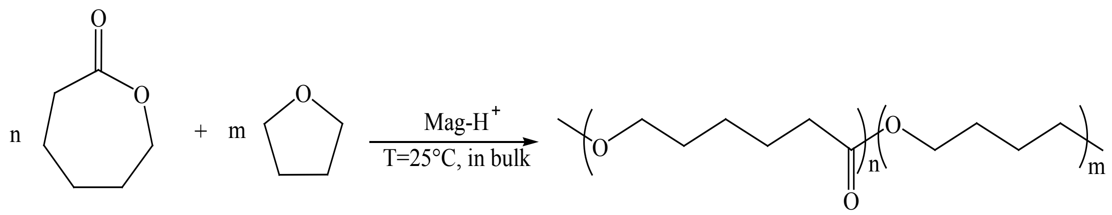


Figure 2: Effect of the amount of the catalyst on copolymerization of ε-caprolactone (0.03mol), with THF (0.03mol).

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 copolymerization yield of ε-caprolactone with THF. Indeed, using various amounts of Maghnite-H^+, 1, 2, 3, 5, 7.5, and 10% by weight, this copolymerization was carried in bulk at 60°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, a number that is pro rata to the amount of catalyst used in reaction.

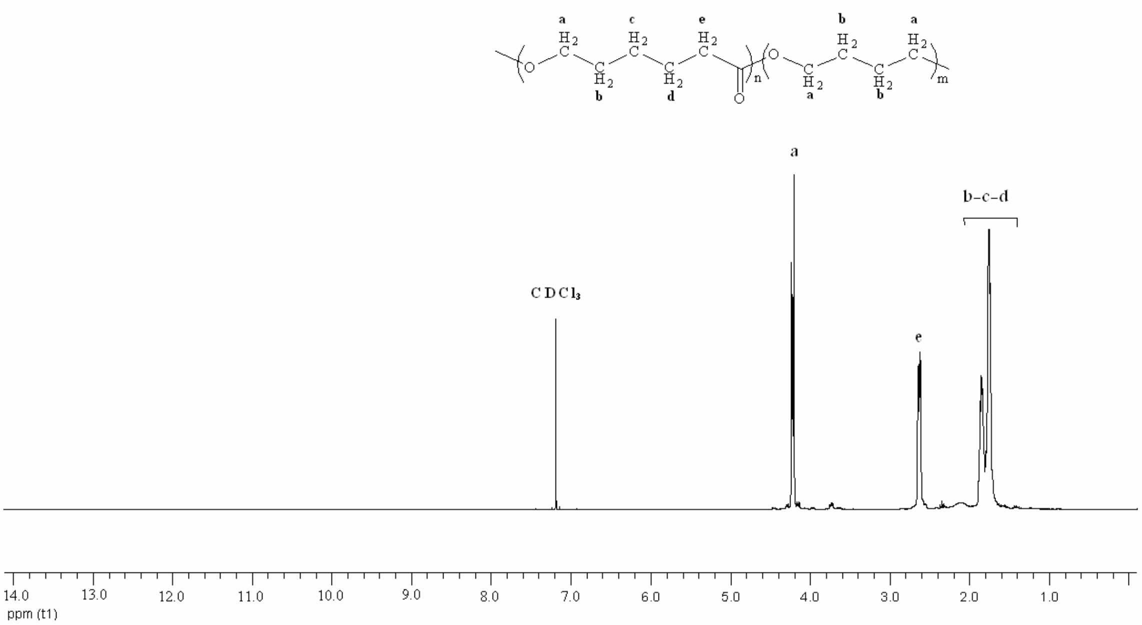
3.4. Characterization of products. The formation of the copolymer was confirmed by ^1H NMR spectroscopy at 300 MHz (Figure 4). The reaction taking place is shown in the following scheme:



ε- caprolactone THF poly (ε- caprolactone-co-THF)

The signals corresponding to the three methylene in position 3, 4 and 5 of ε-caprolactone (-O-CH_2-C**H_2**-C**H_2**-C**H_2**-CH_2-CO-) and in position 3 and 4 of THF(-O-CH_2-C**H_2**-C**H_2**-CH_2-). Lie between δ = 1.74 ppm and δ = 1.76 ppm. The peak appears to δ = 2.61 ppm corresponds to the proton carried by the carbon in position 2 of ε-caprolactone (-O-CH_2-CH_2-CH_2-CH_2-C**H_2**-CO-). The-methylene in position 2 and 5 of THF (-O-C**H_2**-CH_2-CH_2-C**H_2**-) and 6-position of the ε-caprolactone (-O-C**H_2**-CH_2-CH_2-CH_2-CH_2-CO-) give One refers to δ = 4.21 ppm.

Figure 3: ^{1}H NMR spectrum of poly (ε-caprolactone-co-THF) in $CDCl_3$



Product obtained from copolymerization of ε-caprolactone with THF was analyzed after purification by IR, and he gave the spectrum in Figure .4, which shows the existence of: one intense absorption band around 1723.29 cm-1 corresponds to the carbonyl group (C = O) ester; a band at 1162.81 cm-1 confirms the presence of the ester function; 1050.50cm^{-1} to and 1089.36 cm $^{-1}$ two bands characterizing the ether function; the two bands at 2865.10 cm^{-1} and 2936.59 cm^{-1} indicate the existence of links (C-H).

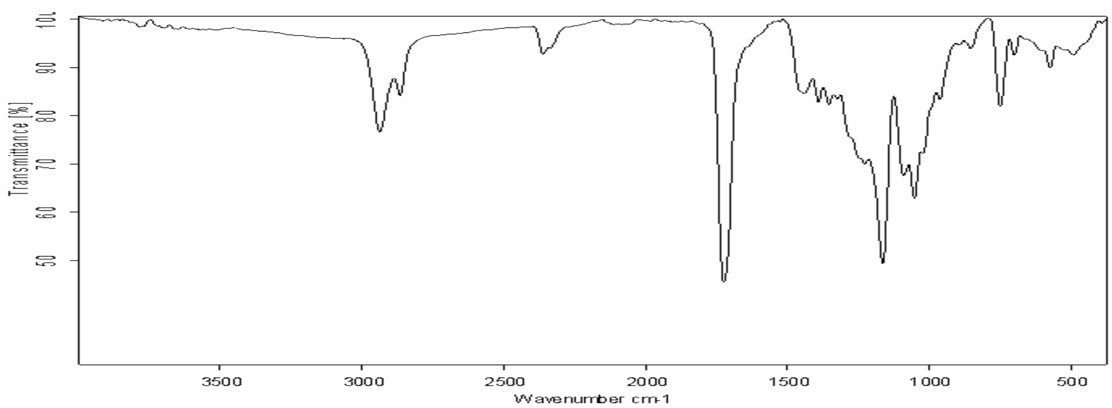


Figure 4: IR spectrum of poly (ε-caprolactone-co-THF)

4. Conclusions

Maghnite-H+, a proton exchanged montmorillonite clay is effective as an acidic catalyst for the copolymerization of ε-caprolactone with THF. The balance of copolymerization moves towards the formation of copolymer with the rise in the temperature and the increase in the quantity of catalyst. The copolymerization proceeds smoothly, and a simple filtration is sufficient to recover the catalyst.

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