

Research Article

Copolymerization of ϵ -caprolactone with Epichlorohydrin by a Green Catalyst, Maghnite

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Received: 24th September 2011, Revised: 12nd December 2011; Accepted: 9th January 2012

Abstract

Most of the cationic initiators used in the synthesis of 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. 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 epichlorohydrin (ECH). The effects of the amounts of Mag-H⁺ and the temperature on the synthesis of poly (ϵ -caprolactone-co-epichlorohydrin) were studied. Increasing Maghnite-H⁺ proportion and temperature produced the increase in copolymerization yield. The copolymer obtained was characterized by ¹H-NMR and IR spectroscopy. Copyright © 2012 BCREC UNDIP. All rights reserved.

Keywords: Maghnite; Montmorillonite; Epichlorohydrin; epsilon-caprolactone; Ring opening polymerization

How to Cite: A. Bouchama, M.I. Ferrahi, and M. Belbachir. (2012). Copolymerization of ϵ -caprolactone with Epichlorohydrin by a Green Catalyst, Maghnite. *Bulletin of Chemical Reaction Engineering & Catalysis*, 7 (1): 43-48

Permalink: <http://ejournal.undip.ac.id/index.php/bcrec/article/view/1211>

1. 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 Brønsted 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-benzoyloxycarbonyl-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,

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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 [17,18].

The purpose of this paper is to study the copolymerization of ϵ -caprolactone with epichlorohydrin, catalyzed by Maghnite-H⁺ [19], a proton exchanged Montmorillonite clay. 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⁺ and the temperature on the synthesis of poly (ϵ -caprolactone-co-epichlorohydrin) are also discussed.

2. Materials and Methods

2.1. General

The ¹H-NMR spectra were recorded on Bruker Avance-300 spectrometer in deuteriochloroform. 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. Epichlorohydrin was purified by fractional distillation. Chloroform was dried on CaH₂ anhydrous and distilled before use. Raw-Maghnite: Algerian Montmorillonite clay was procured from BENTAL (Algerian Society of Bentonite).

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

Maghnite-H⁺ was prepared according to the

process similar to that described by Belbachir et al. [19]. Raw-Maghnite (20 g) was crushed for 20 minutes 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 become sulfate free and then dried at 105 °C.

2.4. Copolymerization and products characterization

Copolymerizations were carried out in stirred flask at 25 °C. The catalyst was dried in a muffle oven at 120 °C overnight and then transferred to a vacuum desiccator containing P₂O₅. After cooling to room temperature under vacuum, the mineral was added to the ϵ -caprolactone (0.026 mol), epichlorohydrin (0.026 mol) mixtures previously kept in the stirred flask at 25 °C. After the required time (24 hours) 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 (0.026 mol), with epichlorohydrin (0.026 mol) induced by "Maghnite-H⁺ 0.25 M" 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 epichlorohydrin induced by "Maghnite-H⁺ 0.25M"

Experi- ment	Mag-H ⁺ (0.25 M) (%)	Yield (%)	Mn ^a	Mw ^b	Mn/Mw ^c
1	10	58.45	518	3462	6.63
2	5	42.92	712	4527	6.36

Mag-H⁺ (0.25 M) (%): the proportions by weight relative to all the reaction reagents

a Mn: The Number Average Molecular Weight.

b Mw: The Weight Average Molecular Weight.

c Mw/Mn: polydispersity index (PDI).

3.2. Effect of temperature on copolymerization

The effect of temperature on the copolymerization of ϵ -caprolactone (0.026) with epichlorohydrin (0.026) initiated by Maghnite-H⁺ (5% by weight) for 5 hours, is shown in Fig. 1.

The copolymerization yield reach maximum value around 65–75 °C. On the other hand, with the increase in the reaction temperature above 65 °C the molecular weight of the obtained copolymer decrease progressively, suggesting the possible occurrence of thermal degradation. On the basis these results, subsequent copolymerizations were carried out at 65 °C.

3.3. Effect of the amount of Maghnite-H⁺ on the Copolymerization

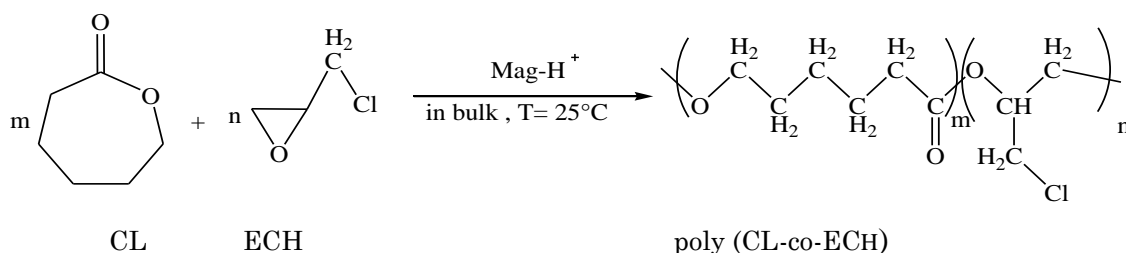
Fig. 2 shows the effect of the amount of Maghnite-H⁺ on the copolymerization yield of ϵ -caprolactone with epichlorohydrin. Indeed, using various amounts of Maghnite-H⁺, 1, 2, 3, 5, 7.5, and 10 % by weight, this copolymerization was carried in bulk at 65 °C, for 5 hours.

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 3).

The reaction taking place is shown in the following scheme:



¹H NMR spectroscopy at 300 MHz (Solvent deuterated CDCl₃) (Fig. 3) showed different peaks, in which the three methylene in position 3, 4 and 5 of ϵ -caprolactone (-O-CH₂-CH₂-CH₂-CH₂-CH₂-CO-), lie between $\delta = 1.57$ ppm and $\delta = 1.78$

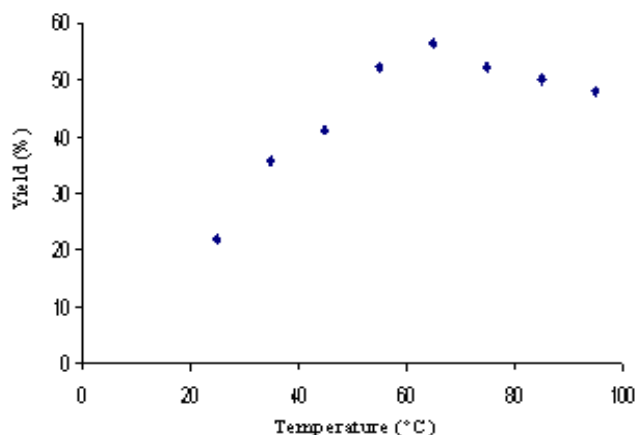


Fig. 1: Effect of temperature on copolymerization of ϵ -caprolactone (0.026 mol), with epichlorohydrin (0.026 mol).

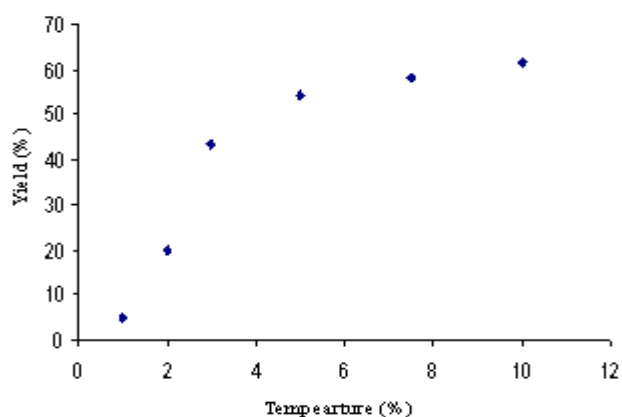


Fig. 2: Effect of the amount of the catalyst on copolymerization of ϵ -caprolactone (0.026 mol), with epichlorohydrin (0.026 mol).

ppm. The proton carried by the carbon in position 2 and 6 of ϵ -caprolactone (-O-CH₂-CH₂-CH₂-CH₂-CH₂-CO-) at $\delta = 4.22$ ppm and $\delta = (2.39 - 2.58)$ ppm respectively, the methylene in position 3 of ECH (-O-CH(CH₂Cl)-CH₂-) at $\delta = 3.81$ ppm, the proton carried by the carbon in position 2 of ECH

Table 2. Results of products analysis by ^1H NMR spectroscopy

Proton type	a	bcd	e	f	g	h
δ in ppm	4.22	1.57-1.78	2.39-2.58	4.98	3.81	3.66

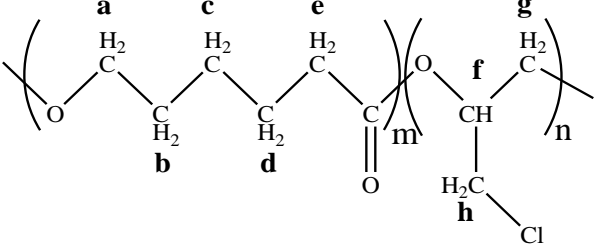
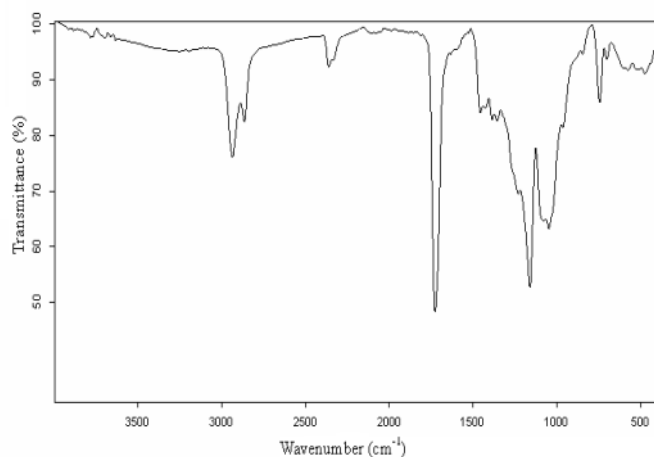



Figure 4: IR spectrum of poly (ϵ -caprolactone-co-epichlorohydrin)

at 4.98 ppm and the methylene carried by the carbon adjacent to the Cl at 3.66 ppm.

Product obtained from copolymerization of ϵ -caprolactone with epichlorohydrin was analyzed after purification by IR, and he gave the spectrum in Figure .4, which shows the existence of:

- Two absorption bands located at 1726.68 cm^{-1} and 1159.91 cm^{-1} show the presence of the ester function in our copolymer
- Bands that come out between 2865.11 cm^{-1} and 2936.17 cm^{-1} correspond to liaison (-CH) of methylene present in the poly (ϵ -

caprolactone-co-ECH). The ether is characterized by the absorption band that appears to 1046.28 cm^{-1} .

- the absorption band at 743.88 cm^{-1} corresponds to liaison (-C-Cl).

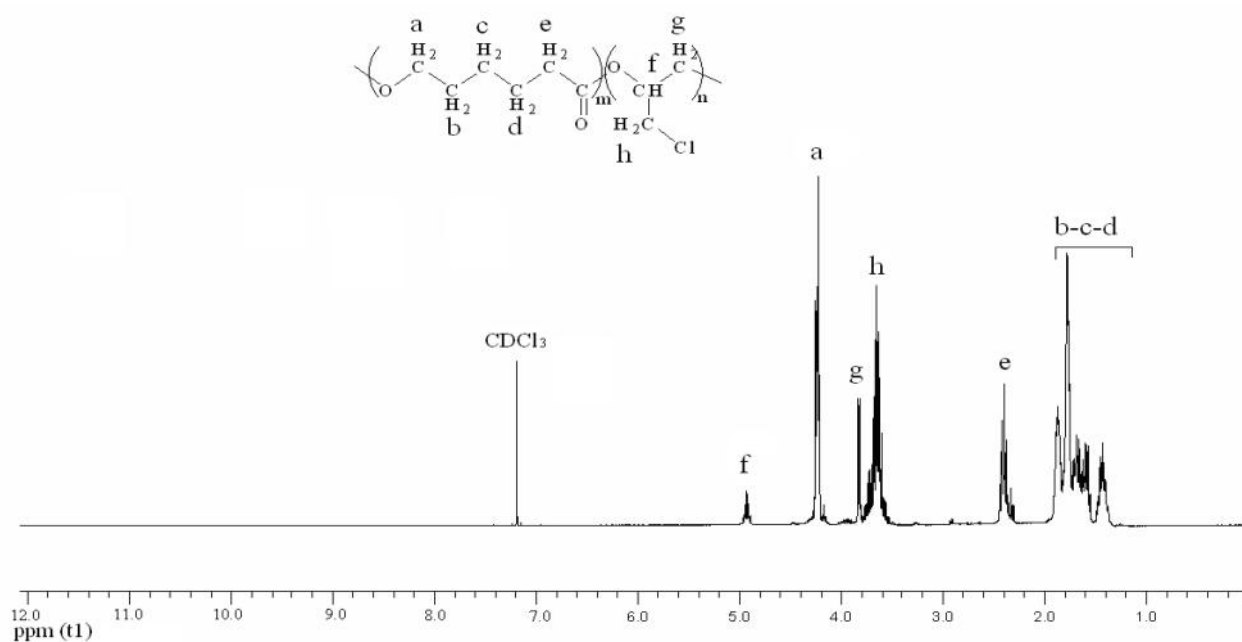


Figure 3: ^1H NMR spectrum of poly (ϵ -caprolactone-co-epichlorohydrin) in CDCl_3

4. Conclusions

Maghnite-H⁺, a proton exchanged montmorillonite clay, is effective as an acidic catalyst for the copolymerization of ϵ -caprolactone with Epichlorohydrin. 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.

Acknowledgements

We thank all laboratory staff of polymer chemistry from the University of Oran for their kind cooperation.

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