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SYNTHESIS OF POLY -CAPROLACTONE-CO-PROPYLENE OXIDE BY A GREEN CATALYST, MAGHNITE

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Synthesis of poly (ϵ -caprolactone-co-propylene oxide) by a green catalyst, Maghnite

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Abstract - In the present work the copolymerization of ϵ -caprolactone (CL) with propylene oxide (PO) using proton exchanged Montmorillonite clay as initiator is reported. The effects of the amounts of Maghnite-H⁺ and the temperature on the synthesis of poly (ϵ -caprolactone-co-propylene oxide) were studied. The copolymer obtained was characterized by 1H-NMR spectroscopy.

Keywords : Epichlorohydrin, Epsilon - caprolactone, Maghnite, Montmorillonite, Ring opening polymerization.

I. 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-benzoyloxycarbonyl-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 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-propylene oxide) are also discussed.

II. EXPERIMENTAL

a) General

The 1H-NMR spectra were recorded on Bruker Avance-300 spectrometer in deuteriochloroform. Chemical shifts are shown in δ values.

b) Materials

ϵ -Caprolactone (grade 99%) was used as purchased from Aldrich. Propylene oxide 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).

c) 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 become sulfate free and then dried at 105 °C.

d) Copolymerization and products characterization

The bulk copolymerizations were carried out in stirred flasks at 25 °C for 24 hours. The catalyst was dried in a muffle furnace 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), propylene oxide (0.026 mol) 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

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mineral, and then dried by evaporation to remove solvent and remaining monomer.

III. RESULT AND DISCUSSION

a) Copolymerization and products characterization

The result of bulk copolymerization experiment of ϵ - caprolactone (0.026mol), with propylene oxide

(0.026mol) induced by "Maghnite-H+ 0.25M" is reported in Table 1.

For all these experiments the temperature was kept constant at 23°C for 24 hours.

Table 1. Copolymerizations of ϵ - caprolactone with propylene oxide induced by "Maghnite-H+0.25M"

Experiment	Mag-H ⁺ 0.25M (%)	Time (Hours)	Yield %	Mn *	Mw **	Mw/Mn ***
1	10	24	56.12	613	3702	6.04
2	5	24	41.63	682	4317	6.33

* Mn: The Number Average Molecular Weight.

** Mw: The Weight Average Molecular Weight.

*** Mw/Mn: polydispersity index (PDI).

b) Effect of temperature on copolymerization

The effect of temperature on the copolymerization of ϵ - caprolactone (0.026mol) with propylene oxide (0.026mol) initiated by Maghnite-H⁺ (5% by weight) for 5 hours, is shown in Fig. 1. The copolymerization yield reach maximum value around 90-100°C. On the other hand, with the increase in the reaction temperature above 90°C the molecular weight of the obtained copolymer decrease progressively, suggesting the possible occurrence of thermal degradation. On the basis of these results, subsequent copolymerizations were carried out at 90°C.

c) 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 propylene oxide. Indeed, using various amounts of Maghnite-H⁺, 1, 2, 3, 5, 7.5, and 10% by weight, this copolymerization was carried in bulk at 90°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.

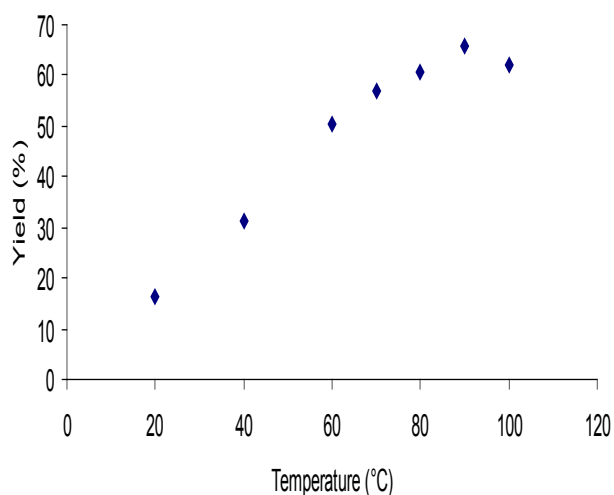


Fig. 1. Effect of temperature on copolymerization of ϵ - caprolactone (0.026mol), with propylene oxide (0.026mol).

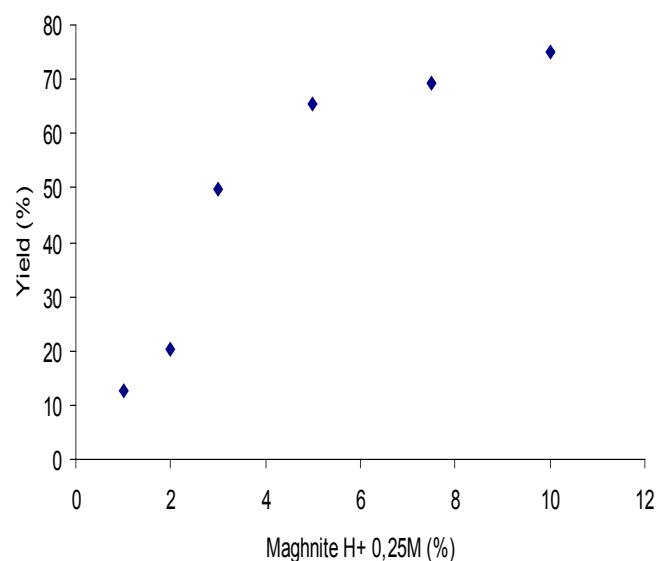


Fig. 2. Effect of the amount of the catalyst on copolymerization of ϵ - caprolactone (0.026mol), with propylene oxide (0.026mol).

d) 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:

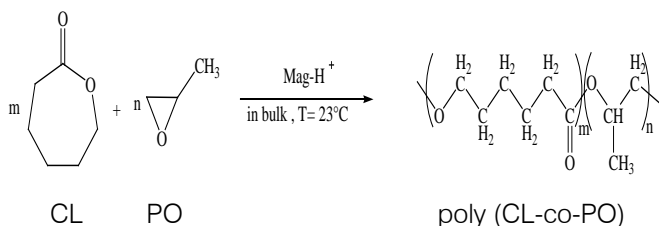


Table.2. Results of products analysis by ^1H NMR spectroscopy.

Proton type	a	b c d	e	f	g	h
δ in ppm	4.21	1.41–1.78	2.24	4.98	3.63	1.20

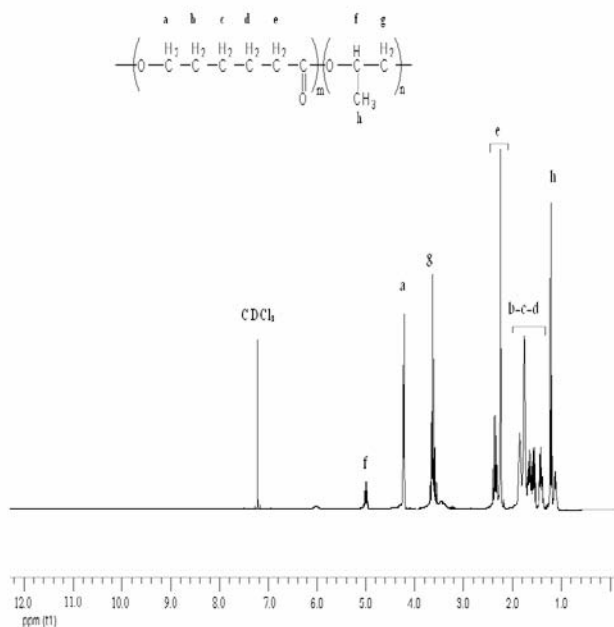


Fig.3. ^1H NMR spectrum of poly (ϵ -caprolactone-co-propylene oxide) in CDCl_3 .

^1H NMR spectroscopy at 300 MHz (Solvent deuterated CHCl_3) (Fig4) showed different peaks, the three methylene in position 3, 4 and 5 of ϵ -caprolactone ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$), lie between $\delta = 1.41\text{ppm}$ and $\delta = 1.78\text{ppm}$, the proton carried by the

carbon in position 2 and 6 of ϵ -caprolactone ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$), ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$) at $\delta = 4.21\text{ppm}$ and $\delta = 2.24\text{ppm}$ respectively, the methylene in position 3 of PO ($-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-$) at $\delta = 3.63\text{ppm}$, the proton carried by the carbon in position 2 of OP at 4.98 ppm and the Methyl group of OP at 1.20 ppm.

IV. CONCLUSION

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

REFERENCES

- Chen. J. H., Huang. C. X. and Chen. Z. L., (2000). Study on the biocompatibility and toxicology Of biomaterials poly(ϵ -caprolactone). *J Biomed Eng.* 17:380–382.
- Le Ray. A. M., Chiffolleau. S., looss. P., Grimandi. G., Gouyette. A., Daculsi. G. and Merle. C. (2003). Vancomycin encapsulation in biodegradable poly(epsilon-caprolactone) microparticles for bone implantation. Influence of the formulation process on size, drug loading, in vitro release and cytocompatibility. *Biomaterials.* 24:443–449.
- Pitt. C. G., Jeffcoat. A. R., Zweidinger. R. A. and Schindler. A. (1979). Sustained drug delivery systems I. The permeability of poly(epsilon-caprolactone), poly(DL-lactic acid), and their copolymers. *J Biomed Mater Res.* 13: 497–507.
- Ye. W.P., Du. F.S., Jin. W.H., Yang. J.Y. and Xu. Y. (1997). In vitro degradation of poly(caprolactone), poly(lactide) and their block copolymers: Influence of composition, temperature and morphology. *React Funct Polym.* 32:161–168
- Yavuz. H., Babac. C., Tuzlakoglu. K. and Piskin. E. (2002). Preparation and degradation of l-lactide and unknown caprolactone homo and copolymer films. *Polym. Degrad. Stab.* 75:431–437
- Storey. R.F., Mullen. B.D. and Melchert. K.M. (2001). Synthesis of novel hydrophilic poly(ester-carbonates) containing pendent carboxylic acid groups. *J. Macromol. Sci. Pure. Appl. Chem.* 38:897–917.
- Guan. H.L., Xie. Z.G., Tang. Z.H., Xu. X.Y., Chen. X.S. and Jing. X.B. (2005). Preparation of block copolymer of epsilon-caprolactone and 2-methyl-2-carboxyl-propylene carbonate. *Polymer.* 46:2817–2824.
- Pêgo. A.P., Luyn. M.J.A.V., Brouwer. L.A., Wachem. P.B.V., Poot. A.A. and Grijpma. D.W. (2003). In vivo behavior of poly(1,3-trimethylene carbonate) and

- copolymers of 1,3-trimethylene carbonate with D,L-lactide or ϵ -caprolactone: Degradation and tissue response. *J. Biomed. Mater. Res.* 67(A):1044–1054.
9. Albertsson, A.C. and Eklund, M. (1995). Influence of molecular structure on the degradation mechanism of degradable polymers: In vitro degradation of poly(trimethylene carbonate), poly(trimethylene carbonate-co-caprolactone), and poly(adipic anhydride). *J. Appl. Polym. Sci.* 57:87–103.
 10. Barakat, I., Dubois, Ph., Grandfils, Ch. and Jérôme, R. (2001). Poly(ϵ -caprolactone-b-glycolide) and poly(D,L-lactide-b-glycolide) diblock copolyesters: Controlled synthesis, characterization, and colloidal dispersions. *J. Polym. Sci. Part A: Polym. Chem.* 39: 294–306.
 11. Bero, M., Czapla, B., Dobrzynski, P., Janeczek, H. and Kasperczyk, J. (1999). Copolymerization of glycolide and ϵ -caprolactone, 2. Random copolymerization in the presence of tin octoate. *Macromol. Chem. Phys.* 200: 911–916.
 12. Dzhavadyan, E.A., Rozenberg, B.A. and Yenikolopyan, N.S. (1973). Kinetics of the copolymerization of tetrahydrofuran with ϵ -caprolactone. *Science. U.S.S.R.* 15: 2235–2242.
 13. Ge, H., Hu, Y., Jiang, X., Cheng, D., Yuan, Y., Bi, H. and Yang, C. (2002) Preparation, characterization, and drug release behaviors of drug nimodipine-loaded poly (ϵ -caprolactone)-poly(ethylene oxide)-poly(ϵ -caprolactone) amphiphilic triblock copolymer micelles. *J. Pharm. Sci.* 91:1463–1473.
 14. He, F., Li, S., Vert, M., Zhuo, R. (2003) Enzyme-catalyzed polymerization and degradation of copolymers prepared from ϵ -caprolactone and poly(ethylene glycol). *Polymer.* 44: 5145–5151.
 15. Brown, D.R., Carpathica, G. (1994) Clays as catalyst and reagent supports. *Ser. Clays.* 45: 45.
 16. Laszlo, P. (1987). *Preparative Chemistry Using Supported Reagents.* Academic. Press. San Diego.
 17. Belbachir, M. and Bensaoula, A. (2006). Composition and method for catalysis using bentonites. *US Patent 6,274,527 B1.*
 18. Harrane, A., Meghabar, R. and Belbachir, M. (2002). A Protons Exchanged Montmorillonite Clay as an Efficient Catalyst for the Reaction of Isobutylene Polymerization. *Int. J. Mol. Sci.* 790–800.
 19. Meghabar, R., Megherbi, A., and Belbachir, M. (2003). An ecocatalyst for cationic polymerization of N-vinyl-2-pyrrolidone. *Polymer.* 2397.