SYNTHESIS OF COPOLYMER FROM 1,3,5-TRIOXANE AND ε-CAPROLACTONE CATALYSED BY TREATED BENTONITE AS ECO-CATALYST

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Abstract. This study presents a novel green method for copolymerizing 1,3,5-trioxane (TOX) with ε-caprolactone (CL). This technique uses Maghnite-H$^+$ (Mag-H$^+$) as a bulk green catalyst. Various techniques were used to confirm the structure of the resulting copolymer. The influencing factors on the copolymerization reaction were also studied. The results show that the best copolymer yield (46.3 %) was obtained *via* bulk copolymerization at a temperature of 353 K for a reaction time of 8 h.

Keywords: copolymerization, 1,3,5-Trioxane, Maghnite-H$^+$, polyoxymethylene, ε-caprolactone.

1. Introduction

Polyoxymethylene, also known as acetal, polyacetal resin, and polyformaldehyde (acetal homopolymer),[1-2] is an engineering thermoplastic used in precision parts requiring high stiffness, low friction, and excellent dimensional stability. Like many other synthetic polymers, it is produced by different formulas. Another method is a copolymerization of 1,3,5-trioxane with cyclic ethers or acetals as copolymer synthesis with 1,3-dioxolane[3] or ethylene oxide,[4] preferably with ε-caprolactone. To obtain the reactions catalyzed by clay minerals, montmorillonite was used as a catalyst for the cationic polymerization of several vinyl and heterocyclic monomers.[5-8] The reaction is usually carried out under mild conditions with high yield and high selectivity. The copolymerization of trioxane is of considerable industrial importance. It is a commercially useful engineering plastic as the copolymer has better thermal properties and superior resistance to alkali than homopolymer.

Several studies to date include the effect of catalyst amount (Mag-H$^+$), trioxane (TOX), and copolymerization time on yield and temperature. The best yield (46.3 %) was obtained using bulk copolymerization at room temperature (353 K) for a reaction time of 8 h. Harane[9] reported a correlation between the acid activation of Maghnite with different concentrations of H$_2$SO$_4$ and its catalytic activity. It has been found that the best results are obtained by acid activation with H$_2$SO$_4$ (0.25M) solution because the cationic exchange of Maghnite by protons (Mag-H$^+$) is complete without destroying its structure. This solid catalyst is widely used in ring-opening polymerizations as an effective catalyst and demonstrates good results published in many international reviews.[10-13] In addition, compared to other catalysts, it has many advantages, such as very low cost, easy removal from the reaction mixture, and regeneration by heating to a temperature above 373 K.[14]

This paper presents a new copolymerization of trioxane with ε-caprolactone, catalyzed by a new non-toxic catalyst Maghnite-H$^+$ and eco-catalyst to replace toxic catalysts prepared through a simple exchange process. Mag-H$^+$ can be easily separated from the polymer product. The effects of different synthesis parameters, such as the amount of montmorillonite Maghnite-H$^+$, and reaction time, are also discussed. Copolymerization experiments were performed in solution Mag-H$^+$. The copolymer obtained was characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance (^{1}H NMR), and Thermo Gravimetric Analysis (TGA). The thermal properties were defined by Differential Scanning Calorimetry (DSC).

2. Experimental

2.1. Materials

1,3,5-Trioxane (98 %) and caprolactone (99 %) were purchased from ALDRICH (Algeria) and used upon

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reception. The montmorillonite Maghnite-H^{+} was procured from Bental (Algerian Society of Bentonite).

2.2. Structural Analysis

The chemical structure of the products was determined by FT-IR. Two FT-IR apparatuses (PerkinElmer) with UATR sampling accessories were used. X-ray diffraction (XRD) was conducted at room temperature using a Bruker AXS D8 advanced X-ray diffractometer (40 kV, 30 mA) with $K\alpha$ radiation ($\lambda = 0.154$ nm) at the rate of 2° min[-1] in the 2θ range of 2.0–80°. The ^{1}H NMR measurements were carried out at room temperature using an Avance Bruker NMR spectrometer at 300 and 99.35 MHz, the spinning speed for cross-polarization magic angle spinning (CPMAS) was 4 MHz for NMR. The chemical shift reference was tetramethylsilane (TMS); a 4 mm zirconia rotor was used. TGA was performed by Perkin Elmer STA 6000 under air and nitrogen in the temperature range of 293–1073 K with a heating rate of 283 K/min. The mass of the sample to be analyzed was 5–7 mg. The DSC analysis was performed by a universal VA.5A TA instrument, with an average site scan between 173 K and 373 K and with a heating rate of 283 K/min, using 6 mg of the copolymer.

2.3. Preparation of Maghnite-H^{+} (0.25 M)

Maghnite-H^{+} was prepared according to the process reported in the literature.[15] Maghnite was activated with a sulfuric acid solution giving a Maghnite exchanged with protons. Raw-Maghnite (20 g) was crushed for 20 mm using a ceramic balls grinder. Then, it was dried for 24 h at 378 K in an Erlenmeyer flask, together with 500 mL of distilled water; the mixture was stirred using magnetic stirring. Then a solution of sulfuric acid (0.25 M) was added. The solution obtained was maintained for 2 days at room temperature. The mineral was filtered and washed several times with distilled water (up to pH 7). After filtration, the Maghnite-H^{+} was dried in an oven for 24 h, at 378 K, and then crushed. The catalyst structure was characterized by FT-IR and XRD.

Table1. Chemical composition of Raw-Maghnite and Maghnite-H^{+}

Species	Raw Maghnite (wt %)	Maghnite-H^{+} (wt %)
SiO_2	69.32	71.70
Al_2O_3	14.65	14.03
Fe_2O_3	1.15	0.81
Na_2O	0.60	0.21
MgO	1.72	0.81
CaO	0.35	0.24
K_2O	0.68	0.60
TiO_2	0.93	0.32
SO_3	0.87	0.38

2.3. Copolymerization Preparation

In a 50 mL beaker containing 4.5 g of trioxane (0.05 mol), mixed with 5.7 g of ε-caprolactone (0.05 mol), we added 10 wt % of dried Mag-H^{+} and the catalyst (0.1 g). The mixture was stirred at a temperature of 353 K. After the required time was reached (8 h), the resulting mixture was removed in such a manner as to exclude any clay mineral. The precipitates (TOX-co-CL) were characterized by ^{1}H NMR, IR (FT-IR), DSC, and TGA. Fig. 1 shows the copolymerization reaction.
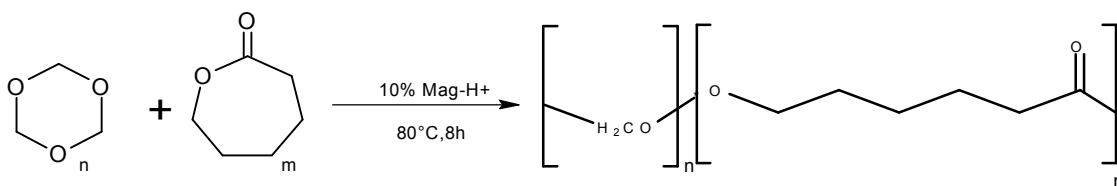

Fig. 1. Synthesis of Copolymer (TOX-CL)

3. Results and Discussion

3.1. Characterization of Mag-H^{+}

3.1.1. XRD Analysis

Fig. 2 illustrates the X-ray diffractograms of the Raw-Maghnite and the Mag-H^{+}. The increase of interlayer distance d (001) = 11.20 Å in Raw-Maghnite is a characteristic of a single water layer between the sheets to a d (001) = 15Å. The distance is attributed to two interlayer water layers in Mag-H^{+}. This increase indicates a cationic exchange of the cation ions (Na^+, Ca^{++}, K^+, NH_4^+, and Mg^{2+}) and a substitution of the H^{+} ions into the leaves of montmorillonite. This increase in basal spacing is explained by substituting single water between the sheet of Raw-Maghnite with two interlayer water layers in Mag-H^{+}.[15]

3.1.2. FT-IR Analysis

The FT-IR spectrum of Mag-H^{+} was compared to that of the Raw-Maghnite. Fig. 3 shows that the hydrated structure of Maghnite-H^{+} results in characteristic vibrations of hydroxide groups around 3400 and 3600 cm^{-1}. The intense band 1004 cm^{-1} corresponds to the valence

vibration of Si-O in the tetrahedral layer. Other absorption bands at 780, 520, and 500 cm^{-1} can be attributed to the montmorillonite clay structure. All these expected absorption bands confirm that the structure of the compound is in good agreement with vibration values reported in the literature.[16]

3.2. Product Characterization

3.2.1. Nuclear Magnetic Resonance of the Proton (^{1}H NMR)

The copolymer obtained was characterized by 300 MHz ^{1}H NMR in CDCl$_3$. The polyoxymethylene copolymer (TOX-CL) comprises oxymethylene units (-O-C$\underline{H}_2$-). Fig. 4 shows the chemical shifts between 1.3 ppm and 1.7 ppm corresponding to three methylene in positions 3.4, and 5 of ε-caprolactone (-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CO-). That at 2.4 ppm for the methylene in position 2 of (CL) (-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CO-), and the intense peak at 4.1 ppm is attributed to the methylene in position 6 of (CL) (-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CO-). There is also a signal at 5.1 ppm corresponding to the methylene proton in position 1 of oxymethylene in the copolymer (O-C$\underline{H}_2$-). The same results were obtained by Bloufaet *et al.*[17] with a small offset of the peak due to the presence of 1,3,5-trioxane.
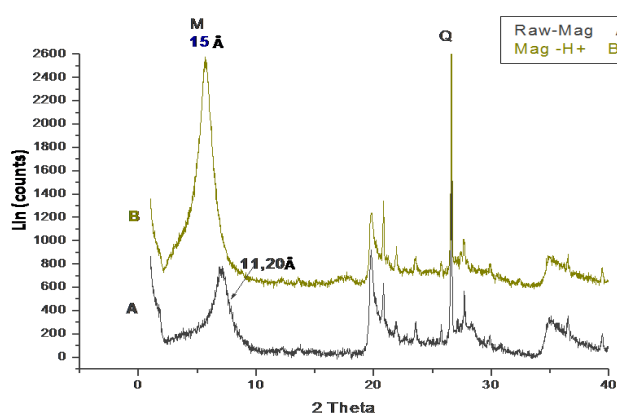

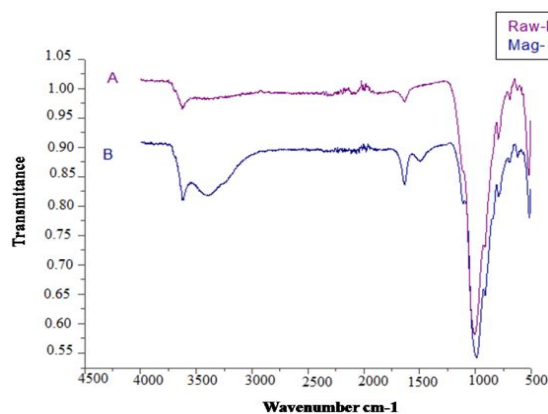**Fig. 2.** X-ray diffractogram of Raw-Maghnite (A) and Mag-H$^+$ 0.25 M (B)

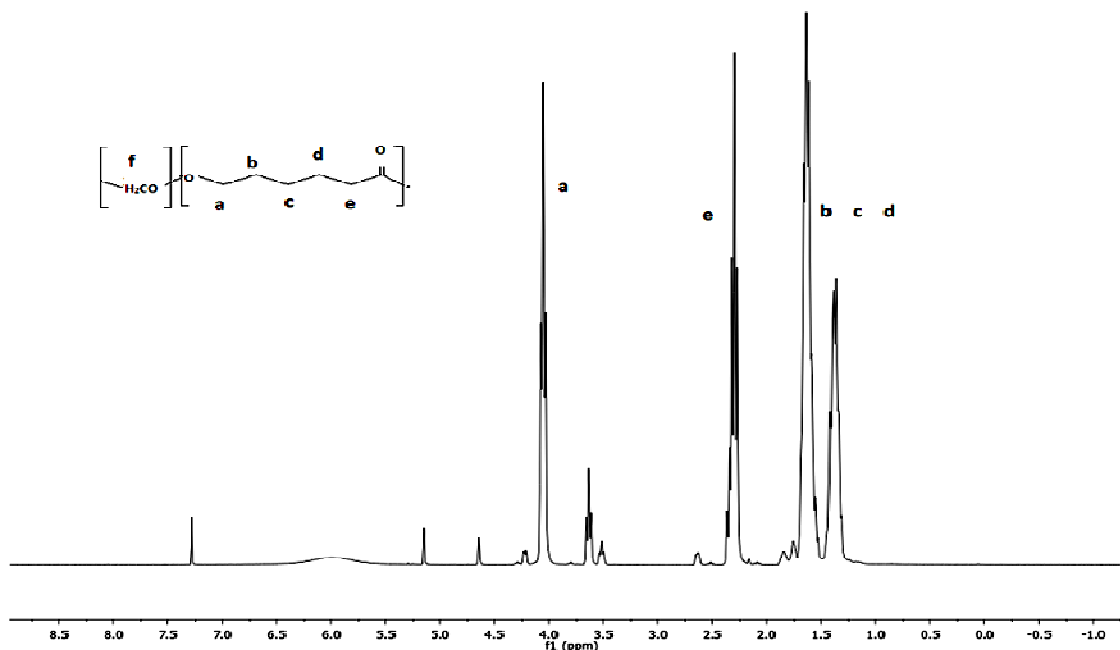**Fig. 3.** FT-IR spectrum of Raw-Maghnite (A) and Mag-H$^+$ 0.25 M (B)

Fig. 4. ^{1}H NMR spectrum (300 MHz) of copolymer (solvent, CDCl$_3$)

3.2.2. FT-IR Spectroscopy

Fig. 5 illustrates the results of the FT-IR spectroscopy. The results allow us to confirm the nature of the polymer. An intense absorption band is observed around 1723.29 cm^{-1} corresponding to the ester's carbonyl group (C=O), another – at 1162.81 cm^{-1} for (-CO-O-), and the last – at 734.22 cm^{-1} for the deformation in the plan of (CH). The two bands appear in the region of 2865.10 cm^{-1} and 2900 cm^{-1}, which is assigned to (C-H) stretching vibration. The ether function appears clearly at 1050.50 cm^{-1} and 1089.36 cm^{-1}, the large band at 3492.22 cm^{-1}, is attributed to the bond (OH).
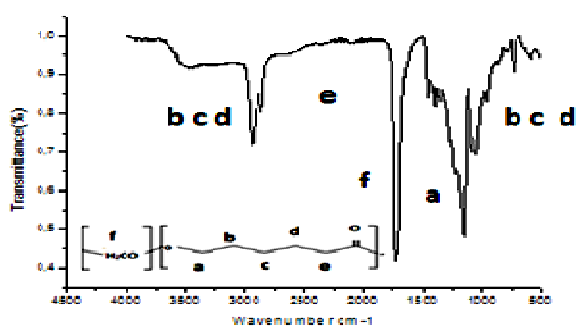

Fig. 5. FT-IR spectra of poly(TOX-co-CL)

3.2.3. DSC Analysis

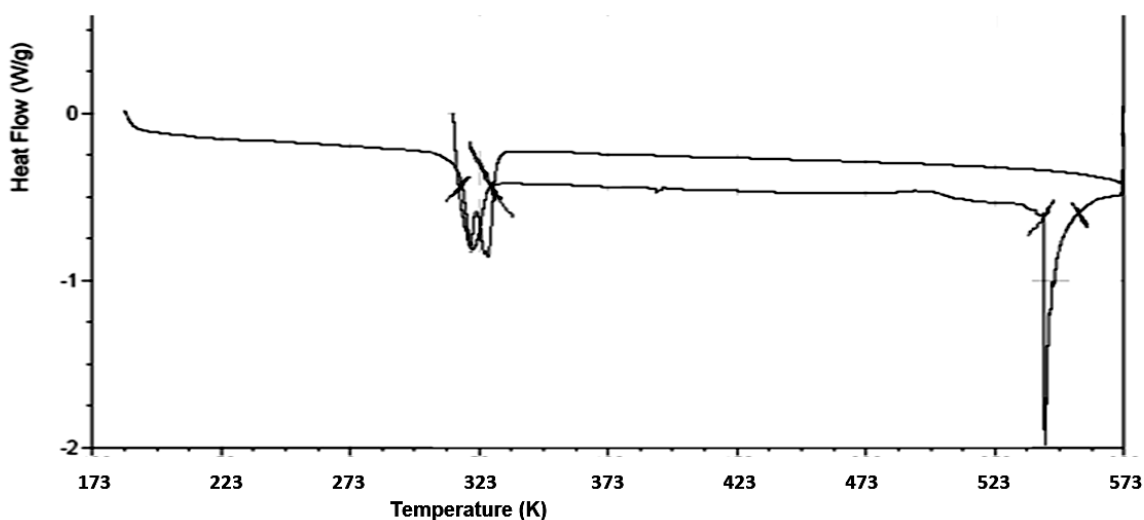Fig. 6 shows the degradation of the polymer. The thermogram of the sample from the previous experiment was obtained with a heating rate of 283 K/min (program from 253 to 473 K). The DSC analysis of the copolymer was performed to give a glass transition temperature obtained at 538 K. It characterizes the melting temperature T_m of the copolymer. This T_m is an intermediate between the melting temperature of two polymers, which is 438 K for PTOX and 329 K for PCL. This proves that we have only one compound, which shows that the copolymer is crystalline. With the increased proportion of monomers, the samples enthalpy of fusion and crystallization decreased.[18]

3.2.4. TGA

TGA was used to monitor the thermal stability of the resulting product (the thermogravimetric curve in Fig. 7). The analysis indicates that the polymer is thermally stable with an onset of degradation temperature above 443 K. The curve (Fig. 7) consists of a single distinct part associated with a single mass loss, indicating that the resulting product is made of a single type of polymer and not a mixture. Also, from the curve, it can be said that the polymers contain no trace of base products. The boiling point of the 1,3,5-trioxane monomer was 385 K, and for the ε-caprolactone, it was 508 K. These two temperatures differ from those shown on the curve, confirming the formation of new products that are not the starting products. The product reached its maximum degradation point at about 747 K (the endpoint of degradation). This result could be related to the chains containing a higher proportion of trioxane[19] (oxymethylene units) and a lower proportion of monomer.
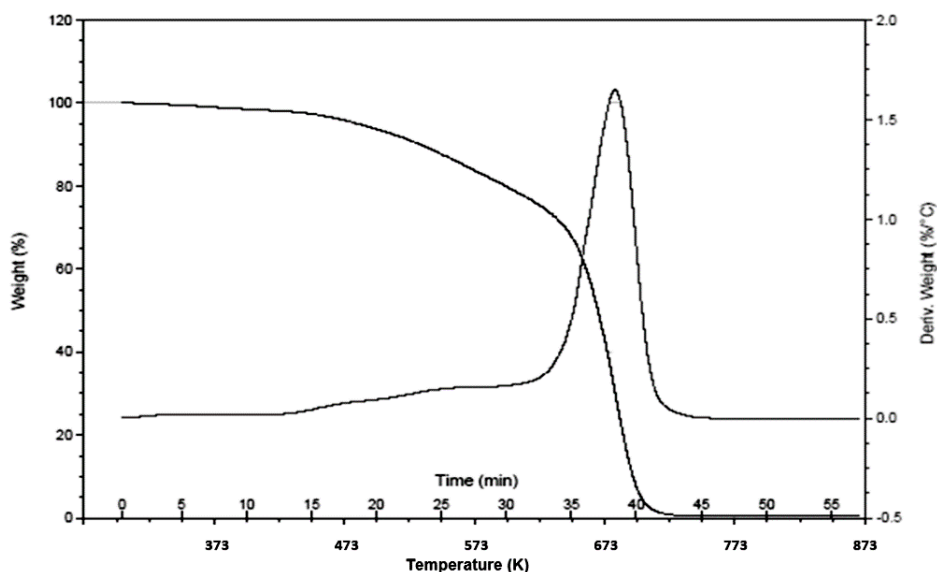

Fig. 6. Thermogram DSC of poly(TOX-co-CL), 10 wt % of Mag-H$^+$, at 353 K for 8 h

Fig. 7. TGA curves of the obtained products

3.3. Kinetic Study of the Copolymerization of Trioxane and ε-Caprolactone

For the kinetic study of this copolymerization, one of the following parameters (time, temperature, the quantity of catalyst, and proportions of the monomers) are fixed to know their influences on the yield of the copolymer obtained. The yield was calculated using Eq. (1), as follows:

$$Yield\,(\%) = (M_0/M_1)\,x100 \quad (1)$$

where M_0 is the weight of the obtained copolymer (TOX with CL) and M_1 is the overall mass of the two monomers (TOX and CL).

3.3.1. Temperature Effect on the Copolymer Yield

To investigate the influence of temperature on the synthetic yield of the studied copolymer, we performed reactions catalyzed by 10 wt % of Mg-H$^+$ with equimolar proportions of two monomers for 8 h at different temperatures: 273, 293, 313, 333, 353, and 373 K. Fig. 8 shows that the yield of the reaction increases with the temperature. It reached a maximum value of 46.3 % for a temperature of 353 K. At this temperature (optimum point), a transparent copolymer with a high yield was formed. In contrast, the yield decreased at 373 K. Also, at high temperatures, the appearance of the Copolymer changed; the color became light brown. It is important to note that the temperature greatly influences the yield of the product.
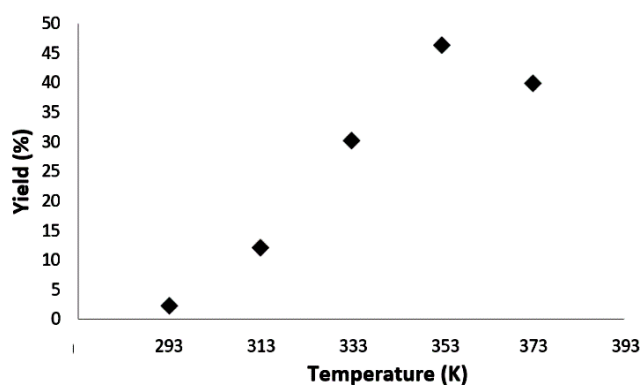

Fig. 8. Temperature effect on the poly(TOX-co-CL) yield, 10 wt % of Mag-H$^+$, time 8 h

3.3.2. Time Effect on TOX Yield with CL

We carried out a series of mass copolymerization of 1,3,5-trioxane with ε-caprolactone using equimolar proportions of each monomer and 10 % of Maghnite-H$^+$ at a temperature of 353 K, varying only the reaction time. Changes in yield over time were monitored by weighing the product at each experiment. Fig. 9 shows that the change in yield as a function of time is regular and rapid until it reaches 32.5 % after 5 h, then it slows down. A yield of 46.3 % was obtained after 8 h of the reaction. The slowing down of the evolution of the yield from 6 h is possibly due to the increase of the medium viscosity, which impedes the movement of the molecules.
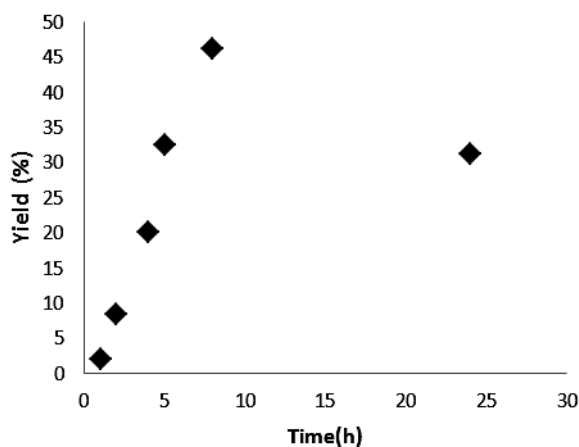
Fig. 9. Effect of the time on the poly(TOX-co-CL) yield, 10 wt % of the Mag-H^{+}, 353 K

Fig. 10 shows that polymerization is the first order to the monomer. The polymerization of GPTMS initiated by Mag-H^{+} can be obtained using Eq., as follows:

$$\vartheta_p = -\frac{d[M]}{dt} = k_p$$

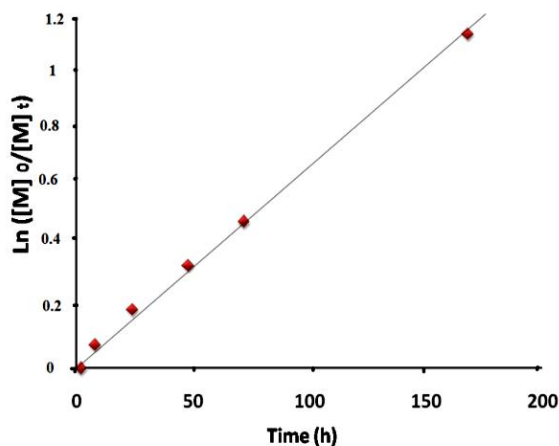where k_p is the polymerization rate constant at 353 K; the k_p value is 1.53 10^{-6} s^{-1}.

Fig. 10. ln ($[M]_0/[M]_t$) as a function of time for *T*=353 K in bulk conditions; $[M]_0$ = 0.005 mol/L for Mag-H^{+}/TOX-co-CL 10 wt %

3.3.3. Effect of Mag-H^{+} Amount on the Yield of Copolymer

The polymerization was carried out at 353 K for 6 h, using various amounts of Mag-H^{+} (2, 3, 5, 8, and 10 wt %). The results in Fig. 11 indicate that the yield of the copolymer represents the evolution of the mass yield of the copolymerization 1,3,5-trioxane with ε-capro-

lactone catalyzed by Maghnite-H^{+}, depending on the amount of the catalyst. The yield increases according to the quantity of Maghnite-H^{+} up to the optimal point of 46.3 %, which corresponds to 10 wt %. This behavior is explained by the increase of active sites available in Maghnite-H^{+} responsible for the initiation and acceleration of the reaction until the saturation of these sites. Similar results were obtained by Belbachir *et al.*[20]
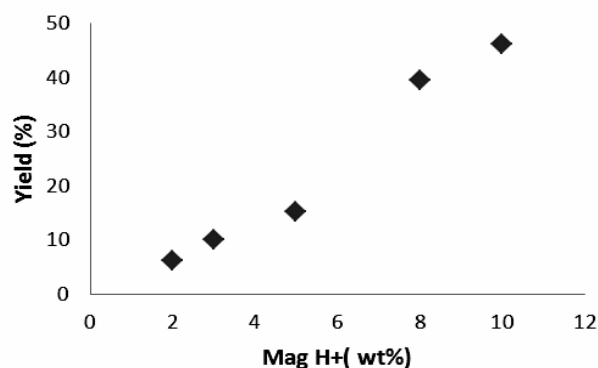

Fig. 11. Effect of Mag-H^{+} amount on the yield of the copolymer at 353 K for 8 h

4. Conclusions

This paper presents the preparation of the copolymer (TOX-co-CL), which was successfully obtained in bulk and solution using Maghnite-H^{+} (proton exchange process) as a green solid catalyst. The FTIR and XRD analyses show that this clay is a part of the montmorillonite family. FT-IR, ^{1}H NMR, DSC, and TGA analyses perfectly characterized the synthesized product. The structure of the obtained polymer was confirmed, and TGA and DSC analyses were used to study the thermal stability of the obtained copolymer.

Moreover, the sample with retarders revealed a higher crystallinity than the samples without them. This work aims to synthesize the copolymer (TOX-co-CL) using Maghnite-H^{+} as a catalyst, which is less expensive and environmentally friendly. The polymerization proceeds *via* a cationic mechanism due to the presence of protons in the lamellar structure of Maghnite. However, bulk polymerization remains a preferred technique for synthesizing TOX-co-CLs to be in line with the principles of green chemistry.

Acknowledgments

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СИНТЕЗ КОПОЛІМЕРУ З 1,3,5-ТРИОКСАНУ Й ε-КАПРОЛАКТОНУ, КАТАЛІЗОВАНИЙ ОБРОБЛЕНИМ БЕНТОНІТОМ ЯК ЕКОКАТАЛІЗАТОРОМ

Анотація. *У цій роботі наведено новий зелений метод кополімеризації 1,3,5-триоксану з ε-капролактоном. У цій методиці використано Maghnite-H$^+$ (Mag H$^+$) як об'ємний зелений каталізатор. Різні методики були використані для підтвердження будови отриманого кополімеру. Також досліджено фактори, які впливають на реакцію кополімеризації. Одержані результати показали, що найкращий вихід кополімеру (46,3 %) отримано для полімеризації в блоці за температури 353 K протягом 8 годин.*

Ключові слова: *кополімеризація, 1,3,5-триоксан, Maghnite-H$^+$, поліоксиметилен, ε-капролактон.*