

Polymerization of DL-Lactide induced by Protonated Montmorillonite clay as a solid catalyst: Mechanism study

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Maghnite- H⁺ is Algerian montmorillonite sheet aluminosilicate clay, exchanged with protons (H⁺). This solid non-toxic catalyst was successfully used as cationic catalyst for the polymerization of D,L-Lactide at 100°C. Interactions between Maghnite-H⁺ platelets and the monomer (D,L-Lactide) were studied by solid state ¹H, ²⁷Al and ²⁹Si NMR spectroscopy. The results show that, the mechanism of the reaction involves both Brønsted and Lewis acid sites on Maghnite surface.

Keywords: D, L-Lactide, poly (D,L-Lactide), PLA, Solid state NMR, , Montmorillonite, Solid Catalyst.

1. Introduction

Poly(D,L-Lactide), (PLA) is a biodegradable and biocompatible polymer. It is usually used in biomedical applications such as controlled drug release matrix, scaffolds for tissue engineering, sutures and constructing medical devices¹⁻³. Conventionally PLA is synthesized by the polymerization of D,L-Lactide. This reaction is mostly induced by the use of metallic or organometallic catalysts, such as, organostannous derivatives^{3,4}. These homogenous catalysts are efficient, but have some disadvantages: they are corrosives which makes them difficult to handle and it is so difficult to remove them from the resulted products. In recent years, the growth of the environmental requirements, have resulted in a demand for alternative catalytic processes. In this regard, many studies have been carried out on the development of new solid acids, such as "Keggin-type Heteropolycompounds"⁵⁻⁸ or acidic clay catalysts⁹⁻¹¹, to replace corrosive homogeneous acids and to resolve the problems related to the purification of the resulted polymers. Therefore, the replacement of classic homogeneous catalysts (such as Lewis acid) by heterogeneous system can offer many advantages: besides of the respect of green chemistry basis, heterogeneous catalysts give easier separation, possible higher product yields and mild reaction conditions⁸.

In our previous works, we have already reported about polymerization reactions catalyzed by Maghnite-H⁺, a proton exchanged montmorillonite clay. This new non-toxic available eco-catalyst exhibited higher efficiency via the cationic polymerization of vinylic and heterocyclic monomers¹⁰⁻¹⁸. The aim of this study is to elucidate the interactions between the monomer (D, L-Lactide) and the inorganic platelets of Maghnite occurring upon the reaction of polymerization. For this reason we have used solid state NMR spectroscopy to elucidate the action of Maghnite-H⁺ such as Brønsted and Lewis acid catalyst upon the polymerization reaction.

Techniques such as ¹H NMR, GPC and viscosimetry were also used to confirm the structure of the resulted polymer.

2. Experimental Procedure

2.1. Materials

Raw-Maghnite: Algerian Montmorillonite clay, was procured from "Algerian Society of Bentonite". D,L-Lactide was purchased from Aldrich Co, it was purified by crystallization from dried ethylacetate and dried under reduced pressure before use. Methanol was dried over magnesium sulphate MgSO₄ and distilled. Ethylacetate was used as received. Dichloromethane was dried over MgSO₄ and distilled on the day of experiment.

2.2. Preparation of the Maghnite-H⁺

Raw-Maghnite (20g) was crushed for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105°C for 2 hours. The Maghnite was then weighted and placed in an Erlenmeyer flask together with 500ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 500 ml sulphuric acid solution (0,5M). Until saturation was achieved over 2 days at room temperature, the mineral was washed with distilled water until became sulphate free and then dried at 105°C.

2.3. Polymerization and kinetics procedure

PLA was prepared by a ring opening bulk polymerisation of D,L-Lactide catalysed by Maghnite-H⁺. The reaction was carried out at 100°C. Each mixture was prepared with 1.44g (10mmol) of D,L-Lactide and an amount of Maghnite-H⁺ and introduced in a sealed tube. The mixture of (Lactide) and Maghnite-H⁺ was stirred under dry nitrogen with a magnetic stirrer. After a required period of time, the reaction of polymerization was terminated by adding Methanol and then the mixture was cooled. For kinetics measurements, the

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resulting polymer was extracted with adequate amount of Dichloromethane, precipitated in Methanol, filtered, washed for several times and dried at 50°C under reduced pressure. The yield of the reaction was determined gravimetrically.

2.4. Polymer characterizations

Spectroscopic ^1H NMR measurements were recorded, under ambient temperature and using DMSO- d_6 as solvent, on an “AM 300 FT Bruker spectrometer. Tetramethylsilane was used as internal standard. GPC, Gel-permeation chromatography, was performed on “Spectra-Physics” chromatograph, equipped with four columns of Ultrastaygel (10^3 , 10^4 , 10^5 and 10^6 Å). The used solvent is THF and the calibration of the apparatus was carried out with polystyrene of known molecular weights. Measurements of “Average viscosimetric Molecular weight” were carried out with an “Ubbelohde capillary viscosimeter” (Semantec ViscologicT11, V 3-1). Intrinsic viscosity, $[\eta]$ (mL/g), was measured in THF at 25°C. The relationship between the viscosity – average molecular weight M_v and the intrinsic viscosity (Staudinger index) is given for PLA (in CHCl_3 , at 25°C), by the Mark-Houwink equation¹⁹:

$$[\eta] = 2,21 \cdot 10^{-4} M_v^{0,77}$$

2.5. Solid state NMR Characterization

Solid state ^{27}Al , and ^{29}Si NMR spectra were recorded with a Bruker spectrometer (Avance 500) using Tetramethylsilane for ^1H and ^{29}Si , and $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in water for ^{27}Al as the 0 ppm external references for the chemical shifts. MAS experiments were performed, with a probe having 2.5 mm ZrO_2 rotors, at a spinning rate of 30 KHz for ^1H and ^{27}Al and 10 kHz for ^{29}Si .

2.6. XRD and XRF Characterization

X-Ray Diffraction (XRD) profiles for pressed powder samples were recorded on a Philips PW 1710 diffractometer using $\text{Cu-K } \alpha$ radiation ($\lambda = 1.5418$ Å). Samples for X-Ray Fluorescence (XRF) analysis were prepared using the LiB_4O_7 fusion method. The resulting beads were analysed on a Philips PW 2400XRF spectrometer.

3. Results and Discussion

3.1. Maghnite Structure.

The composition and the structure of Maghnite- H^+ were reported in a previous works^{10,18}, in which we have demonstrated that Maghnite is a Montmorillonite clay with basic repeating unit: $[\text{Si}_4\text{O}_{10}\text{Al}^{3+}(2-x)\text{Mg}^{2+}x(\text{OH})_2]$ (Figure 1). Table 1 shows the chemical composition of Maghnite- H^+ obtained by XRF analysis. The results show the aluminosilicate nature of the material.

XRD measurements of Maghnite- H^+ (Figure 2) show a broad peak of H^+ -MMT centered on a value of 15.8Å , indicating that the layer distance in Maghnite- H^+ is 15.8Å . Such as they were attributed in a previous work¹⁰, the other peaks are related to the structure of Montmorillonite aluminum-oxygen octahedron and silicon-oxygen tetrahedron^{10,20}.

The comparison between the diffractograms of Maghnite (figure 2(a)) and Maghnite/Polymer mixture after the reaction (figure 2(b)), shows that there are no significant changes on the crystallographic structure of Maghnite- H^+ after the reaction. We can then conclude that the polymerization occurs only on the surface of Maghnite- H^+ .

3.2. Polymerization of DL-Lactide by Maghnite- H^+

The bulk cationic ring opening polymerization of DL-Lactide was catalyzed by Maghnite- H^+ at 100°C (scheme 1). The results are reported in Table 2. The structure of the prepared PLA was confirmed by ^1H NMR (figure 3)¹¹. As shown in table 2, increasing of Maghnite- H^+ /Monomer weight ratio causes increasing in the rate of the polymerization (expressed by the yield) and decreasing in the average viscosimetric molecular weight (M_v) of the resulted polymer. These results show clearly, the effect of Maghnite- H^+ as a cationic catalyst for D,L-Lactide polymerization. Similar results are obtained in our previous work in the polymerization of Isobutylene by Maghnite- H^+ which polymerizes only by cationic process¹⁰.

3.3. ^1H MAS NMR Spectroscopy

The ^1H MAS NMR spectrums of Maghnite- H^+ (figure 4) show two broad peaks at chemical shift values at 2.2 and 6.9 ppm. The peak at 2.2 ppm is attributed to protons of hydroxyl groups in the octahedral sheet of Maghnite; this signal is compatible with the di-octahedral nature of the clay²¹. The peak at 6.9 ppm can be assigned to Brønsted acid sites on the surface of catalyst. This signal is in good agreement with those assigned to solid acids²²⁻²³.

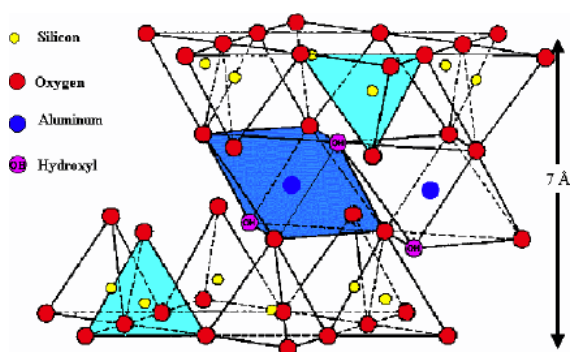


Figure 1. Cristallographic structure of Maghnite (Basic repeating unit is $[\text{Si}_4\text{O}_{10}\text{Al}^{3+}(2-x)\text{Mg}^{2+}x(\text{OH})_2]$)

Table 1. Composition (in %) of Maghnite by X-Ray Fluorescence (XRF) analysis.

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	Water loss at 110°C
Maghnite- H^+	71.70	14.03	0.71	00	0.28	0.80	0.21	0.77	0.15	0.34	11.05

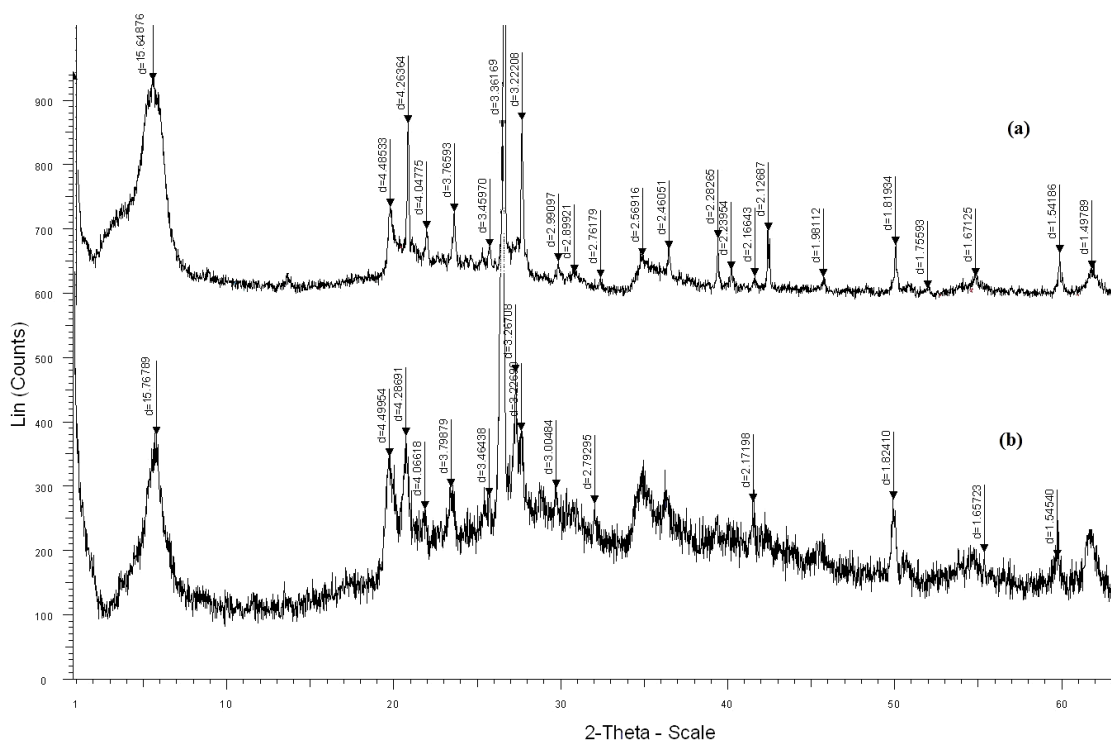
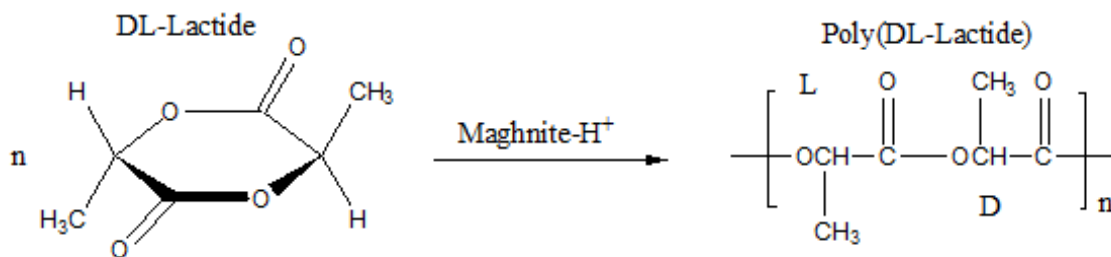


Figure 2. X-ray powder Diffractions of Maghnite-H⁺ (a) and Maghnite-H⁺/Polymer mixture after the reaction (b) (recorded on a Philips PW 1710 diffractometer using Cu- K α radiation ($\lambda=1.5418\text{\AA}$), d is reported in \AA)



Scheme 1. Polymerization of D,L- Lactide by Maghnite-H⁺

In a previous work¹⁵, we have demonstrated that 9,6 ppm signal correspond, respectively, to AlOH and SiOH groups in the vicinity of Al atoms. Accordingly, Brønsted acidic protons in Si(OH)Al units should come from some isomorphous Al substitution in the tetrahedral sheets.

3.4. ²⁷Al MAS NMR Spectroscopy

²⁷Al MAS NMR is a useful method to distinguish between tetrahedral AlO₄ and octahedral AlO₆ units in the material²⁴⁻²⁵. Figure 5 shows the ²⁷Al MAS spectra of Maghnite-H⁺ and Maghnite-H⁺/Polymer mixture after the reaction of polymerization respectively. The chemical shifts are summarized in table 3. The spectra provide information about the local environment of the aluminum sites in Maghnite,

two small bands of two tetra-coordinated AlO₄ (Al_{Td1} and Al_{Td2}) at 58–60 ppm and 68–71 ppm, and another signal at 3–4 ppm attributed to octahedral AlO₆ (Al_{Oh})²⁵. AlO₄ sites in the maghnite structure are the consequence of isomorphous ions substitution within the silicate layers^{10, 15-17}.

Meanwhile, the ²⁷Al NMR spectra of Maghnite-H⁺ and of Maghnite-H⁺/Polymer mixture after the reaction were closely identical, two very significant differences were observed in the ²⁷Al NMR spectra. The (D,L-Lactide) polymerization induced by Maghnite-H⁺ leads to an increase in the proportion of Al in the hexa-coordinated site and a decrease in the proportion of Al in only one tetra-coordinated site (Al_{Td1}) at ~70 ppm. This result suggests that the signal at ~60 ppm corresponds to non-reactive sites of the layered alumino-silicate, while

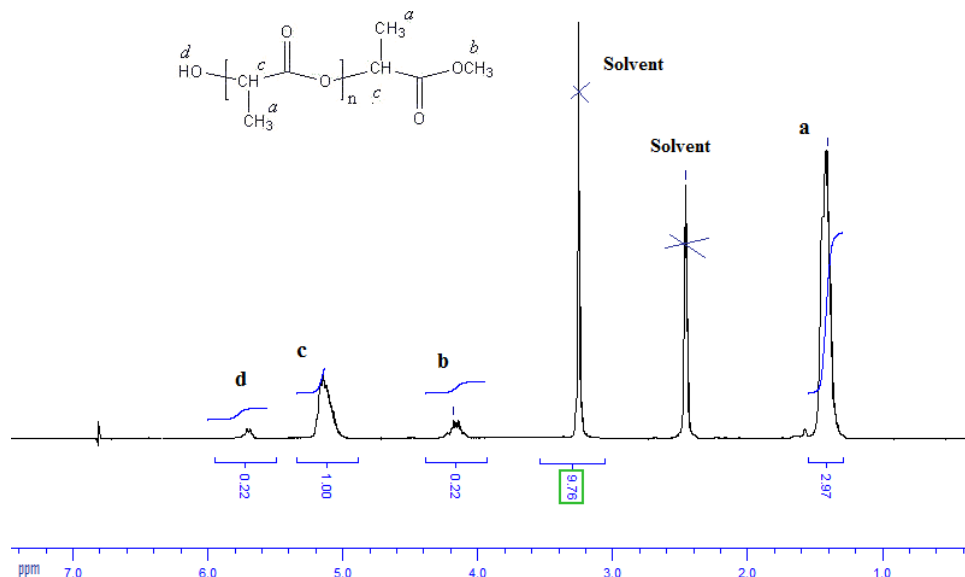


Figure 3. ^1H NMR spectrum of poly (D,L-Lactide) in DMSO- d_6

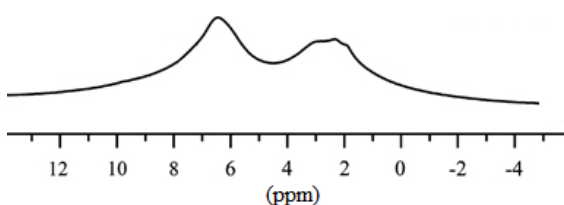


Figure 4. ^1H MAS spectrum of Maghnite- H^+ (recorded with a $\pi/4$ pulse of 3.4 μs , 80 scans, a recycle delay of 4 s and spinning frequencies of 30 kHz).

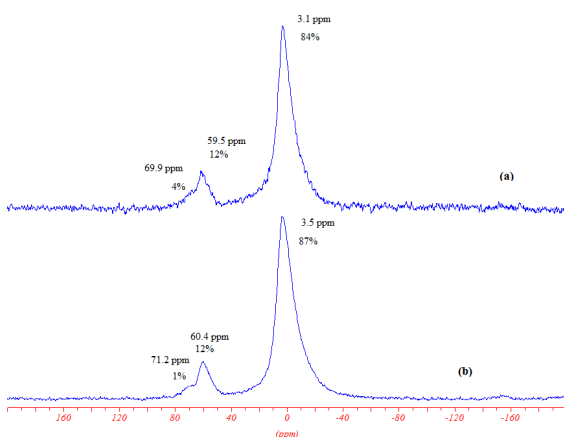


Figure 5. ^{27}Al MAS spectra of the different samples, (a) Maghnite- H^+ ; (b) Maghnite- H^+ /Polymer mixture after the reaction, spinning frequency: 30 kHz.

the signal at ~ 70 ppm is rather due to different reactive sites²⁵⁻²⁶. We can then conclude that polymerization reaction occurs specifically on the active specific tetra-coordinated Al sites, which transforms it into hexa-coordinated Al sites. This result shows that AlO_4 tetrahedral aluminum on the surface of Maghnite contributes to the polymerization reaction of Lactide as Lewis acid catalyst.

Table 2. Kinetics of D,L-lactide polymerisation catalysed by Maghnite- H^+ ($T=100^\circ\text{C}$)

Maghnite/ Lactide w %	Time(h)	Yields %	Mv x 10^{-3}	Mw/Mn
5	3	03.5	2.3	1.10
5	4	15	4	1.16
5	5	18	6.3	1.21
5	7	37	8.4	1.26
5	9	41	9.5	2.10
10	3	05	2.8	1.11
10	4	21	3.5	1.23
10	5	25	4.5	1.19
10	7	52	5.1	1.29
10	9	56	6.3	2.36
15	3	7	1.1	1.10
15	4	35	2	1.28
15	5	37	2.2	1.37
15	7	57	2.5	1.36
15	9	64	3.1	2.20

3.5. ^{29}Si MAS NMR Spectroscopy

^{29}Si MAS NMR spectra provide supporting evidence for no change occurring on silicate sites of the Maghnite- H^+ . ^{29}Si MAS NMR [Figure 6(a)] of Maghnite- H^+ exhibits a strong signal at -94.5 ppm that corresponds to the Q4(1Al)²⁷.

3.6. Mechanism of polymerization

According to theoretical studies on acid catalytic properties of montmorillonite structure²⁸⁻³², the Brønsted acidity alone seems therefore not enough to explain the observed high acid-catalytic activity of the material. Lewis acidity is then of importance for such a catalytic reaction. Indeed, it has been concluded that the reaction occurs at places having both the hydroxyl group and an accessible

Table 3. ^{27}Al NMR Chemical Shifts and Signal Area (%) in Maghnite- H^+ and Maghnite/Polymer mixture after reaction

Sample	(Al_{Oh})		(Al_{Td1})		(Al_{Td2})	
	$\delta(\text{ppm})$	Area (%) ^a	$\delta(\text{ppm})$	Area (%) ^a	$\delta(\text{ppm})$	Area (%) ^a
Maghnite- H^+	3.1	84	59.5	12	69.9	4
Maghnite/Polymer mixture after reaction	3.5	87	60.4	12	71.2	1

^a By spectral decomposition using dmfit software program.

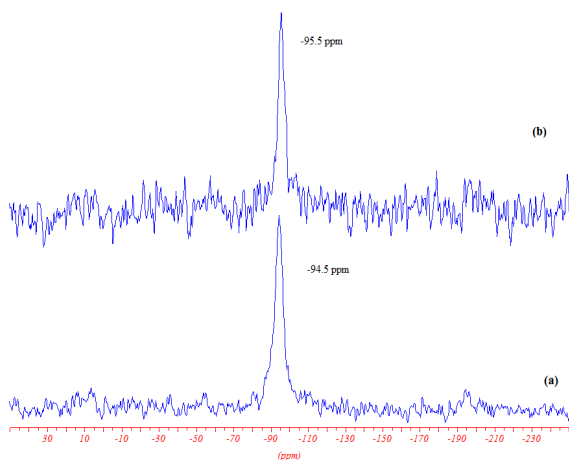


Figure 6. ^{29}Si MAS spectra of the different samples, a) Maghnite- H^+ ; (b) Maghnite- H^+ /Polymer mixture after the reaction, spinning frequency : 10 kHz.

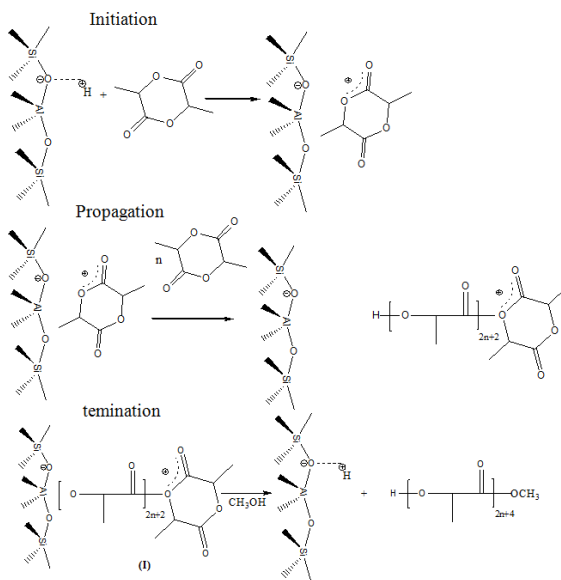
aluminum site acting concertedly as co-localized strong Brønsted and Lewis acidic sites^{31, 32}.

Our present study is consistent with a mechanism involving the initiation of the cationic polymerization of (D,L-Lactide) at the surface of the clay, by the monomer addition on an aluminum Lewis acidic site and assisted by a subsequent neighbor Brønsted acidic site. Thus, the activation of the monomer occurs on Al-O tetra-coordinated sites of the clay as indicated by ^{27}Al NMR. The driving force of cationic polymerization reaction is therefore the ability of these active sites to direct the supported propagation process.

Scheme 2 shows the proposed schematic mechanism of acid catalyzed polymerization of (D,L-Lactide) onto clay surface.

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Scheme 2. Mechanism of D,L-Lactide polymerization catalyzed by Maghnite- H^+

4. Conclusions

The present work shows that D,L-Lactide polymerization can be induced in heterogeneous phase by proton exchanged montmorillonite clay called Maghnite- H^+ . Poly (D,L-Lactide) was produced by an available non-toxic cationic catalyst and by an easy-to-handle procedure in one batch process. This study clearly demonstrates the effectiveness of Brønsted/Lewis acidic sites on the clay interface to induce D,L-lactide polymerization. Solid NMR measurements demonstrate that, the polymerization is therefore consistent with a concerted Brønsted/Lewis acid catalyzed mechanism. This chemistry may be a potential direct method to produce poly(D,L-Lactide)/montmorillonite nanocomposites.

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