



Preparation of PLA blends by polycondensation of D,L-lactic acid using supported 12-tungstophosphoric acid as a heterogeneous catalyst



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ABSTRACT

Poly(lactic acid) (PLA) is a significant polymer that is based on renewable biomass resources. The production of PLA by polycondensation using heterogeneous catalysis is a focus for sustainable and economical processes. A series of samples comprising 12-tungstophosphoric acid (H_3PW) supported on activated carbon, silica, and alumina induced the catalytic polymerization of D,L-lactic acid to form blends of PLA. The catalysts were characterized by multiple techniques to confirm the integrity of the Keggin anion as well as the acidity, which is the key property for relating structure to activity. The best reaction conditions were established for H_3PW/C and tested for the other supported catalysts. The obtained polymer was a blend that was characterized as an enantiomeric excess (ee) of as much as 95% L-PLA (PLLA) with a mass average molar mass (M_w) of approximately 14,900 daltons. The role of H_3PW in these polymerizations was demonstrated, i.e., without the Keggin acid, only oligomeric units ($M_w < 10,000$ daltons) could be obtained. Additionally, inverse relationships between the M_w of PLA and the enthalpy ($-\Delta H$) of the strongest sites of the catalysts were distinguished, i.e., $PLA_{Mw-H_3PW/C} > PLA_{Mw-H_3PW/Al_2O_3} > PLA_{Mw-H_3PW/SiO_2}$, whereas the acidity ($-\Delta H$) order was as follows: $H_3PW/SiO_2 > H_3PW/Al_2O_3 > H_3PW/C$. These findings could be attributed to the correct tuning of strength and the accessibility of the sites to produce longer polymeric chains.

1. Introduction

Poly(lactic acid) (PLA) is one polymer among many that is based on renewable resources and may be used in sustainable plastics. PLA is considered a promising biopolymer due to its properties and its estimated costs [1]. The precursor in the production of PLA is lactic acid ($C_3H_6O_2$), which is an enantiomeric molecule with two isomers: L- or (S)-, and D- or (R)-lactic acid. The known and possible applications of PLA [2] depend on the characteristics of the produced material, such as the mechanical resistance, molding capability, and the abilities to be shaped into thin films, fibers, composites, and membranes. Some of these attributes depend on the properties obtained after its synthesis, e.g., the average molar mass distribution, glass transition (T_g), and melting temperature (T_m). Also, modifications of PLA by different processes (e.g., surface activation, copolymerization, and blending) affect PLA applications [3].

Currently, the most frequently used process to obtain PLA is based on the ring-opening polymerization (ROP) of lactate (obtained from lactic acid) using tin(II) bis(2-ethylhexanoate) (also known as tin octoate (II))

as the catalyst [4, 5]. However, this process is homogeneous, and recovery of the catalyst is not economically feasible. Consequently, PLA applications appropriate for this method are limited to those that are not sensitive to tin contamination, which may prevent, for example, use in some medical devices [6]. A broader application of PLA for medical devices requires reducing production costs as well as improving the quality of the manufactured polymer. The presence of contaminating metals in the PLA matrix can lead to an increase in the rate of degradation, which renders certain applications impossible [7].

Reducing costs in the production of PLA may be achieved through the use of less expensive monomers. The majority of reports in the literature include pure L- or D-lactic acid or L- or D-lactide as the starting source of PLA synthesis [8, 9, 10, 11, 12]. In contrast, the use of a racemic mixture (D,L-lactic acid) as the starting material for PLA is much less explored. Kaitan et al. [13] studied the polymerization of lactic acid and lactide (both D,L) and obtained low (500–2300 Da) and high (8×10^3 - 150×10^3 Da) molecular mass PDLLA. In both cases, only amorphous polymers were synthesized according to differential scanning calorimetry (DSC)

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results. Du et al. [14] prepared atactic PLA from rac-lactide using a Schiff base ligand on aluminum ethyl and isopropoxide complexes with different chiralities. Kucharczyk et al. [15] synthesized carboxyl-functionalized PLA by the direct melt polycondensation of lactic acid and pentetic acid without any catalyst and concluded that there was a direct influence of the optical purity of the lactic acid monomer (i.e., L or D,L). Pure lactic acid created longer branches with unreacted carboxylic groups compared with D,L-lactic acid, which generated a higher concentration of COOH-end groups. Again, the D,L-lactic acid produced non-crystalline PLA. These examples explain the relatively low level of attention that the use of D,L-lactic acid has received as a possible source of PLA, which is mainly because amorphous materials were created.

Recently, we found that carbon-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ could be used as a catalyst in the conversion of D,L-lactic acid to enantioselective blends of PLA [16]. Keggin heteropolyacid (HPA) is an important class of solid acids among which 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, H_3PW) is particularly important because it can be used in acid catalysis for greener processes [17, 18, 19, 20, 21]. It has been shown that the $\text{H}_3\text{PW}/\text{C}$ catalyst is an alternative for use in such reactions involving an inexpensive monomer of D,L-lactic acid. Different loadings of $\text{H}_3\text{PW}/\text{C}$ and calcination temperatures have been studied to optimize PLA formation. Precise experimental conditions have been developed and have resulted in the formation of PLA blends with a high level of enantiomeric excess (85%) [16].

Based on these results, we considered whether there are more economical or efficient supports for H_3PW that could be used efficiently for the same polycondensation reaction. Moreover, we wondered if the same level of enantioselectivity would be possible and whether there could be some additional effect of the carrier or the acidity of the catalyst used. Thus, the objective of this work was to examine cheaper supports (silica and alumina) for H_3PW catalysts that, under similar conditions of the polycondensation reaction, could produce PLA with the same high enantioselectivity. A comparison was conducted with the carbon-supported system, and we verified the properties of the obtained PLA polymers via $^1\text{H}/^{13}\text{C}$ NMR spectroscopy, powder X-ray diffraction (XRD), specific optical rotation, gel permeation chromatography (GPC), and DSC.

2. Materials and methods

2.1. Preparation of the supported catalysts

The supported catalysts were obtained by the impregnation technique. Solutions of H_3PW ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, 99.9%, obtained from Sigma, USA) in 0.1 mol L^{-1} hydrochloric acid (HCl, acquired from Vetec, Brazil) were prepared to attain 20, 30, and 40 wt.% H_3PW on the supports (activated carbon, silica, and alumina, purchased from Aldrich, USA). The detailed procedure can be found elsewhere [16]. The prepared catalysts were subjected to different calcination temperatures (200, 300, and 400°C) in a muffle furnace (EDG model 3P-S, Brazil) for 4 h. The supported catalysts were analyzed by elemental analyses (EDXRF spectrometer from Shimadzu, model EDX 720, Japan) according to a method that has already been described in the literature [22, 23]. The results confirmed that the actual and nominal loadings were similar ($\pm 2\%$). Also, no chloride was detected after the calcination.

2.2. Characterization of the materials

X-ray powder diffraction patterns (XRD) were obtained in a Bruker powder diffractometer (model D8 Focus, 0-20, Germany) using $\text{CuK}\alpha = 0.15418 \text{ nm}$ radiation, operating at 40 kV and 30 mA, a scanning rate of 1° min^{-1} at increments of 0.02° for all of the samples. For the supported catalysts, the 2θ ranges were from 5 to 50° and 5 to 35° for the PLA materials.

The infrared spectra were obtained in a Thermo Scientific Nicolet 6700 model FT-IR spectrometer (USA) in transmittance mode (KBr

pellets) with 256 scans, resolution of 4 cm^{-1} , at room temperature (25°C), from 4000 to 400 cm^{-1} .

The nuclear magnetic resonance (NMR) spectra were obtained for the solid (catalysts) and liquid (PLA) samples. For the solid catalysts, a Bruker, Avance III HD-Ascend model (14.1 T, 600 MHz for ^1H) spectrometer (Germany) was used. Magic angle spinning solid state nuclear magnetic resonance (MAS NMR) spectroscopy was performed in a 4-mm CP/MAS probe with zirconia rotors. The conditions for ^{31}P were the following: 243.1 MHz, spin rate of 10 kHz, pulse duration of 4.75 μs , 10 s interval between pulses, and 512 acquisitions. The reference used was $\text{NH}_4\text{H}_2\text{PO}_4$ ($\delta = 0.9 \text{ ppm}$), which was corrected to H_3PO_4 85% ($\delta = 0 \text{ ppm}$). For the liquid samples, a Varian Mercury Plus spectrometer (USA) was used at 7.05 T (300 MHz for ^1H) with a 5-mm glass tube and 20-Hz spin rate. The acquisition conditions of the NMR spectra were the following: i) ^1H , 300 MHz, single pulse of 4.5 μs duration, acquisition time of 0.1 s, interval between pulses of 1 s, minimum of 20 acquisitions, and internal reference of CDCl_3 ($\delta = 7.3 \text{ ppm}$); ii) ^{13}C , 75.459 MHz, single pulse of 4.5 μs duration, acquisition time of 0.1 s, ^1H decoupling, interval between pulses of 1 s, minimum of 1000 acquisitions, and internal reference of CDCl_3 ($\delta = 77.0 \text{ ppm}$).

The textural data were obtained through gaseous N_2 physisorption at -196°C in ASAP 2020C equipment from Micromeritics, USA. The specific surface areas and volumes of the pores were evaluated from the adsorption and desorption isotherms of nitrogen, which were calculated according to the known Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The fitting models were obtained using the software provided by the manufacturer (ASAP 2020, V3.01). The degasification operation was performed in 0.5 g of the catalyst, under vacuum at 100°C , for 12 h, immediately before the adsorption measurements.

The acidities of the catalysts were obtained with microcalorimetric pyridine (Aldrich, Sure/Seal, minimum of 99%, USA) adsorption in the liquid phase using cyclohexane (Vetec, 99%, Brazil, purified by distillation under P_2O_5 , Merck, Germany). The calcined supported H_3PW (0.5 g) was suspended in anhydrous cyclohexane (50 mL), and a pyridine solution (0.1 mol L^{-1}) in cyclohexane was incrementally added by a syringe pump to the slurry. After each addition, the heat evolved from the reaction of the base with the solid was measured using a calorimeter (model ISC 4300 from Calorimetry Sciences Corporation, USA). Between additions, we waited 4–5 min, which was sufficient to reach system equilibrium. Additional experimental details can be found in the literature reported by our group [24, 25, 26, 27, 28].

Gel permeation chromatography (GPC) profiles were obtained for PLA at 40°C in a Malvern Instruments model Viscotek RImax (UK) equipped with a refractive index detector, a 60-position autosampler, and three GPC columns ($8 \text{ mm} \times 30 \text{ cm}$) in KF-802.5, KF-804L, and KF-805L ovens that were compatible with tetrahydrofuran (THF). The mobile phase was eluted at 1 mL min^{-1} with THF ($\text{C}_4\text{H}_8\text{O}$, Aldrich, inhibitor-free for HPLC, 99.9%, USA). The system was calibrated using polystyrene. The samples were prepared using 1.6–2.0 mg of synthesized PLA per mL THF and filtered through a $0.45\text{-}\mu\text{m}$ membrane filter.

The specific optical rotation ($[\alpha]_D^{25}$) was determined with an automatic Bellingham + Stanley model ADP220 polarimeter (UK) with a 50-mm filling tube. The measurements were performed at a wavelength of 589.3 nm (sodium D-line) at 25°C in a solution of chloroform using concentrations of 1 g dL^{-1} . The enantiomeric excess (ee) was calculated according to the following equation: $\text{ee} (\%) = [\alpha_{\text{Polymer}}^{25} / \alpha_{\text{PLA (pure)}}^{25}] \times 100$; where α_{Polymer} and $\alpha_{\text{PLA (pure)}}$ are the specific optical rotations of the obtained polymer and the pure PLLA (both at 25°C), respectively. The value for PLLA was taken as -156° [1].

The DSC curves were constructed with a Shimadzu Scientific Instruments device (model DSC-60, Japan) from -50 to 250°C at $10^\circ\text{C min}^{-1}$ using approximately 5 mg of sample in a closed aluminum crucible under helium flow (30 mL min^{-1}). During the cooling of the samples, a nitrogen flow (100 mL min^{-1}) was used as the drag gas. Two scans were obtained for each sample, and for the analyses, the results of the curves of

the second scans were used. The temperature at the midpoint of the change in slope of the DSC heat-capacity change was taken as the glass transition temperature (T_g).

2.3. Catalytic polycondensation of D,L-lactic acid

The initial reaction occurred by obtaining a pre-polymer without the addition of catalyst. The reaction was performed using a round-bottom three-necked glass flask (50 mL) containing 15 mL of D,L-lactic acid (Vetec, 84.5–85.5%, Brazil). With the aid of a condenser coupled to the flask. The system was maintained at 160 °C for 4 h under a constant flow of nitrogen gas (White Martins, industrial grade, 99.998%, Brazil) to facilitate the release of water during this step. After completion, the condenser was removed, and approximately 0.1 wt.% of catalyst was inserted into the flask. The system was placed under vacuum, and the other two necks of the flask were hermetically sealed. Each reaction was kept at a constant temperature of 180 °C for 15 h. The obtained PLA was then dissolved in 10 mL of chloroform (Cromoline, p.a., 99.8%, Brazil) and further centrifuged (4000 rpm) for the recovery of the heterogeneous catalyst. The recrystallization procedure was performed via the addition of 50 mL methanol in a 100-mL round-bottomed glass flask. The material was placed in a rotary evaporator to ultimately obtain the solid polymer. The average yield was approximately 60% as calculated gravimetrically. Additional details of the procedure can be found elsewhere [16].

3. Results and discussion

3.1. Structures and properties of the catalysts

The good results obtained with 20 wt.% H₃PW/C in the polycondensation of D,L-lactic acid [16] prompted us to study other supported H₃PW systems. The choices of silica and alumina supports were based on the following: i) their wide availability and low cost, and ii) they are catalysts with loadings of 20 wt.% H₃PW on silica or alumina that have been studied and characterized by our group [24, 25, 26]. Thus, the good and reliable characterizations of the catalysts enabled us to choose the best for testing.

Thermal studies have demonstrated compromises between the temperature of calcination, the integrity of the Keggin anion, and the acidity [27, 28]. For the supported catalysts, complete characterizations by XRD, FT-IR, and ³¹P MAS NMR have been accomplished [25, 26, 29, 30]. Essentially, calcinations far beyond 400 °C are not recommended (especially for long times) because decomposition of the Keggin structure becomes evident.

The XRD patterns and FT-IR spectra of the H₃PW supported on silica, alumina, and carbon exhibited some similar aspects. All the profiles are practically independent of the H₃PW loading from 20 to 40 wt.% and thermal treatments from 200 to 500 °C [25, 26, 29] for H₃PW/support (support = carbon or Al₂O₃). Powder XRD of H₃PW, in its hexahydrated form, displayed main peaks at $2\theta = 10.4$; 25.4 and 33.5°, corresponding to the (110), (222) and (422) planes, respectively [24]. However, it is well known in the literature that the hydration degree concerning the secondary structure changes very much the pattern, because different crystalline systems are detected for each actual hydrated proton present in the structure [24, 27].

The XRD patterns (Figs. 1 and 2) revealed a halo from the respective support and a poor crystalline pattern of 20 wt.% H₃PW/support (support = carbon or Al₂O₃), except for a large peak at $2\theta = 8.5^\circ$ in the XRD of H₃PW/carbon. This reflection for H₃PW was assigned to the presence of hydrated polyanions that were either isolated molecular moieties or small crystallites containing a few Keggin units [31, 32, 33]. Using the Scherrer equation, it was possible to calculate a nanocrystal size of approximately 3 nm. For the 20 wt.% H₃PW/Al₂O₃, it was not possible to detect any characteristic peak of H₃PW. However, the H₃PW on the silica support (Fig. 3) had peaks of crystalline H₃PW for loadings as low as 10 wt.% [25]. In these cases, the crystallite size was also approximately 3 nm

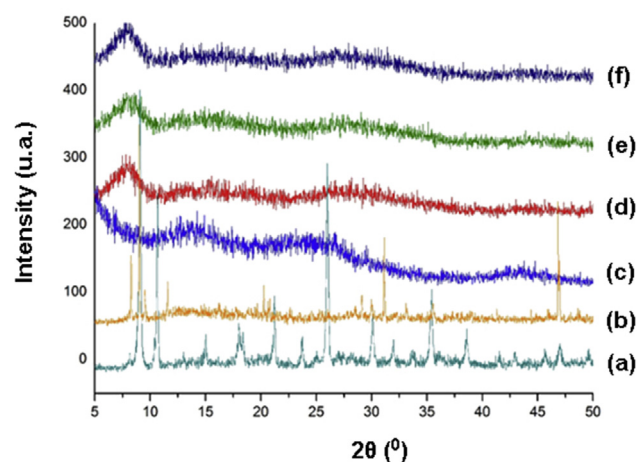


Fig. 1. XRD of: (a) H₃PW not calcined; (b) H₃PW calcined at 300 °C; (c) activated carbon not calcined; and 20% H₃PW/C calcined at: (d) 200 °C; (e) 300 °C; (f) 400 °C.

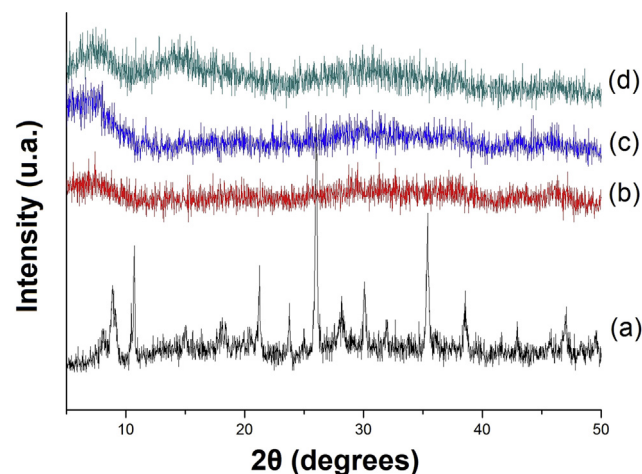


Fig. 2. XRD of X% H₃PW/Alumina calcined at 400 °C with X: (a) 100%; (b) 20%; (c) 30% and (d) 40% H₃PW.

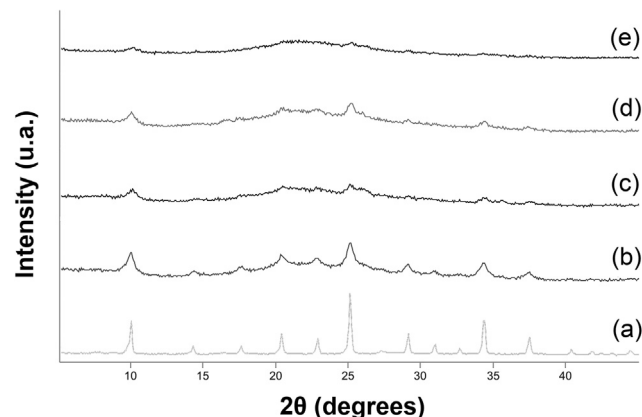


Fig. 3. XRD of X% H₃PW/Silica calcined at 400 °C with: (a) 100%; (b) 30%; (c) 20%; (d) 15% and (e) 10% H₃PW.

(calculated from $2\theta \sim 8.5^\circ$). Upon treatments at 500 °C, the peaks of crystalline WO₃ were observed on all three supports, which confirmed the decomposition of pure H₃PW at that temperature [28, 29].

The FT-IR spectra of the non-calcined H₃PW showed the fingerprint

bands of the Keggin structure at 1080 cm^{-1} (vas-(P=O)), 983 cm^{-1} (vas-(W=O)), 892 cm^{-1} (vas-(W-Oc-W)) and 797 cm^{-1} (vas-(W-Oe-W)), which agreed with the literature [23]. The FT-IR spectra of the $\text{H}_3\text{PW/C}$ (Fig. 4) clearly demonstrated the presences of the Keggin anions on the composites, whereas, in the thermal treatments, the fragmentations of the polyanion could be detected either by the presence of bands from the lacunary phase derivative of Keggin anions or the stretching bands of W–O from the WO_3 moieties [29]. However, for the alumina and silica supports, the superposition of the Keggin fingerprint bands with those in the same region of the materials made it more difficult to observe the primary structure of the H_3PW [25, 26]. In those cases, one may either subtract the spectra of the support (which requires cautious experimental data) or carefully analyze the bands. In these cases, the analyses were more difficult with lower loadings. For example, for alumina, the presence of the actual bands at 981 cm^{-1} (W=O) and 892 cm^{-1} (W–O–W) became more visible with increasing H_3PW loading (e.g., approximately 40 wt.%).

In this sense, to prove the structure of the H_3PW on any of these composites, ^{31}P MAS NMR is more effective than other methods (Fig. 5). The spectra of 20% H_3PW /support (carbon, SiO_2 , or Al_2O_3) calcined at 400°C demonstrated the maintenance of the Keggin structure with different degrees of interaction that depended on the support. Clearly, there was a widening of the ^{31}P signal that was characteristic of the Keggin structure and centered at -14.5 ppm for $\text{H}_3\text{PW/C}$, which indicated a strong interaction with this support. A strong interaction was also observed for the alumina-supported system with much lower widening, but a shift of the original H_3PW signal from -15.1 ppm to -13.5 ppm was present [26]. For $\text{H}_3\text{PW/SiO}_2$, the signal at -14.9 ppm was practically unaffected, independent of the H_3PW loading [25]. The ^{31}P spectrum of pure H_3PW has been demonstrated to be dependent on hydration, which

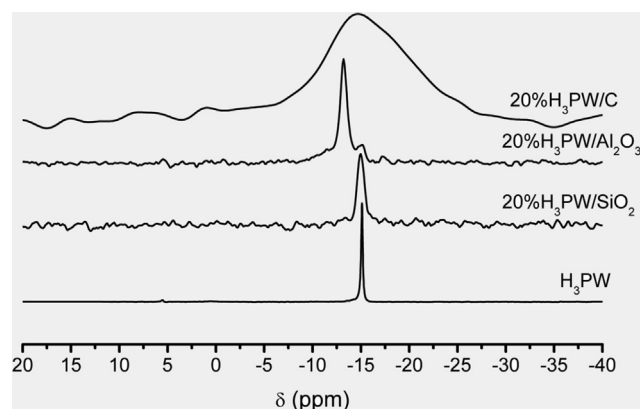


Fig. 5. ^{31}P MAS NMR spectra of H_3PW and supported (20%), calcined at 400°C .

can range from -11 to -16 ppm (i.e., the anhydrous to the hydrated form, respectively), according to the literature [24, 34]. Thus, the chemical signal related to the ^{31}P environment of H_3PW shifted to more positive values (low field) due to the interaction of the support with the Keggin anion. This behavior has been widely established in the literature for H_3PW supported on silica, alumina, zirconia, and niobia [22, 23, 25, 26]. The same trend has been observed for supported catalysts calcined at 200 and 300°C , which demonstrates that, in all cases, the Keggin structure was maintained under those preparation conditions. These results are important because they substantiate the acidity properties of these materials. The main effect is the high electronic delocalization on the Keggin

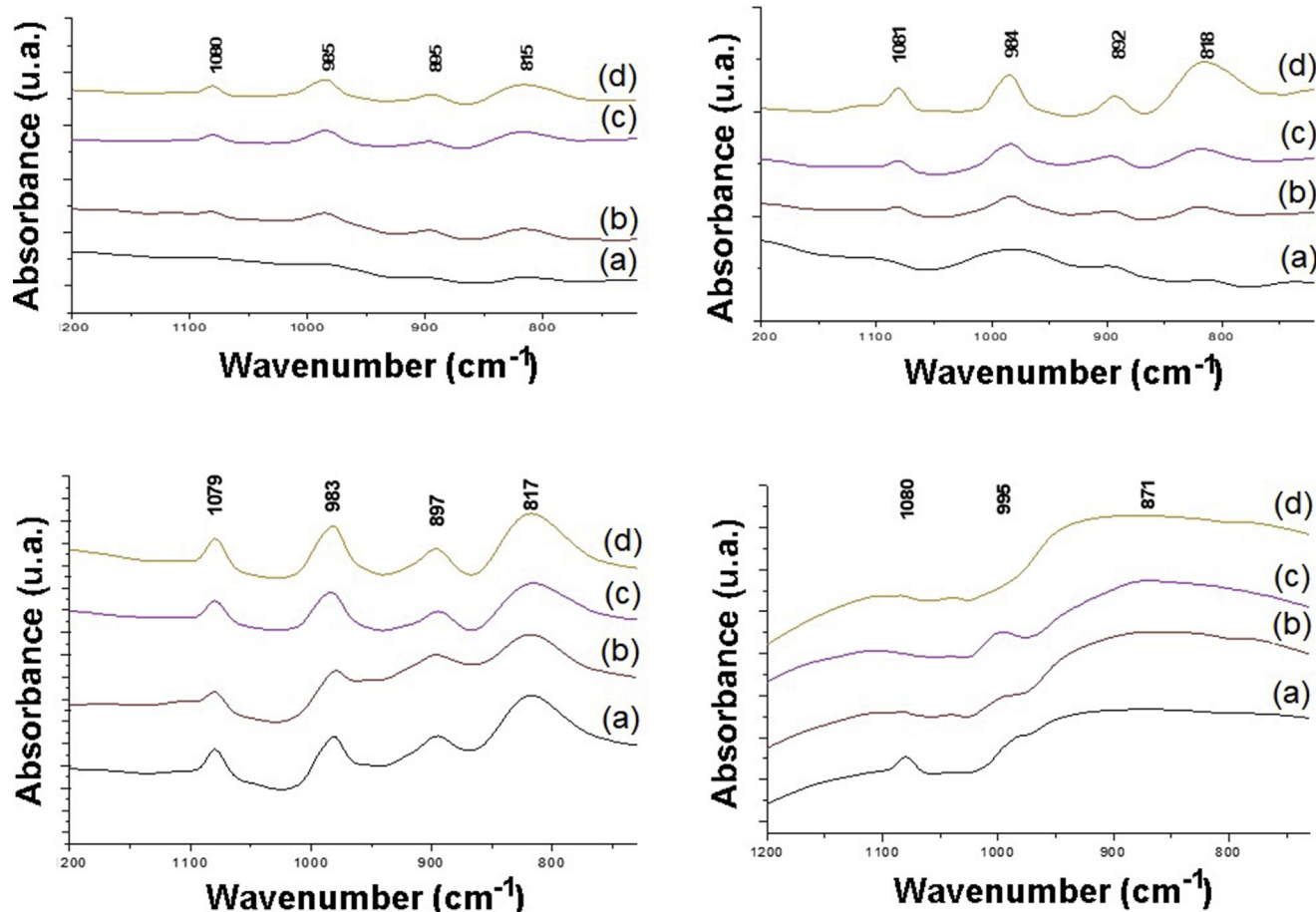


Fig. 4. FT-IR of X% $\text{H}_3\text{PW/C}$ calcined at (a) 200°C ; (b) 300°C ; (c) 400°C and (d) 500°C .

anion in the donor capacity of H₃PW protons. Once the protons are kept on the secondary structure of H₃PW after thermal treatment, a higher potential acidity will be reached based on the negative charge distribution of the anion on the intact Keggin structure [35].

The proposed interaction observed by ³¹P MAS NMR could be confirmed by measurements of the heating of pyridine adsorption on the solids by microcalorimetry. Table 1 displays the average enthalpies (−ΔH₁) and the numbers of the strongest sites of the catalysts (n₁). The leveling effect on the strength and enhanced accessibility to the protons of H₃PW on the different supports have been demonstrated by calorimetry and adsorption (Cal-Ad) method [24, 25, 26]. Supporting H₃PW on different carriers caused their originally strong Brønsted sites to become weaker, which was expected because a fraction of the protons of H₃PW reacted with the mostly basic surface sites of the supports. The order of the measured acid strengths (−ΔH₁) was H₃PW > H₃PW/SiO₂ > H₃PW/Al₂O₃ > H₃PW/C, which corresponds to the average enthalpies of 143, 114, 98, and 95 kJ mol^{−1}, respectively. However, the accessibility (n₁) to the strongest acid sites was significantly increased with the supports. The n₁ ordered was H₃PW/Al₂O₃ > H₃PW/C > H₃PW/SiO₂ > H₃PW with the numbers of sites equaling 0.15, 0.13, 0.10, and 0.08 mmol g^{−1}, respectively. Thus, the strengths and the numbers of sites might be important parameters of the catalysts that correlate with some properties of the PLA polymer preparation.

The textural properties of the supported catalysts were obtained (Table 2) using low temperature N₂ adsorption. The nitrogen adsorption-desorption isotherms of the catalysts were determined to be predominately type IV according to the BET model and IUPAC classification. A decrease of the BET specific surface from the parent support was observed, which could be attributed to the deposition of the nanocrystalline H₃PW on the pore opening, which blocked the entrance of the molecular nitrogen during adsorption. Additionally, the reductions of the original BET specific surfaces from the pure supports were 17%, 18%, and 45% for carbon, alumina, and silica, respectively. Considering that the amount of dispersed H₃PW was the same (20 wt.%), these findings may indicate a possible effect on the activities of the materials.

3.2. Catalytic polycondensation and polymer characterization

The polycondensation of D,L-lactic acid was optimized for the 20% H₃PW/C catalyst via TG/DTG analysis of the temperature of the maximum derivative mass loss for the degradation of the polymer (T_D) [16]. Based on these best conditions, the supported catalysts on silica and alumina were tested (i.e., at a temperature of 180 °C for 15 h, 0.1 wt.% catalyst, 20 wt.% H₃PW/support calcined at 400 °C). Thus, the PLA produced in each reaction was characterized by ¹H/¹³C NMR, XRD, GPC, and specific optical rotation.

Table 1

Calculated enthalpies (−ΔH₁, kJ·mol^{−1}) and numbers (n₁, mmol·g^{−1}) of the strongest sites obtained by microcalorimetry of the pyridine adsorption on the supported catalysts that were calcined at different temperatures.

Catalyst	Temperature (°C)	−ΔH ₁ ^a (kJ·mol ^{−1})	n ₁ (mmol·g ^{−1})
H ₃ PW	200	148	0.08
H ₃ PW	300	150	0.08
H ₃ PW	400	130	0.07
20% H ₃ PW/C	200	96	0.13
20% H ₃ PW/C	300	93	0.13
20% H ₃ PW/C	400	91	0.12
20% H ₃ PW/SiO ₂	200	114	0.10
20% H ₃ PW/SiO ₂	300	116	0.11
20% H ₃ PW/SiO ₂	400	110	0.09
20% H ₃ PW/Al ₂ O ₃	200	98	0.15
20% H ₃ PW/Al ₂ O ₃	300	100	0.14
20% H ₃ PW/Al ₂ O ₃	400	97	0.12

^a The enthalpies measured in this work are the averages of the first additions of pyridine (limiting reagent) in the calorimetric titration. The standard deviation is ±1 kJ mol^{−1} in all cases.

Table 2

Textural properties of supported H₃PW on carbon, silica, and alumina calcined at 400 °C. The catalysts were activated at 200 °C/4 h before the N₂ adsorption measurements.

Catalyst	S _{BET} (m ² ·g ^{−1})	P _V (cm ³ ·g ^{−1})
H ₃ PW	4	0.02
Carbon	687	0.51
Silica	260	0.75
Alumina	155	0.38
20% H ₃ PW/C	572	0.41
20% H ₃ PW/SiO ₂	142	0.32
20% H ₃ PW/Al ₂ O ₃	127	0.17

The PLA produced was first analyzed by ¹H and ¹³C NMR. Fig. 6a–d shows the ¹H NMR spectra of the polymers obtained after the catalytic reaction using pure silica and 20 wt.% H₃PW/SiO₂ calcined at 200, 300, and 400 °C. In the spectra, the singlet at 7.3 ppm refers to the CDCl₃ solvent, and the quartet between 5.0 and 5.3 ppm is attributable to the hydrogen atoms of the methine group (−CH−CH₃). This quartet appeared with high resolution even though it had small multiplets located between 5.2 and 5.3 ppm. Additionally, there was a doublet at approximately 1.60 ppm that was related to the hydrogen atoms of the methyl group (−CH₃). The observed signals between 4.2 and 4.5 ppm may refer to the presence of oligomeric units. For the polymers catalyzed by 20% H₃PW/SiO₂ and calcined at 200, 300, and 400 °C, it was possible to observe very low signals between 3.6 and 3.9 ppm, which were not evident in the spectra of the polymers obtained from pure silica. For the PLA obtained from pure silica, there was a low signal at approximately 2.3 ppm that was related to the hydrogen atoms associated with the carboxylic acids. Therefore, it was plausible to infer that the PLA obtained by the catalysis with pure silica presented a certain number of monomers in the final structure.

The ¹³C NMR spectra of the PLA obtained from pure silica and 20% H₃PW/SiO₂ calcined at 200, 300, and 400 °C were similar to those obtained with H₃PW/C (Fig. 7a–d). The signals observed at 66.8 ppm were attributable to the carbon of the −CH group of the D isomer, and the signals at 69.0 ppm were attributable to the −CH carbon of the L-isomer in the equimolar mixture of D,L-lactic acid [16]. Additionally, the signals appearing at 16.7 ppm were attributable to the carbon of the −CH₃ group of the L-isomer. At 20.3 ppm, the signals were attributable to the carbon of the −CH₃ group of the D isomer. At 169.7 ppm, the signals were

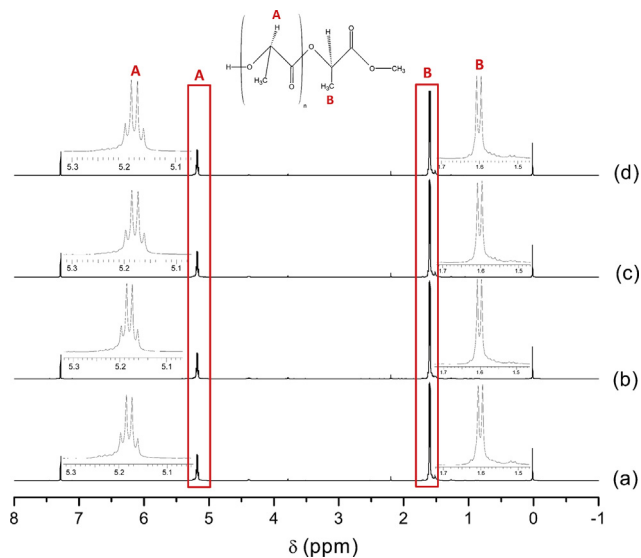


Fig. 6. ¹H NMR spectra of PLA catalytically obtained with the following: (a) pure silica and 20% H₃PW/silica calcined at (b) 200 °C, (c) 300 °C, and (d) 400 °C.

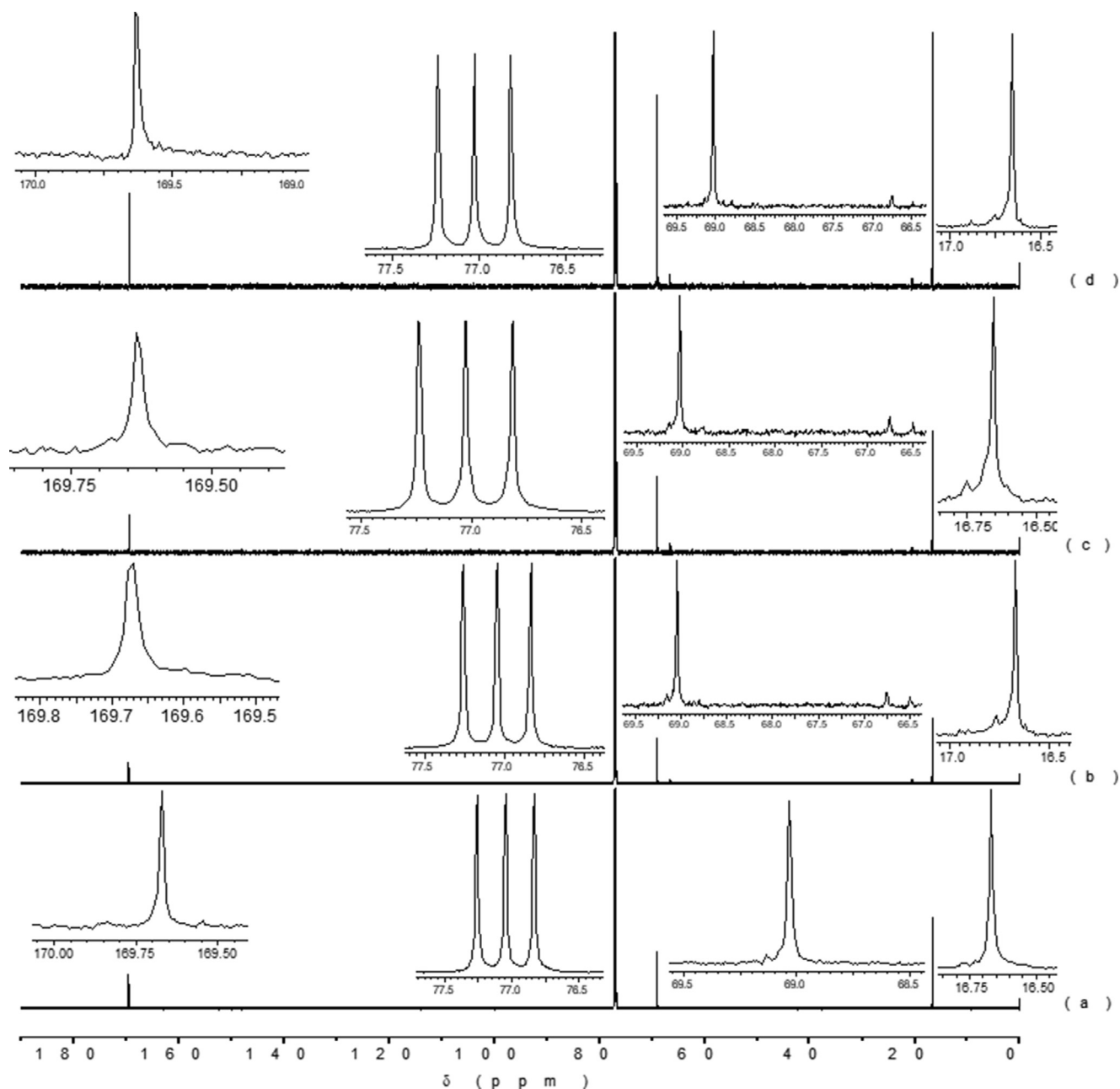


Fig. 7. ^{13}C NMR spectra of PLA catalytically obtained with the following: (a) pure silica and 20% $\text{H}_3\text{PW}/\text{silica}$ calcined at (b) 200 $^\circ\text{C}$, (c) 300 $^\circ\text{C}$, and (d) 400 $^\circ\text{C}$.

attributable to the carbon of the carboxyl group ($-\text{C}=\text{O}$). As the calcination temperature of the supported catalysts was increased, an increase in the intensity of the L-isomer signals was observed, which suggests a slight increase in racemization during the polymerization of samples obtained with catalysts that were subjected to higher calcination temperatures.

The ^1H NMR spectra of the PLA obtained with pure alumina and 20% $\text{H}_3\text{PW}/\text{Al}_2\text{O}_3$ catalysts are shown in Fig. 8a–d. All spectra revealed a singlet at 7.3 ppm (CDCl_3) and a quartet between 5.0 and 5.3 ppm that were attributable to the hydrogen atom of the carboxylic group chain end and the hydrogens of the methine group ($-\text{CH}-\text{CH}_3$), respectively. The observed doublet at approximately 1.60 ppm was related to the hydrogen of the methyl group ($-\text{CH}_3$). The signals between 4.2 and 4.5 ppm referred to the presence of oligomeric units. The spectra revealed a low resolution for the sample catalyzed by pure alumina; however, the resolution sharpened as the calcination temperature increased for the supported catalysts. The signals that appeared at approximately 3.6 and 3.9

ppm for the polymers obtained from 20% $\text{H}_3\text{PW}/\text{C}$ and 20% $\text{H}_3\text{PW}/\text{SiO}_2$ were not evident for those obtained with 20% $\text{H}_3\text{PW}/\text{Al}_2\text{O}_3$, but instead generated a low intensity signal at 2.2 ppm (which was possibly related to hydrogen atoms associated with carboxylic acids) for pure alumina. These findings suggest that little or no racemization occurred when 20% $\text{H}_3\text{PW}/\text{Al}_2\text{O}_3$ was applied.

Nonetheless, the quartet for the methine group at approximately 5.2 ppm was observed with significantly greater resolution in the ^1H NMR spectra of the PLA obtained from pure and supported alumina catalysts than from those obtained from the catalysts using silica or carbon supports. This finding is corroborated by the ^{13}C NMR spectra acquired from the same polymers (Fig. 9). In summary, the spectra of the ^1H and ^{13}C NMRs of the PLA attained by catalytic reactions using supported H_3PW on silica and alumina revealed a potential system for the synthesis of enantioselective PLA and possible blends. Importantly, this is an initial qualitative analysis, and complementary techniques will confirm these points.

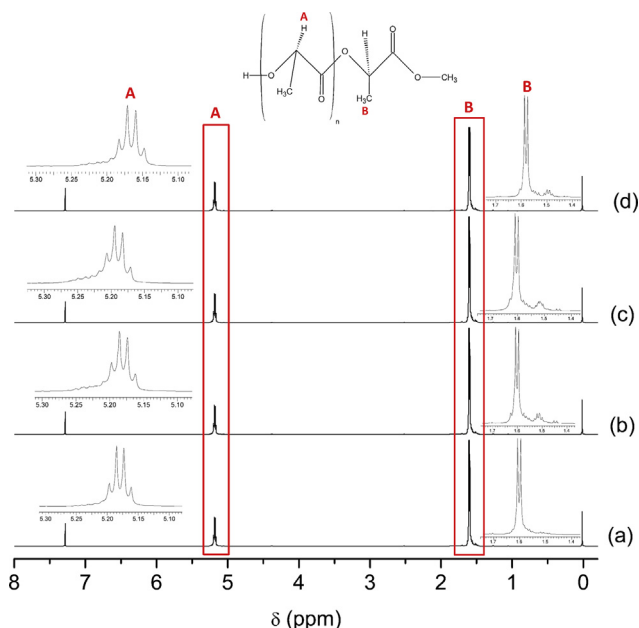


Fig. 8. ^1H NMR spectra of PLA catalytically obtained with the following: (a) pure alumina and 20% H_3PW /alumina calcined at (b) 200 °C, (c) 300 °C, and (d) 400 °C.

The PLA products appear to be enantiomeric in form. To prove their crystallinities, X-ray diffraction patterns (Figs. 10 and 11) were acquired for the polymers obtained by the catalytic reaction using pure silica, alumina, and their supported H_3PW . In all cases, two intense peaks at $2\theta = 19.1^\circ$ and 16.7° were observed for planes hkl (203) and (110/200), respectively, and two less intense peaks at approximately $2\theta = 22.4^\circ$ and 14.8° were observed for planes hkl (015) and (010), respectively [36]. These results indicated that one or more of the crystalline enantiomers of PLA formed because patterns of racemic PLA exhibit no XRD peaks [36, 37]. No peaks related to H_3PW [38] or halos from the supports (i.e., silica or alumina) were observed in any synthesized polymer.

Polarimetry is a more specific technique for demonstrating the enantioselective formation of molecules. Table 3 shows the *ee* achieved for the polymers obtained by the catalytic reactions with H_3PW supported on silica and alumina and by the pure supports. There is a marked increase in the conversion towards the L-lactic isomer in the polymer chain at the expense of the D-lactic moiety. It is interesting to note the blank experiments (pre-polymer) and polymer obtained without catalyst (i.e., catalyzed only by the auto-ionization of the carboxylic acid). In all cases, an enantiomeric excess was formed from the beginning of the reaction (produced pre-polymer for 4 h). These results are consistent with the $^1\text{H}/^{13}\text{C}$ NMR analyses.

Because the supports by themselves apparently demonstrated the capacity to transform D,L-lactic acid into enantioselective PLA as well as the supported H_3PW catalysts, the role of H_3PW should be clarified. For this purpose, GPC measurements of the produced polymers were important and necessary. Table 4 shows the relative average molar masses of the polymers obtained with the different catalysts under the same reaction conditions. Based on these results, the important role of H_3PW on the polycondensation reactions was confirmed. The acidities of the catalysts were fundamental to obtain a higher relative molar mass of the PLA. In other words, without H_3PW , the produced PLA is much more accurately described as a mixture of oligomers. Here, we adopted the criterium used by Garlotta [6], which considered a molar mass of up to 10,000 daltons to indicate oligomeric chains.

Another concern regards the possible formation of blends, as has been observed for PLA obtained via a catalytic reaction using H_3PW /carbon [16]. The analysis of the polymers by DSC allows the visualization of important polymeric properties. Using this technique, it is possible to

measure temperatures in which physical and morphological transitions occur, and these transitions are critical parameters in the engineering of polymeric materials. For the formed polymers, the DSC curves (Fig. 12) suggested first-order transitions that exhibited two melting peaks (i.e., one associated with the PDLA chains and the other with PLLA; $T_m \geq 138^\circ\text{C}$). Notably, the presence of only a second-order transition related T_g denotes that the blends are formed by amorphous and crystalline domains, which accords with the behavior of semicrystalline materials [6, 36]. The data related to the crystallization and melting enthalpies (ΔH_c and ΔH_m) of the polymers from each process using pure solids and heterogeneous-supported catalysts are listed in Table 5.

3.3. Correlations of catalyst structures and polymer properties

There are some important correlations that can be observed and analyzed based on the properties of either the catalysts or the produced PLA. Those most prominent properties of the catalysts that involve their structures (i.e., preparation method) are the following: the acidity, the number of acid sites, and the accessibilities of these sites. In contrast, the quality of the PLA produced may be measured by the relative average molar mass (M_n and M_w) and the enantiomeric excess in the blends. To make this correlation easier to compare, Table 6 provides and organizes these data.

Before a straight comparison is performed, some remarks should be considered. The pre-polymerization step aimed to remove as many water molecules as possible to form the highest number of oligomers. The reaction medium was maintained in an inert atmosphere (under nitrogen flow) to ensure that the equilibrium of the reaction was displaced towards the product (PLA). After the addition of the catalyst, the polycondensation reaction began under reduced pressure (vacuum). The oligomers then reacted with each other through a Fischer esterification, which is a nucleophilic substitution. Briefly, the acidic catalyst furnished a proton to react with the acyl group of one oligomer, which allowed it to be more electrophilic. Subsequently, the substitution of an O–H group with an O–R group of a second oligomer and the release of a water molecule after the formation of a tetra-coordinated intermediate occurred [7, 39, 40]. A proposed schematic of this mechanism is represented in Fig. 13.

The GPC results were essential to understand the H_3PW action in the preparation of PLA. Without any catalyst, only low molar mass oligomers [6] ($M_w < 10,000$ daltons) were formed (Table 6, entries 1 to 3). With pure supports (carbon, silica, and alumina), the average molar mass of the formed PLA decreased as the acidity ($-\Delta H_1$) of the support increased (Table 6, entries 4 to 6). Pure H_3PW (Table 6, entry 7), which had reacted under homogeneous conditions, was too strong of a solid acid for the polymerization because a low M_w was obtained. Secondary reactions with strong acids have been commonly observed in previous works [41, 42]. The separation process was more difficult in this case, and the purification of PLA using pure H_3PW demanded more care, because it was a homogeneous catalytic reaction.

The inverse relationship between the acidity of the supports and the relative molar mass of PLA demonstrated that the polycondensation of D,L-lactic acid depended on the acidity of the catalyst, which was expected based on the described mechanism (Fig. 13). The strengths of the catalytic sites were probably limiting in terms of promoting polycondensation without many side reactions. Thus, this acidity should be carefully tuned to attain the best properties of the PLA. Using supported H_3PW was one such method to tune the original acidity of H_3PW , i.e., to reach the desired strength of the acid sites, to disperse it by increasing the specific surface area, and to enhance the number of the available sites by providing their accessibility over the supports [33, 43].

The hypothesis that better control of the polycondensation process can be achieved by tuning the acidity of the H_3PW catalyst was proved by using different supported H_3PW samples. First, developing the method for the separation of PLA and the supported catalysts was an easier process than that for pure H_3PW . Second, we also observed an inverse

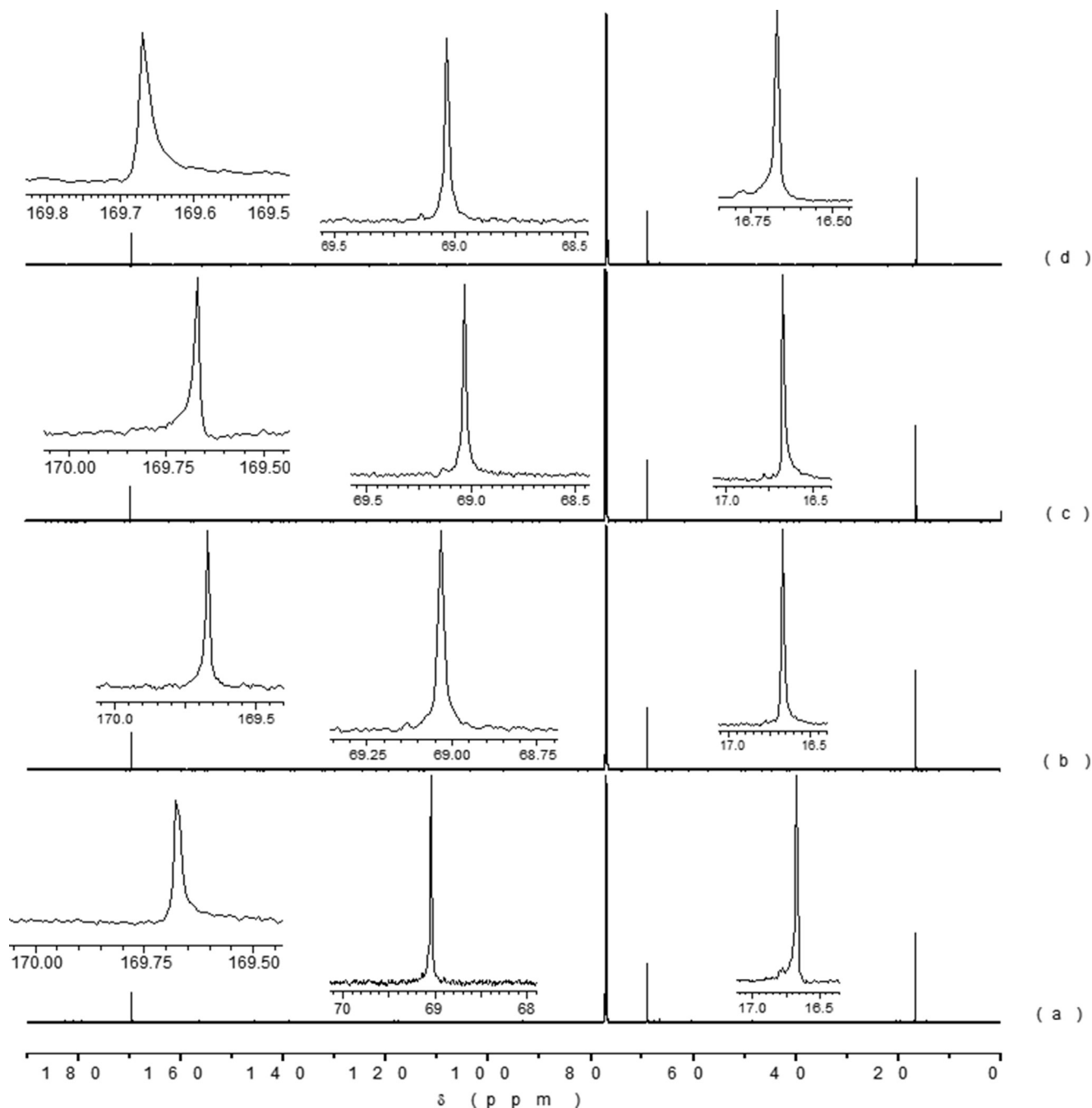


Fig. 9. ^{13}C NMR spectra of PLA catalytically obtained with the following: (a) pure alumina and 20% H_3PW /alumina calcined at (b) 200 $^\circ\text{C}$, (c) 300 $^\circ\text{C}$, and (d) 400 $^\circ\text{C}$.

relationship between the acidity of the supported H_3PW and the relative molar mass of the PLA (Table 6, entries 8 to 10). However, the M_w values were higher than those of the pure supports, and a demonstration that polymerization rather than oligomerization really occurred was achieved. Thus, without H_3PW , only relatively lower average molar mass oligomers were formed ($M_w < 10,000$ daltons).

In addition to acidity, the accessibilities of the sites can be inferred for the supported catalysts. The PLA produced from the supported catalysts with the highest numbers of sites (n_1) exhibited higher relative average molar mass (Table 6, entries 8 to 10). The small difference in M_w between 20% $\text{H}_3\text{PW}/\text{C}$ and 20% $\text{H}_3\text{PW}/\text{alumina}$ might be related to the much higher specific surface (BET) of the former. As is known, the heterogeneous catalysis dispersion of acid sites on the surface of a catalyst is an important property for enhancing reaction yield. For pure supports (C, SiO_2 , and Al_2O_3), this trend of higher M_w may also be directly related to

the higher specific surface ($\text{BET}_\text{C} > \text{BET}_{\text{SiO}_2} > \text{BET}_{\text{Al}_2\text{O}_3}$), due to the higher dispersion of acid sites on larger surfaces.

Another property of PLA with respect to the catalysts pertains to enantioselectivity (ee). A tendency toward the production of selective enantiomers from PLA (PLLA) was observed in the pre-polymer step. In this case, only oligomeric forms of lactic acid were detected as demonstrated by GPC. For pure supports, the general trend involved a decrease of enantioselectivity with increased acidity (Table 6, entries 4 to 6), whereas for supported H_3PW , the same trend was observed (Table 6, entries 8 to 10) except for $\text{H}_3\text{PW}/\text{alumina}$. This decrease might be related to competing side reactions during polycondensation as observed in the polydispersity index (M_w/M_n). A possible scheme of the reaction was presented in Fig. 13, and a more detailed description is provided as follows: the oligomers in the L-form grow blocks that connect to each other via catalyst sites and form longer chains with preferred

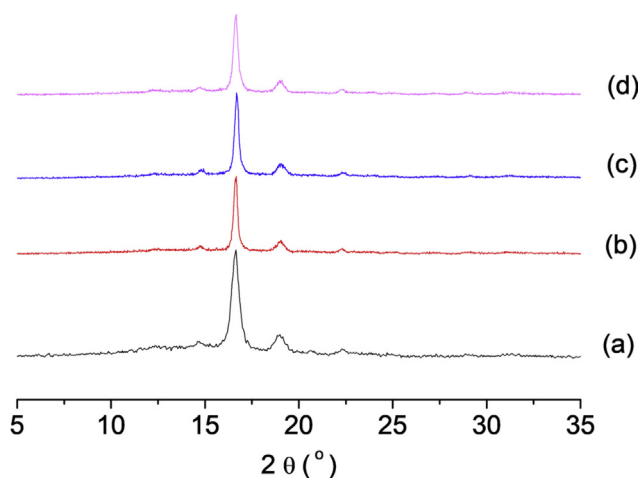


Fig. 10. XRD patterns of the catalytically synthesized PLA using (a) pure silica and 20% H₃PW/silica calcined at (b) 200 °C, (c) 300 °C, and (d) 400 °C.

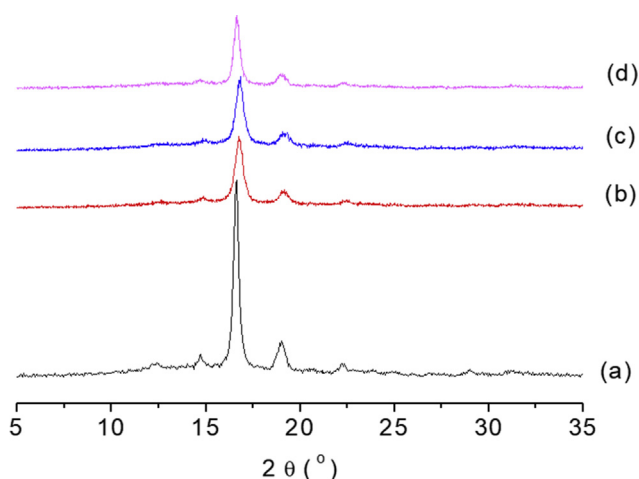


Fig. 11. XRD patterns of the catalytically synthesized PLA using (a) pure alumina and 20% H₃PW/alumina calcined at (b) 200 °C, (c) 300 °C, and (d) 400 °C.

Table 3

Specific optical rotations and enantiomeric excesses (ee) of the D,L-lactic acid starting reagent and different polymers obtained from each catalyst.

Sample	$\alpha_{\text{Polymer}}^{25}(\text{deg})$	ee (%)
D,L-lactic acid	-4	3
PLA (pre-polymer)	-109	70
PLA (no catalyst)	-140	82
PLA (carbon)	-146	93
PLA (silica)	-148	94
PLA (alumina)	-132	84
PLA (H ₃ PW)	-123	79
PLA (H ₃ PW/C-400 °C)	-133	85
PLA (H ₃ PW/Silica-200 °C)	-116	74
PLA (H ₃ PW/Silica-300 °C)	-115	73
PLA (H ₃ PW/Silica-400 °C)	-129	83
PLA (H ₃ PW/Alumina-200 °C)	-137	88
PLA (H ₃ PW/Alumina-300 °C)	-148	94
PLA (H ₃ PW/Alumina-400 °C)	-149	95

enantioselectivity. According to the proposed process [16], a cationic S_N2 mechanism that is compatible to the inversion of the configuration [1] could explain the enhancement of PLLA in the blend formation. The formation of blends was explained by the linking of block structures (D

Table 4

GPC characterizations of the polymers obtained from the different catalytic reactions. Supported H₃PW materials were calcined at 400 °C.

PLA/Catalyst	$M_n(\text{g}\cdot\text{mol}^{-1})$	$M_w(\text{g}\cdot\text{mol}^{-1})$	$D(M_w/M_n)$
PLA/pre-polymer	2278	2705	1.2
PLA/No catalyst	4864	7408	1.5
PLA/Carbon	4893	9672	1.6
PLA/Silica	5285	8350	1.6
PLA/Alumina	5267	7709	1.5
PLA/H ₃ PW	5914	9818	1.6
PLA/(20% H ₃ PW/C)	8469	15189	1.8
PLA/(20% H ₃ PW/Silica)	7982	14273	1.8
PLA/(20% H ₃ PW/Alumina)	8161	14827	1.8

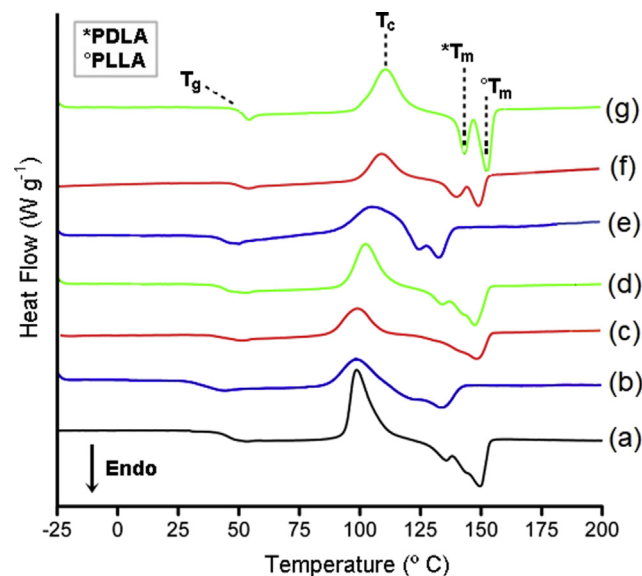


Fig. 12. DSC curves of PLA polymers obtained by polycondensation with the following: (a) H₃PW, (b) SiO₂, (c) Al₂O₃, (d) carbon, (e) 20% H₃PW/SiO₂, (f) 20% H₃PW/Al₂O₃, and (g) 20% H₃PW/C. All H₃PW/support catalysts were calcined at 400 °C.

Table 5

Thermodynamic parameters obtained by DSC analyses of the polymers from each catalytic process using pure supports, H₃PW, and supported H₃PW catalysts.

Polymer/ Catalyst				PDLA		PLLA	
	T _g (°C)	T _c (°C)	ΔH _c (J g ⁻¹)	T _m (°C)	ΔH _m (J g ⁻¹)	T _m (°C)	ΔH _m (J g ⁻¹)
Carbon	53	103	-29	134	0.9	148	14
SiO ₂	30	84	-15	120	1.2	138	12
Al ₂ O ₃	52	100	-25	-	-	149	22
H ₃ PW	47	100	-32	135	-	148	31
20% H ₃ PW/ Carbon	55	111	-33	144	8	153	14
20% H ₃ PW/ Silica	45	106	-8	125	-	138	5
20% H ₃ PW/ Alumina	58	110	-34	135	8	150	13

(-) Represents points where the thermodynamic parameters (T_m or ΔH_m) were attributed to a single PLA species because, in the employed method, that species accounted for the majority contribution, and the other species could not be accurately determined by the program.

and L oligomers) interacting with different protons (sites) on the Keggin structure on the supports. These two protonic sites have been demonstrated with the Cal-Ad method [24]. Hence, the enantiomeric blocks might be connected at these sites, which would lead to different PLA

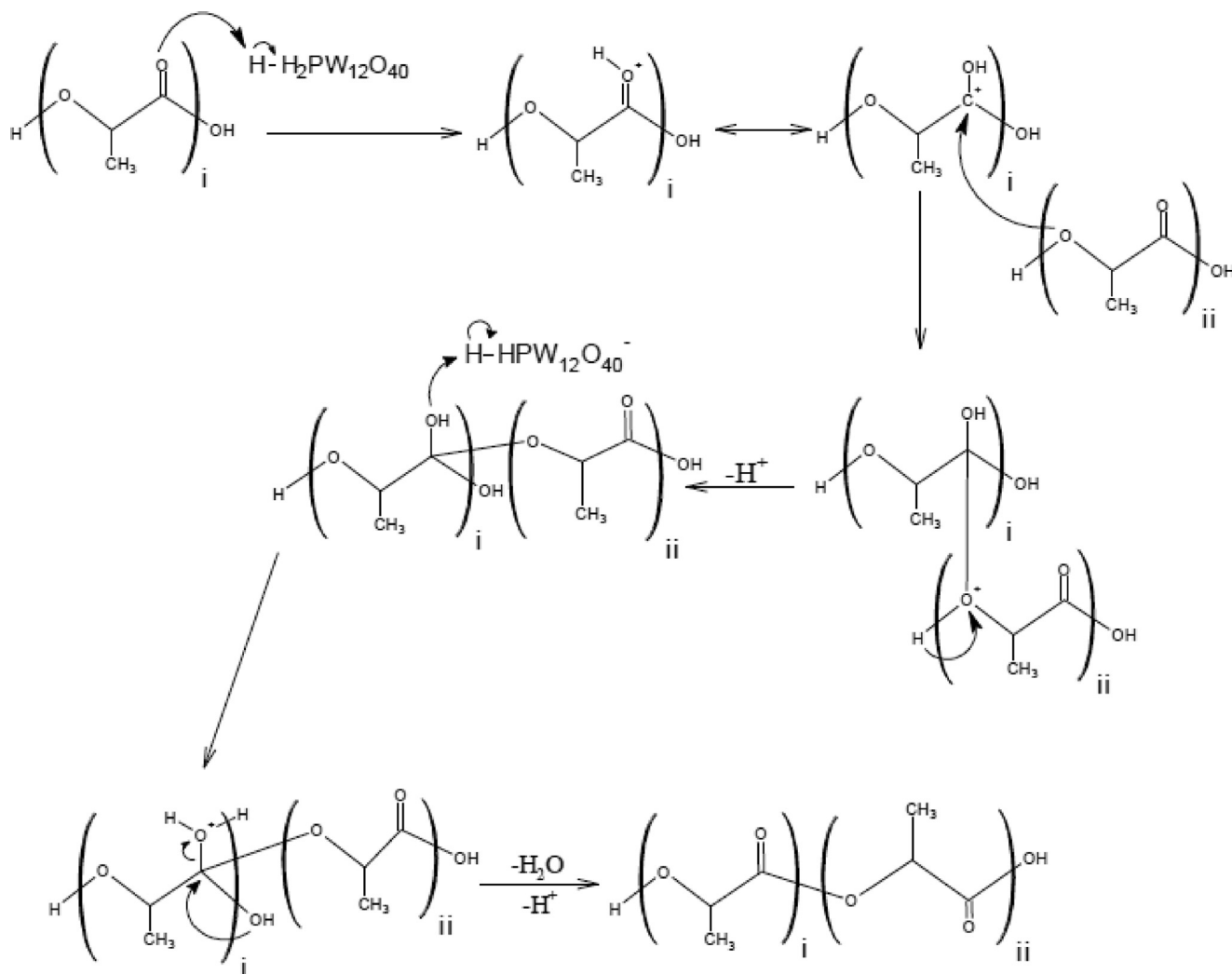


Fig. 13. Reaction scheme of the catalytic polycondensation process of PLLA using H_3PW /support (support = carbon, silica, or alumina).

Table 6

Properties of the catalysts and correlations with some properties of the produced PLA.

#	Sample/polymer	Property (Catalyst) ^a			Property (PLA) ^b		
		$-\Delta H_1$	n_1	n_T	ee	M_n	M_w
1	D,L-lactic acid	-	-	-	3	-	-
2	PLA (pre-polymer)	-	-	-	70	2278	2705
3	PLA (no catalyst)	-	-	-	88	4864	7408
4	Carbon	6	-	-	93	4893	9672
5	SiO_2	53	0.86	1.72	94	5285	8350
6	Al_2O_3	64	0.16	0.41	84	5267	7709
7	H_3PW	130	0.08	0.23	79	5914	9818
8	20% $\text{H}_3\text{PW}/\text{C}$	91	0.12	0.34	85	8469	15189
9	20% $\text{H}_3\text{PW}/\text{Al}_2\text{O}_3$	97	0.12	0.35	95	8161	14827
10	20% $\text{H}_3\text{PW}/\text{SiO}_2$	110	0.09	0.40	83	7982	14273

- data not available.

^a $-\Delta H_1$ ($\text{kJ}\cdot\text{mol}^{-1}$) and n_1 ($\text{mmol}\cdot\text{g}^{-1}$) are for the strongest sites; n_T ($n_1 + n_2$ $\text{mmol}\cdot\text{g}^{-1}$) is the total acid sites obtained by the Cal-Ad method based on a pyridine probe.

^b PLA properties (ee, enantiomeric excess and the average molar masses, M_n and M_w) obtained from the respective process with or without catalysts.

polymers that mix and form a blend at the end of the reaction. Kinetic studies [44] could elucidate the preponderance of PLLA molecules generated by the polymerization, and this idea will be tested soon.

4. Conclusions

Poly(lactic acid) (PLA) is a bio-based polymer of great importance among “green polymers” due to the growing number of applications that result from its biodegradability. The preparation of PLA by heterogeneous catalytic reactions is a prominent research area for the application of this material at industrial scales. The main challenge includes producing an economical material with a high level of enantioselective isomer and a low level of contamination. This work dealt with 12-tungstophosphoric acid (H_3PW) supported on carbon, silica, and alumina as candidates for heterogeneous catalysts for the polycondensation reaction of D,L-lactic acid, which is a much less expensive precursor than L-lactic acid. Optimal conditions were developed to prepare blends of PLA with up to 95% enantiomeric excess for poly(L-lactic acid; PLLA) under the following conditions: 20 wt.% H_3PW /support calcined at 400 °C, 0.1 wt.% of the catalyst relative to the D,L-lactic acid, a temperature of 180 °C, and a 15 h reaction time. Several blank tests were performed with pure H_3PW and the supports to establish the advantages of the supported catalysts. Pure H_3PW was too strong of a solid acid that it induced side reactions that formed only low molecular weight polymers ($M_w \sim 9000$ daltons). The supports themselves (i.e., carbon, silica, and alumina) formed only oligomers with M_w values lower than 10,000 daltons. Supported H_3PW formed PLA products with an average M_w in the range from 14,000 to 15,000 Da. Thus, the presence of H_3PW was fundamental for obtaining higher polymeric units. An inverse relationship between the

M_w of PLA and the enthalpy ($-\Delta H$) of the strongest sites of the catalysts was obtained, i.e., $PLA_{Mw-H3PW/C} > PLA_{Mw-H3PW/Al_2O_3} > PLA_{Mw-H3PW/SiO_2}$, whereas the acidity ($-\Delta H$) order was $H_3PW/SiO_2 > H_3PW/Al_2O_3 > H_3PW/C$. Therefore, an adequate strength of the solid acid with a H_3PW Keggin structure together with the accessibility of these sites was necessary to achieve a successful polycondensation process.

Declarations

Author contribution statement

Liana S. Chafran: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Mateus F. Paiva, Juliene O. C. França: Performed the experiments; Analyzed and interpreted the data.

Maria José A. Sales: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Sílvia C. L. Dias, José A. Dias: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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