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Influence of Catalyst Type on the Structural and Thermal Properties of Poly (ethylene 3,4-pyridinedicarboxylate)

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Research Article

Keywords: 3,4-pyridinedicarboxylic acid, magnesium oxide, sulfuric acid, ethylene glycol, the acid number value, cross-linking agent, higher molecular weights

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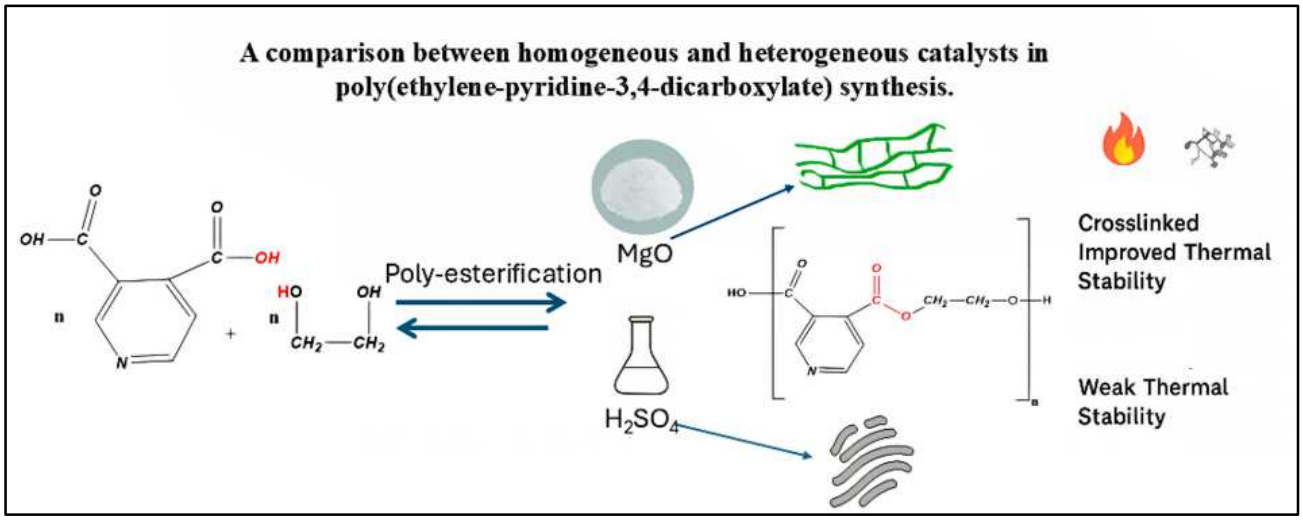
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Abstract

In the context of the global trend toward developing sustainable and high-performance polymeric materials, heterocyclic aromatic-based polyesters have emerged as a promising class due to their superior physical and mechanical properties compared to aliphatic counterparts. In this study, the novel use of 3,4-pyridinedicarboxylic acid as a monomer in polyester synthesis was investigated. The polymerization was carried out through a condensation reaction with ethylene glycol in dimethyl sulfoxide at 120 °C using both homogeneous (sulfuric acid) and heterogeneous (magnesium oxide) catalysts. The progress of the reaction was followed by monitoring the acid number over time. The results demonstrated that magnesium oxide enhanced the conversion and promoted the formation of polyesters with higher molecular weight compared to those obtained using sulfuric acid. Infrared spectroscopy confirmed the successful formation of ester bonds, while differential scanning calorimetry (DSC) revealed improved thermal stability for the polymer synthesized in the presence of MgO. In addition, the polymer prepared using magnesium oxide exhibited increased intermolecular interactions and possible chain crosslinking, which contributed to enhanced structural and thermal properties. Overall, this study highlights the potential of 3,4-pyridinedicarboxylic acid-based polyesters and demonstrates the effectiveness of magnesium oxide as a heterogeneous catalyst for improving polyester properties, suggesting promising applications in advanced polymeric materials.

Keywords:3,4-pyridinedicarboxylic acid, magnesium oxide, sulfuric acid, ethylene glycol, the acid number value, cross-linking agent, higher molecular weights.



1. Introduction:

With the growing environmental concerns, it has become essential to find sustainable, eco-friendly polymers with desirable properties for various applications. Among the most prominent are biodegradable polymers such as polyesters [1], which have become some of the most widely used thermoplastic polymer systems in reinforced plastic and fiber industries due to their good mechanical properties [2], low cost [3], and good corrosion resistance [4], They also offer high toughness and low deformation [5].In recent years, there has been increasing interest in studying the kinetics of polyester polymerization and their various reactions[6]. Kirshanov and colleagues indicated that modeling the kinetics of trans-esterification reactions between polyethylene terephthalate and hydroxy-terminated polyesters is an important tool for understanding the mechanisms of polymer growth and predicting the resulting properties [7]. Similarly, a study published in the Royal Society of Chemistry showed that metal catalysts with Lewis's acidity significantly affect the efficiency of esterification reactions, with the hydrolysis mechanism playing a specific role in controlling both the yield and rate of the reaction [8]. Another recent study focusing on ZnO/polyester composites analyzed thermal kinetics and degradation using thermogravimetric analysis (TGA), demonstrating that the introduction of nanoparticles contributes to improved thermal stability and alters degradation pathways [9].The significant influence of catalyst type on polymerization kinetics and polymer properties has been widely reported, particularly for metal-based catalytic systems, which can enhance reaction rates and improve thermal and structural properties of polyesters[10]. Additionally, another study on unsaturated polyester reinforced with ceramic powder found that inorganic fillers modify the thermal degradation mechanism and impact the calculated activation energies, opening new avenues for the design of composite materials with enhanced properties [11].

Conventional polyesters based on aromatic dicarboxylic acids such as phthalic or terephthalic acid have been extensively studied and are known for their good mechanical properties and industrial applicability. However, these systems primarily rely on π–π interactions between aromatic rings and are typically synthesized using metal catalyst polymerization under high-temperature [12], or homogeneous catalytic systems as dibutyltin dilaurate [13]. While Dicarboxylic 3,4-pyridinedicarboxylic acid is a relatively uncommon aromatic acid used in polyester polymerization, despite its structural importance that enables the incorporation of heteroaromatic cyclic units into the polymer chain [14]. This confers the polymer with distinctive thermal and electrical properties. Recent studies suggest that introducing heteroaromatic rings such as pyridine into the polymer backbone opens new horizons for obtaining materials with higher thermal stability and enhanced electronic conductivity. However, research that specifically uses 3,4-pyridinedicarboxylic acid in polyester polymerization remains scarce and limited compared to traditional dicarboxylic acids like terephthalic or phthalic acids [15].

In this context, the importance of heterogeneous catalysts such as magnesium oxide (MgO) in condensation polymerization processes becomes evident. These catalysts not only accelerate the reaction by activating hydroxyl groups and facilitating ester bond formation but also feature

advantages such as easy separation from the reaction medium, reusability, and reduced pollution from residual homogeneous acidic catalysts like sulfuric acid [16]. Several studies have demonstrated that the use of metal oxides (MgO, ZnO, TiO_2) contributes to increasing the molecular weight of polyester and improving its thermal and mechanical properties [17]. Therefore, the scientific value of selecting a rarely used acid like 3,4-pyridinedicarboxylic acid, combined with an unconventional catalyst such as magnesium oxide, highlights a novel approach that contributes to the development of advanced polymeric materials.

Heterocyclic ring polymers are considered promising materials due to their combination of structural stability and potential applications in advanced industrial fields [18]. However, their final properties such as molecular weight, degree of crosslinking, electrical conductivity, and thermal stability are directly influenced by the polymerization method and the type of catalyst employed [19]. This issue highlights the necessity of systematic investigations to explore the relationship between polymerization conditions and the resulting properties, as well as to provide accurate comparisons that can guide practical applications of these polymers.

Consequently, this research aims to synthesize a polymer from 3,4-pyridinedicarboxylic acid using two different catalysts and to study the effects of these catalysts on its structure and physical and thermal properties.

2.Expermintal:

2.1. Chemicals used:

3,4-Pyridinedicarboxylic acid (99%) and Magnesium oxide (MgO) were purchased from Merck, Ethylene glycol (Carlo Erba / 99%), Sulfuric acid Prepared from Alpha stock / 98%.

2.2. Devices used:

The product was characterized using an FT-IR-4100 infrared spectrometer from Shimadzu, Japan, and a 400 MHz proton NMR spectrometer from Bruker, Switzerland. Additionally, several physical properties of poly(ethylene pyridine-3,4-dicarboxylate) were assessed), including electrical conductivity measured with a Cond 7110 conductivity meter, pH determined using a Sartorius pH meter, particle size analysis performed with an InoLab optical microscope, and thermal properties evaluated through Differential Scanning Calorimetry (DSC) using an analyzer located at the Environmental Engineering Laboratory, Faculty of Civil Engineering, Homs University.

2.3. Synthesis of Poly (ethylene 3,4-pyridinedicarboxylate):

A three-neck round-bottom flask equipped with a reflux condenser, nitrogen gas inlet, and temperature controller were used. 0.1 mol (0.5 gr) of dicarboxylic acid was added to the flask. The solvent was gradually introduced while heating the mixture up to 120 °C until the acid was completely dissolved. Subsequently, (0.05 gr) of a catalyst amounting to 10% by weight of the

acid was added. Then, 0.1 mol (5.5 ml) of ethylene glycol was gradually added. Water formed during the reaction was continuously removed by bubbling nitrogen gas and collected in a designated trap to drive the reaction toward polyester formation.

After the reaction was completed, the solvent evaporated, yielding a yellow powdered polymer. The product was purified by washing with diethyl ether to remove excess ethylene glycol.

2.4. Determine the value of the acid number:

The progress of the reaction was monitored by measuring the acid value, which decreases over time when using different catalysts. The acid value was determined based on the titration of the remaining unreacted acid with a potassium hydroxide solution containing phenolphthalein as an indicator. Samples were taken from the reaction vessel at various time intervals and titrated with potassium hydroxide. then calculated according to the following relationship (1). [20]

$$\mathrm{A_v} = \frac{(V)(0.056)(1000)}{W} \qquad (1)$$

Where: (A_V) is the acid value, defined as the amount of potassium hydroxide required to neutralize the carboxylic groups per gram of the sample. (W) is the weight of the sample taken from the reaction vessel (g), and (V) is the volume of KOH solution used (mL).

The conversion values were calculated from the acid value (A_V) measured at successive time intervals until a constant A_V was observed, according to the following equation:

$$p = \frac{\boldsymbol{A_{v_0} - A_v}}{\boldsymbol{A_{v_0}}} \qquad (2)$$

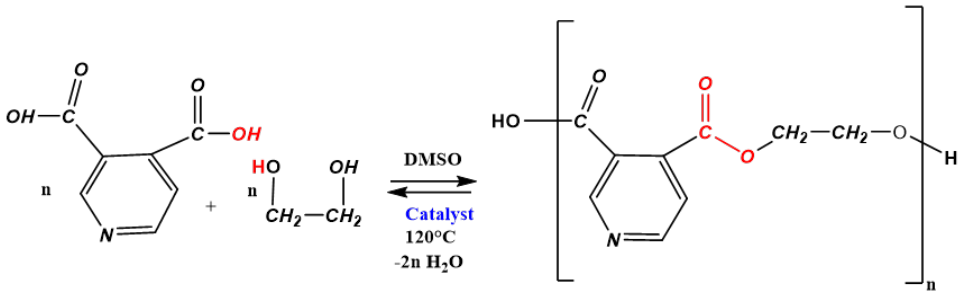
3. Results and Discussion:

The esterification reaction is a reversible process. According to Le Chatelier's principle, reaction conditions can be adjusted to favor the formation of the product—such as by using an excess of reactants, removing the produced water, or changing the catalyst type.

$$RCOOH + R_1OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RCOOR_1 + H_2O$$

Scheme 1: Reversible esterification -reaction between carboxylic acid and alcohol

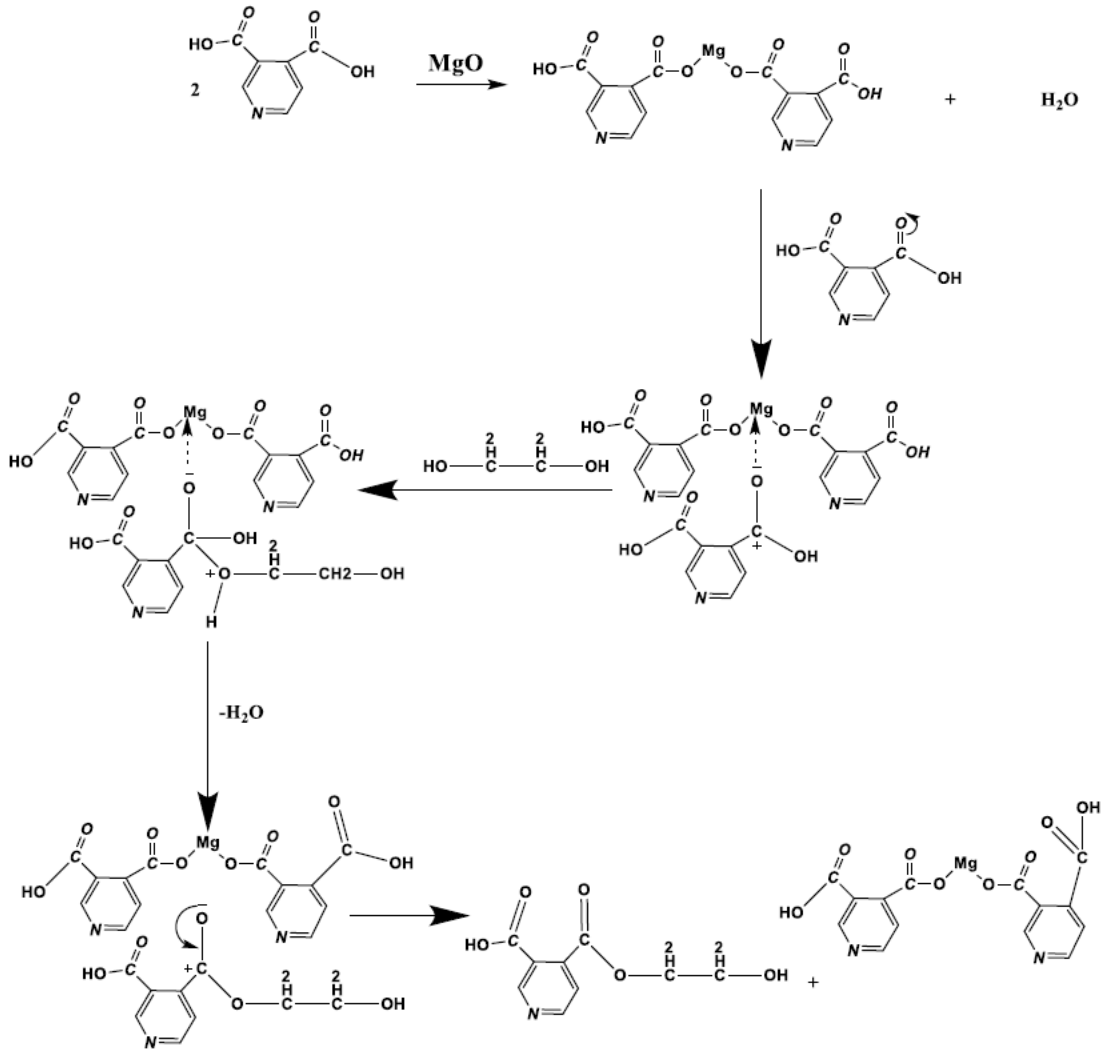
In this study, a 3,4-Pyridinedicarboxylic acid was esterified with an equimolar amount of ethylene glycol to synthesize a polyester. A water trap was employed to continuously remove water from the reaction mixture. Different catalysts were tested, and the progress of the reaction was monitored by titration to determine the acid number at various time points.



Scheme 2: Synthesis of poly (ethylene 3,4-pyridinedicarboxylate) via esterification of 3,4-pyridinedicarboxylic acid with ethylene glycol in DMSO in the presence of a catalyst at 120 °C.

The results showed that the acid number decreased over time for both catalysts at the same concentration, as illustrated in Figure 1. A more pronounced decrease in acid number was observed in the presence of magnesium oxide compared to sulfuric acid over the same reaction time, indicating a higher extent of conversion. It was observed that, in the presence of sulfuric acid, the acid number reached a plateau after approximately five hours, suggesting that the reaction had approached equilibrium and no further significant progress occurred. In contrast, the system catalyzed by MgO did not reach equilibrium within the same time frame and continued to show a decrease in acid number up to seven hours. This behavior indicates that the reaction proceeds for a longer duration in the presence of MgO, allowing for greater consumption of carboxylic groups and consequently higher conversion. The difference in behavior can be attributed to the distinct catalytic mechanisms of the two systems, where the heterogeneous catalyst (MgO) promotes a more sustained esterification process compared to the homogeneous acid catalyst.

Scheme 3. Suggested mechanism for MgO-catalyzed esterification of 3,4-pyridinedicarboxylic acid with ethylene glycol. The mechanism involves the formation of Mg–carboxylate complexes, which enhance the reactivity of carboxylic groups and promote esterification, thereby facilitating polymer chain growth during condensation polymerization. This mechanism is proposed based on experimental observations and supported by literature [21].



Scheme 3: Proposed mechanism for MgO-catalyzed esterification of 3,4-pyridinedicarboxylic acid with ethylene glycol. The mechanism suggests the formation of Mg–carboxylate intermediates that facilitate the activation of carboxylic groups and promote ester bond formation, leading to chain growth during condensation polymerization.

The conversion degree for both catalysts was calculated at the same temperature as shown in figure2. Upon comparison of the results, a conversion rate of up to 76.28% was obtained in the presence of magnesium oxide, while a conversion rate of 61.53% was achieved with sulfuric acid. This difference is attributed to the nature of the catalyst, as magnesium oxide increases the surface area and thus enhances the active sites. Additionally, magnesium oxide reacts with the water produced during the esterification process, forming magnesium hydroxide, so shifts the reaction forward according to Le Châtelier's principle, resulting in a higher conversion percentage. The higher conversion obtained in the presence of MgO may also promote the formation of longer polymer chains compared to the polymer prepared using sulfuric acid.

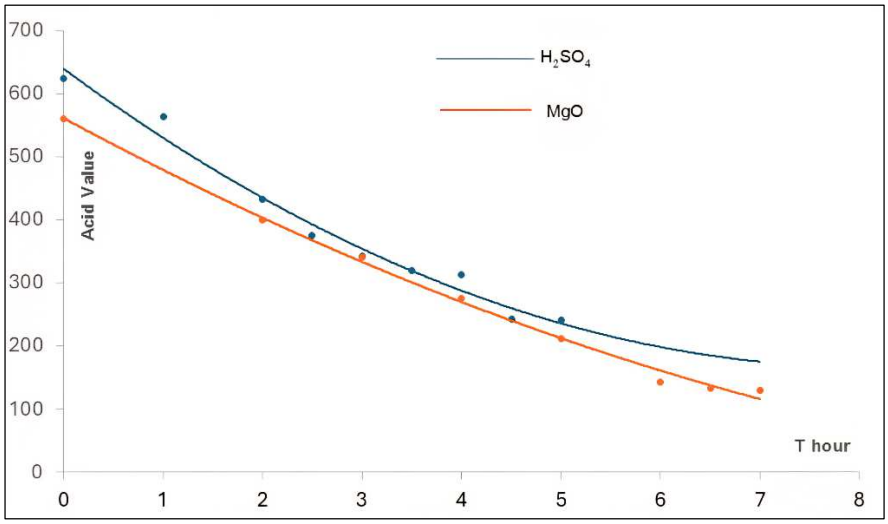


Figure 1: Effect of catalyst type (H_2SO_4 and MgO) on the evolution of acid value with time during the synthesis of poly(ethylene 3,4-pyridinedicarboxylate).

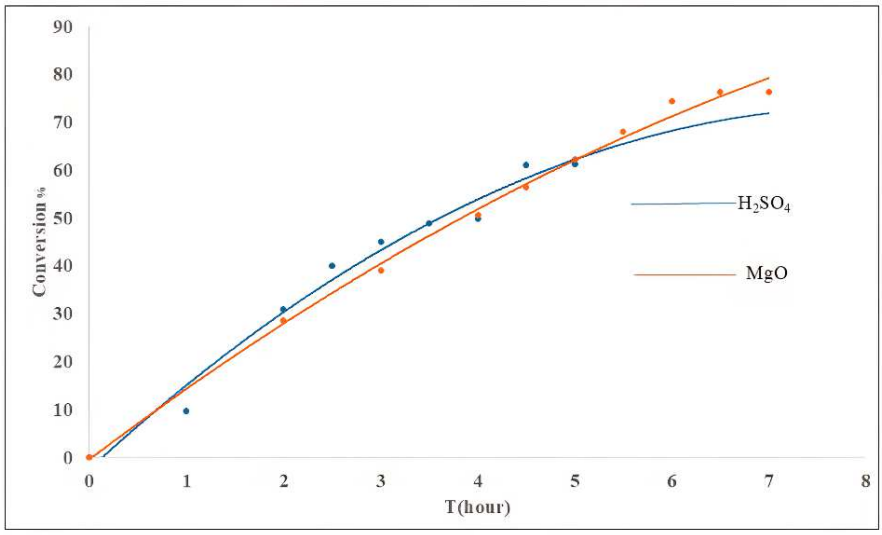


Figure 2: Effect of catalyst type (H_2SO_4 and MgO) on the conversion percentage via time during the condensation polymerization of poly(ethylene 3,4-pyridinedicarboxylate).

Characterizations of Poly (ethylene 3,4-pyridinedicarboxylate):

The synthesized polymer was characterized using Fourier-transform infrared spectroscopy (FTIR) to identify the functional groups formed during the polymerization process. The spectrum exhibited a broad absorption band in the range of 3200–3600 cm^{-1}, attributed to the stretching vibrations of the O–H group. This band was shifted toward lower wavenumbers compared to that of the original monomer, which can be ascribed to the increase in hydrogen bonding interactions among terminal hydroxyl groups because of polymer chain crosslinking. The broadness and red shift of this band indicate the formation of an extended hydrogen-bonding network between neighboring chains.

Furthermore, the carbonyl (C=O) stretching band was also shifted to lower wavenumbers relative to that of the initial acid, confirming the formation of the ester linkage. A characteristic absorption at 1259 cm^{-1} corresponding to the C–O–C stretching vibration further supports the successful formation of the polyester, as illustrated in Figure 3.

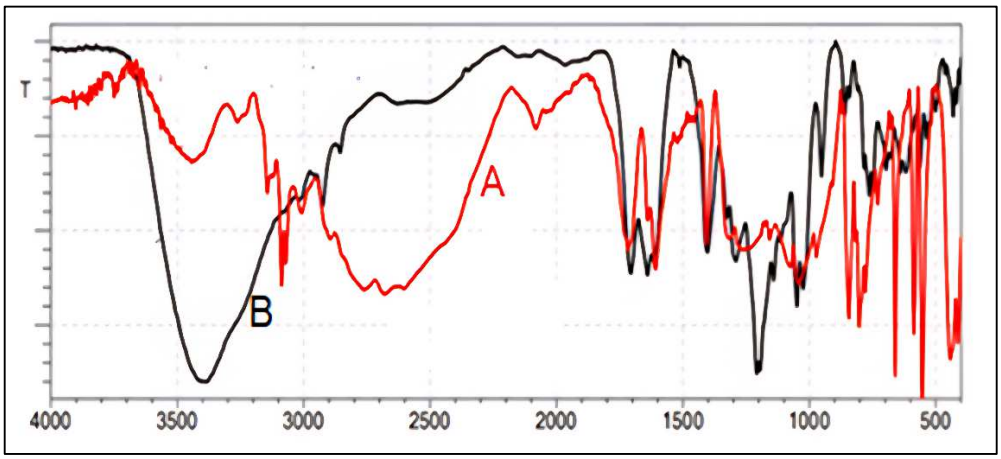


Figure 3: (A) IR spectrum of 3,4−pyridinedicarboxylic acid , (B) IR spectrum of Poly (ethylene 3,4−pyridinedicarboxylate)

A comparative analysis of the FTIR spectra of the polyesters synthesized using sulfuric acid as a homogeneous catalyst and magnesium oxide as a heterogeneous catalyst revealed that both spectra exhibited a characteristic absorption band in the range of 1200–1259 cm^{-1}, corresponding to the C–O–C stretching vibration, confirming the successful formation of the ester linkage in both systems. However, the position of the carbonyl (C=O) stretching band differed noticeably between the two samples. In the case of sulfuric acid catalysis, the band was shifted toward higher wavenumbers, indicating weaker ester linkages or a less polar environment around the carbonyl group. In contrast, the C=O band shifted toward lower wavenumbers in the presence of magnesium oxide, which can be attributed to the formation of stronger hydrogen bonding interactions between the carbonyl and neighboring hydroxyl groups. This observation highlights the crosslinking role of magnesium oxide, which promotes interchain association and enhances structural cohesion within the polymer matrix. Also, the results obtained from the analysis of the absorption spectrum for the OH group indicate that the intensity of the broad band decreased when sulfuric acid was used as a catalyst, with a corresponding shift towards higher wavenumbers. In contrast, the band observed in the polyester spectrum, when magnesium oxide was employed, appeared broader and shifted towards lower wavenumbers. This observation suggests an increase in bonding between the polymeric chains when magnesium oxide is utilized. As shown in Figure 4.

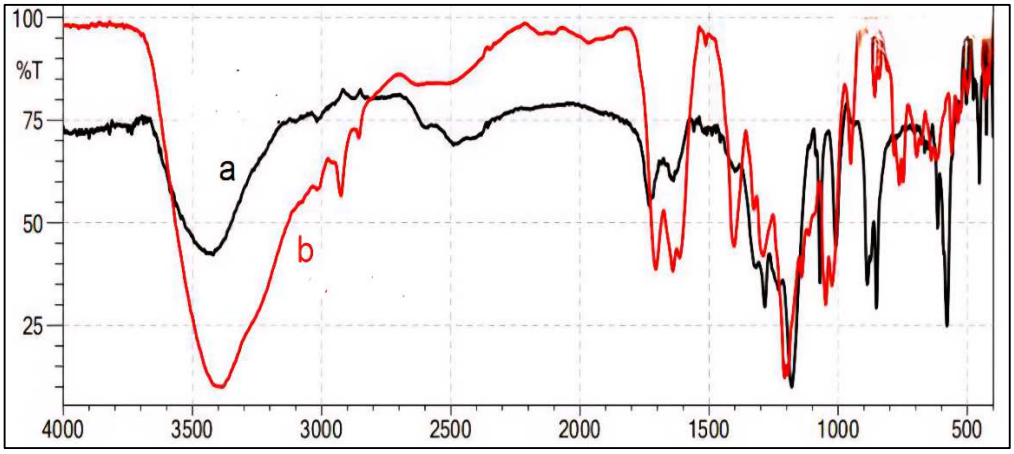


Figure 4: (a) IR spectrum of Poly (ethylene 3,4–pyridinedicarboxylate) Prepared Using Sulfuric Acid Catalyst, (b) IR spectrum of Poly (ethylene 3,4–pyridinedicarboxylate) Prepared Using MgO Catalyst

The chemical structure of the synthesized polymer was confirmed using ¹H NMR spectroscopy (Figure 5). The spectrum exhibits characteristic signals corresponding to the ethylene glycol units at δ = 2.30–2.55 ppm, attributed to the methylene protons (–CH_2–CH_2–). Additionally, the aromatic protons of the pyridine ring appear in the region δ = 8.6–9.4 ppm, confirming the incorporation of the heteroaromatic moiety into the polymer backbone.

The broad nature and multiplicity of the peaks are consistent with the polymeric structure, reflecting different chemical environments along the polymer chains. All the chemical shifts are shown in table 1.

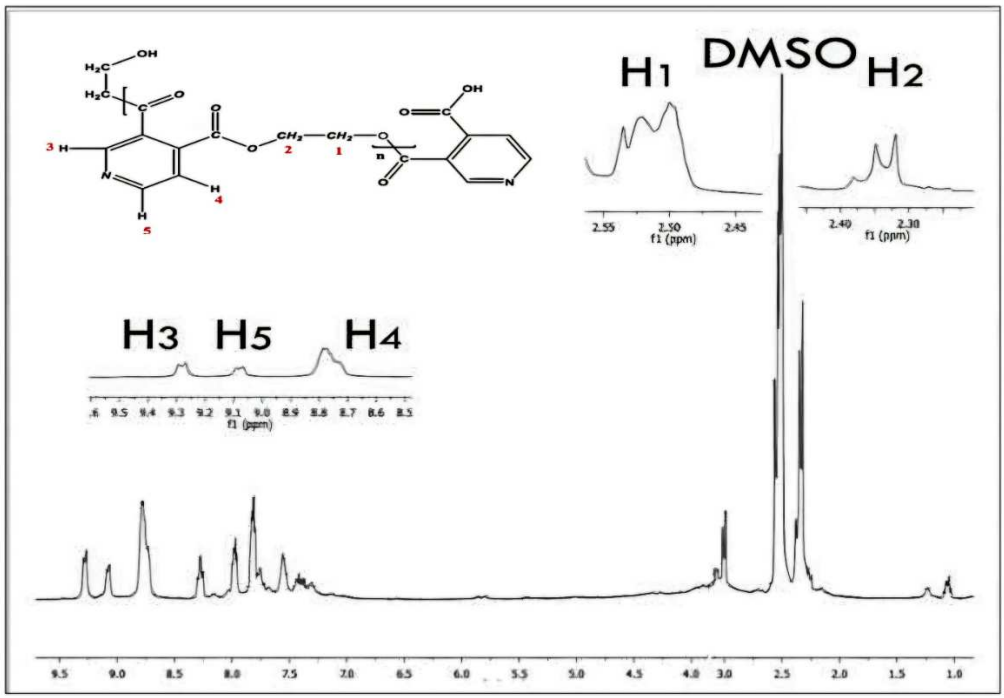


Figure 5: H NMR spectrum of of Poly (ethylene 3,4–pyridinedicarboxylate) in DMSO–d6

Table 1: Assignment of ^{1}H NMR signals for poly(ethylene 3,4−pyridinedicarboxylate).

Proton assignment	δ (ppm)	Description
H1	2.45- 2.55	-CH_2- (ethylene glycol)
H2	2.3-2.4	-CH_2- (ethylene glycol)
H3	9- 9.2	pyridine ring
H4	9.2-9.4	pyridine ring
H5	8.6-8.8	pyridine ring

Physical and Thermal Properties of Poly (ethylene 3,4-pyridinedicarboxylate):

Based on several measurements, the previous result was verified. The dimensions of the molecules were measured using an electron microscope, and it was found that the polymer molecules with magnesium oxide have larger dimensions compared to those with sulfuric acid, as shown in Figures 6 and 7. When measuring the pH and conductivity of the polymer solution dissolved in a mixture of ethanol and water, it was observed that the acidity was lower in the polymer formed in the presence of magnesium oxide compared to that formed in the presence of sulfuric acid. This is attributed to the decreased number of terminal carboxyl groups. The same trend was observed for conductivity, as demonstrated in Table 2.

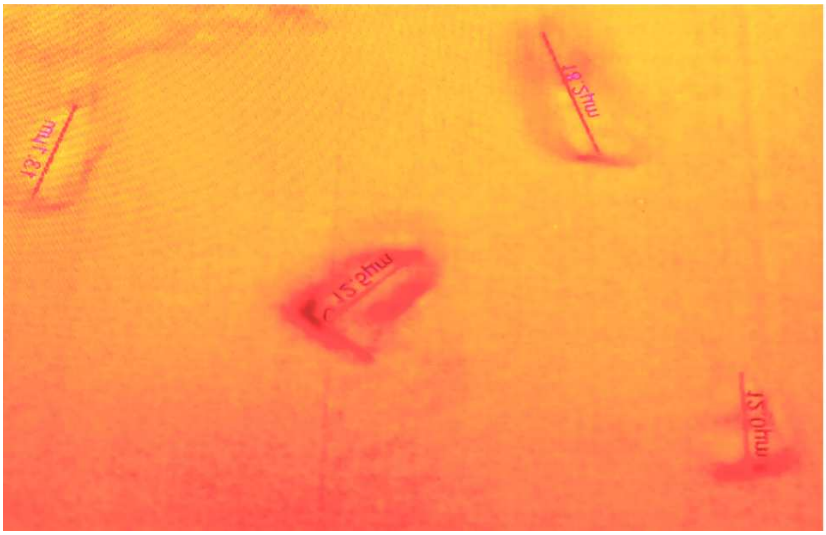


Figure 6: Molecular Dimensions of Poly(ethylene−3,4−pyridinedicarboxylate) Prepared Using Manganese Oxide Catalyst



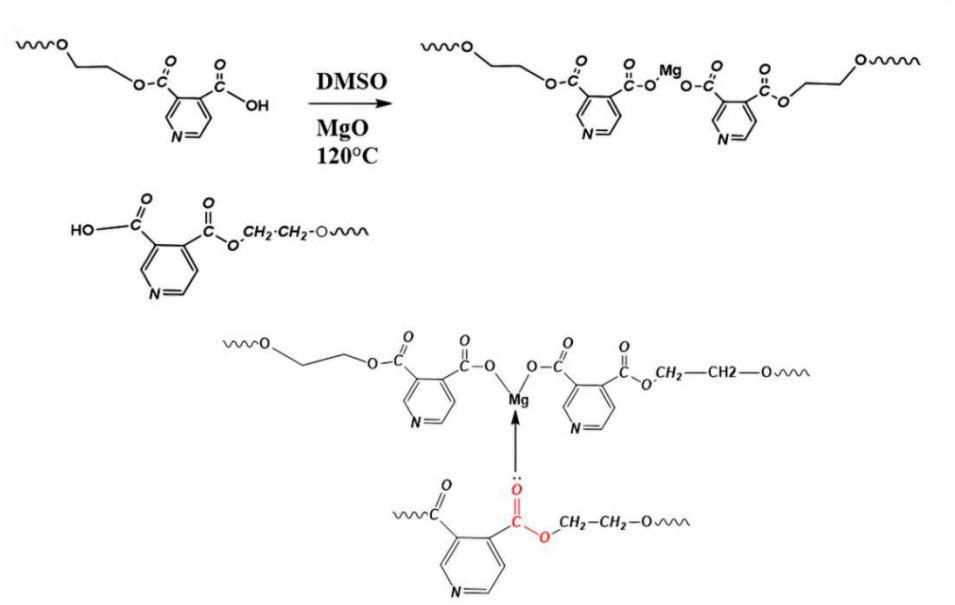
Figure 7: Molecular Dimensions of Poly(ethylene−3,4−pyridinedicarboxylate) Prepared Using Sulfuric Acid Catalyst

Table 2: Physical Properties of Poly(ethylene−3,4−pyridinedicarboxylate)

Polymer prepared using catalyst	pH	Conductivity (µS/cm)	Particle Size (µm)
Magnesium oxide	3.7	237	13.1-15-18.2
Sulfuric acid	1.8	1220	3.7-5.1-7.4

The differential scanning calorimetry (DSC) curves of poly (ethylene 3,4-pyridinedicarboxylate) were recorded in the temperature range of 20–250 °C under a nitrogen atmosphere. The DSC results suggest that magnesium oxide plays an important role in modifying the structural organization of the polymer chains. As illustrated in Scheme 4, MgO may interact with the carboxylate groups of neighboring polyester chains through coordination bonding involving magnesium ions. These interactions promote the formation of intermolecular bridges between polymer chains, causing the chains to become more interconnected and structurally ordered. Consequently, the mobility of the polymer chains decreases, leading to increased rigidity and enhanced intermolecular cohesion. This structural arrangement explains the transition from the predominantly amorphous nature observed in the polymer prepared using sulfuric acid to the more semi-crystalline character obtained in the presence of magnesium oxide. Furthermore, the restriction of chain mobility due to these intermolecular interactions contributes to the significant increase in the thermal transition temperature from 57 °C to 115 °C, along with the appearance of a melting peak at approximately 140 °C as shown in figure 8,9 . These findings indicate that MgO

acts as a linking agent between polymer chains, enhancing the thermal stability and structural integrity of the resulting polyester.



Scheme 4: Mechanism of polymer chain lengthening in the presence of magnesium oxide

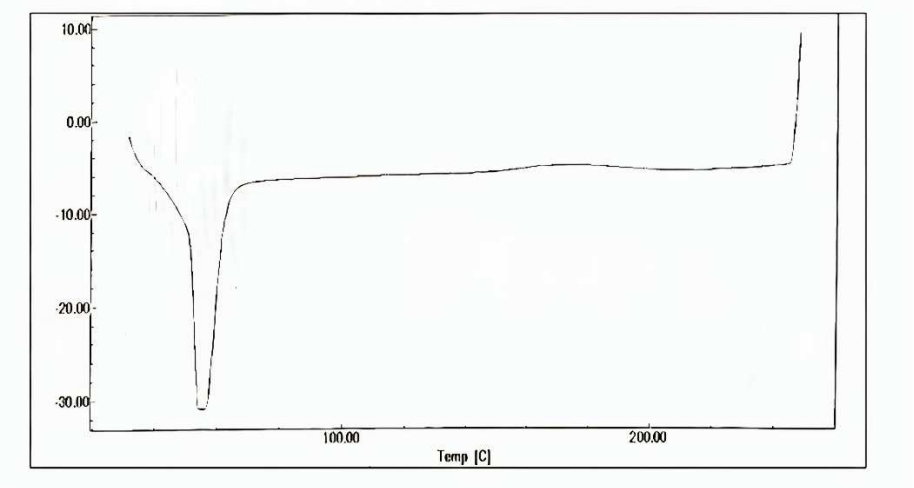


Figure8: The differential scanning calorimetry (DSC) curve of poly(ethylene 3,4−pyridine carboxylate) in presnt H_2SO_4 as catalyst.

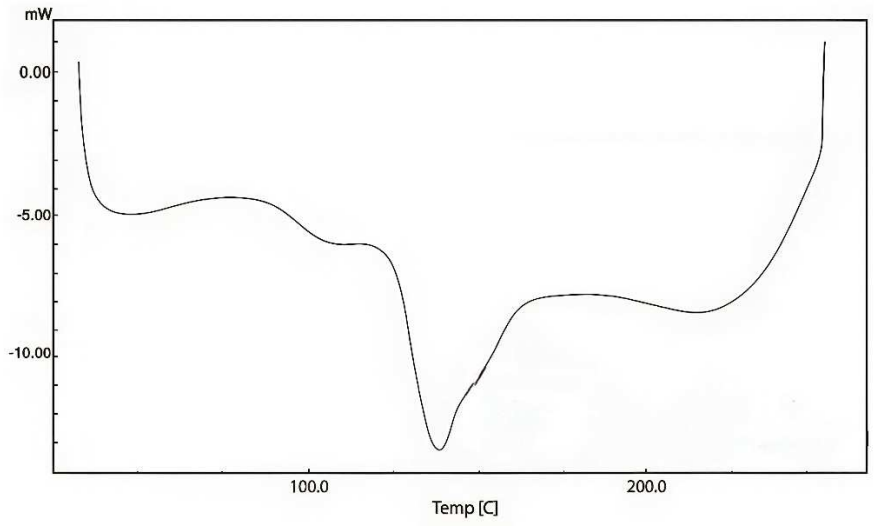


Figure 9: differential scanning calorimetry (DSC) curve of poly(ethylene 3,4–pyridine carboxylate) in presnt MgO as catalyst.

Conclusions:

The present study demonstrated the successful synthesis of poly(ethylene 3,4-pyridinedicarboxylate) using both homogeneous (sulfuric acid) and heterogeneous (magnesium oxide) catalysts. The obtained results showed that the catalyst type plays a significant role in determining the structural and thermal properties of the resulting polyester. The polymer prepared in the presence of magnesium oxide exhibited higher conversion, greater structural organization, and improved thermal stability compared to the polymer synthesized using sulfuric acid. DSC analysis revealed a transition from predominantly amorphous behavior in the sulfuric acid-catalyzed polymer to a more semi-crystalline structure in the MgO-catalyzed polymer, accompanied by a noticeable increase in thermal transition temperature and the appearance of a melting peak. These observations suggest that magnesium oxide promotes stronger intermolecular interactions and possible linking between polymer chains, leading to enhanced rigidity and thermal resistance. The findings highlight the potential of magnesium oxide as an effective heterogeneous catalyst for the preparation of heteroaromatic polyesters with improved structural and thermal properties.

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Declarations

Consent to Publish: Not applicable.

Consent to Participate: Not applicable.

Ethics Approval: Not applicable.

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