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Synthesis and Characterization of Poly (Ester-Imide) S Based on Imide Dicarboxylic Acid with Dihydroxy Heterocyclic Compounds

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ABSTRACT

By using dibutyltine dilaurate as a catalyst in the polycondensation of imide dicarboxylic acid and aromatic diols, two thermally stable and organosoluble poly(ester-imide) s were created. One mole of orthochlorobenzaldehyde and 2,4-dichlorobenzaldehyde was condensed, respectively, with p-hydroxy acetophenone to yield two phenolic compounds. Two Imide compounds were prepared from the reaction of Pyromellitic anhydride, and 3,3,4-benzophenone tetracarboxylic dianhydride with anthranilic acid respectively. The structural properties of the poly (esters-imide)'s were verified by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy analysis of the synthesized polymers.

Keywords: Poly (Esters-Imide) S, Dibutyltine Dilaurate, Diimide-Dicarboxylic, Aromatic Diols, Heterocyclic Moiety.

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INTRODUCTION

A class of high-temperature polymers known as polyimides has grown in importance in a wide range of engineering applications because of its remarkable mechanical, electrical, and thermo-oxidative characteristics at elevated temperatures. However, polyimides' intractability, insolubility, and high melting temperatures—which lead to a host of processing problems—often restricted their applications [1-3]. Numerous fusion polymers, in particular polyamides, polyesters, polyurethanes, and polyureas, can be prepared using interfacial polymerization [3-4].

Polymers made from condensation can be created at low temperatures and few side reactions thanks to interfacial polymerization. This method has gained extensive adoption in a variety of applications, from conducting polymer films to the microencapsulation of medicinal items [5] to the direct generation of completed products such as films, fibers, membranes, etc. [6]. Thermally stable polymers have attracted a lot of attention in the last ten years as the automotive, aerospace, and microelectronic industries increasingly need high-performance polymers to replace metals or ceramics.

Polyimides and their copolymers, one of the most advantageous classes of high-performance polymers, are used in numerous industrial applications. [7-8]. Due to their great thermal stability and advantageous mechanical and electrical properties, polyimides have received a lot of attention [9]. But the infusibility and low flow qualities have limited their utilization due to the difficulty in processing. In order to tackle these issues, poly(ester-imide) s was created [10]. The incorporation of elastic ester linkages may result in a reduction in processing temperature and an enhancement in flow characteristics at the price of thermal stability. Furthermore, a significant number of poly(ester-imide) s have

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been observed to exhibit fluid phases that are crystalline. [11-13]. For them, poly(ester-imide) (PEIs) is of interest to scientists because they combine polyester biodegradability with the good mechanical qualities of polyimides [14]. In addition to serving as disposable bags, farming films, drug carriers, and matrix resins for biological products, PEIs have a wide range of other uses as well. [15-16].

Poly (ester imides) have only ever been studied from the limited viewpoints of sheet fundamentals, such as mechanical properties, solubility, and thermal stability, since its inception. [17]. Several of the previously described poly (ester imide) s were made by directly polymerizing polyester from imide-containing di carboxylic acid with diols rather than through the heat imidization process, which is crucial for spontaneous in-flight orientation. [18][21].

MATERIALS AND INSTRUMENTS

Materials

Ortho chloro benzaldehyde and P-hydroxy acetophenone from (Merck-Schuchardt / Germany), 2,4-dichlorobenzaldehyde, 3,3,4,4-Biphenyl tetra carboxylic dianhydride, Pyromellitic anhydride, Anthranilic acid and 3,3,4-benzophenon tetracarboxylic dianhydride from (SIGM-Aldrich /German).

Instrument

Fourier transform infrared (FTIR) spectroscopy: it was used the fourire transport infrared spectrophotometer of type FT-IR -8400 s supplied by the Bruker company, Germany in the characterization of the recorder preparation compound by the detection the active group, and detect the type of bounds that bind the particles of the mineral, Department of chemical engendering –university of AL-Qadisiyah.

Degree of fusion (Melting points): were measured the penile and lattice Stuart smp30 melting point apparatus **Hotplate stirrer:** model - 81, albinos, the Netherlands.

Vacuum drying oven k-vo27, K&K scientific suppler, Korea.

^{1}HNMR spectroscopy: were recorded at the University of Tehran in Iran using an ultra-shield 400 MHz Bruker spectrometer using DMSO d6 as a solvent.

Synthesis of phenols

Synthesis of (phenol-1)

Using a reflux condenser on a 250 ml round-bottomed flask, combine a mixture of (Ortho chloro benzaldehyde (1.5gm, 10.7mmol), *P*-hydroxy acetophenone (3.31gm ,24.3 mmol), ammonium acetate(7.5gm,97,3mmol), and glacial acetic acid (20ml) was refluxed at 140-142 ºC for 2hs After cooling, the crystals separated, and they were filtered, cleaned twice—first with acetic acid (50%) and then with cold ethanol, and then vacuum-dried at 60 ºC.

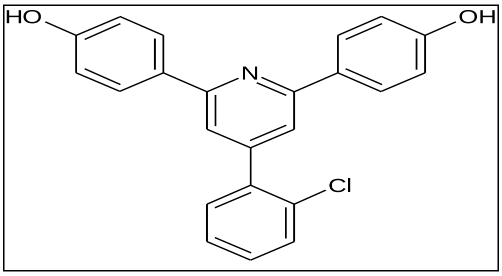


Figure 1- structure of (phenol -1).

Phenol compound	Formula	Substance		Color	m.p /C	Weight (gm)	Yield (%)
Phenol -1	$C_{23}H_{15}ClNO_2$	P-hydroxy acetophenone	Ortho chloro benzaldehyde	Deep Yellow	280-283	2.5	47

Synthesis of (phenol-2)

Using a reflux condenser on a 250 ml round-bottomed flask, combine a mixture of 2.4dichlorobenzaldehyde (1.5gm, 8.57mmol), P-hydroxy acetophenone (3.31 grams, 24.3 moles), ammonium acetate (7.5 grams, 97.3 moles), and glacial acetic acid (20 ml) were refluxed at 140 to 142 °C for two hours. Crystals split after cooling, and these were filtered, washed twice with cold ethanol and acetic acid (50%) before being vacuum-dried at 60°C.

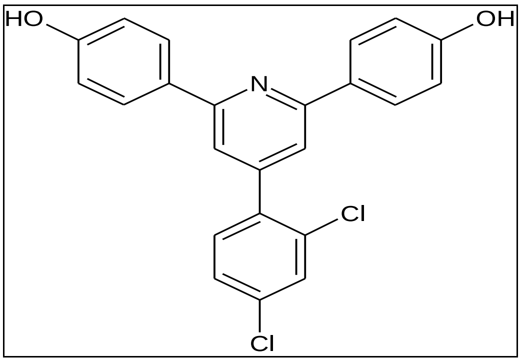


Figure 2- structure of (phenol -2).

Phenol compounds	Formula	Substance		Color	m.p/ C	Weight (gm)	Yield (%)
Phenol -2	$C_{23}H_{15}Cl_2NO_2$	2,4-dichlorobenzaldehyde	P-hydroxy acetophenone	Yellow	56-58	3.7	24

Synthesis of imides compounds

Synthesis of (imide -1)

Pyromellitic anhydride (2gm, 9.16mmol), anthranilic acid (3.84gm, 27.96mmol), and 80 mL of a 3:2 solutions of acetic acid and pyridine were added to a 250 mL round-bottomed flask.

The mixture was swirled for two hours at room temperature before being refluxed for one hour at 60 degrees Celsius. The mixture was then chilled and stirred into 200 mL of water. Filtered, extensively rinsed with methanol, and dried solid.

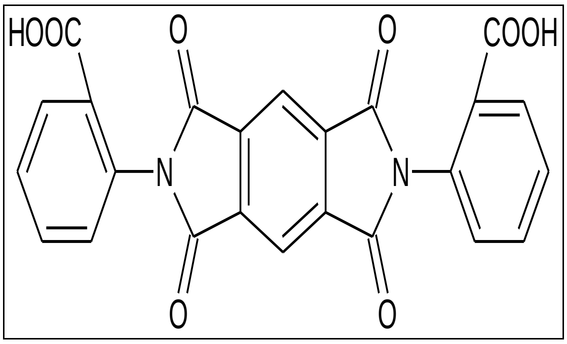


Figure 3- structure of (imide -1).

Imide compounds	Formula	Substance		Color	m.p /C	Weight (gm)	Yield (%)
imide -2	$C_{24}H_{12}N_2O_8$	Anthranilic acid	Pyromellitic anhydride	White	>300	6.2	83

Synthesis of (imide -2)

3.84 grams of anthranilic acid, 2.20 grams of 3,3,4-benzophenon tetracarboxylic dianhydride, and 80 milliliters of a 3:1 solution of acetic acid and pyridine were added to a 250-milliliter round-bottomed flask. The mixture was swirled for two hours at room temperature before being refluxed for one hour at 60 degrees Celsius. The mixture was then chilled and stirred into 200 mL of water. Filtered, extensively rinsed with methanol, and dried solid .

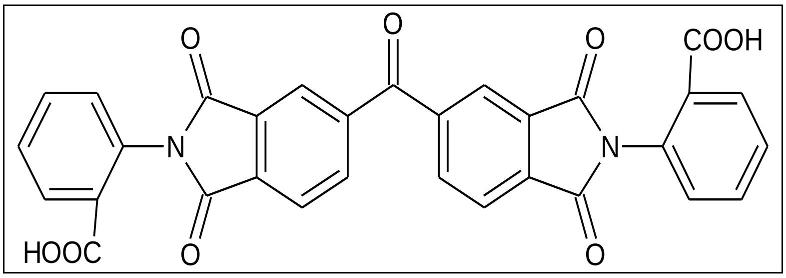


Figure 4- structure of (imide -2).

Imide compound	Formula	Substance		Color	m.p /C	Weight (gm)	Yield (%)
imide -2	$C_{31}H_{16}N_2O_9$	Anthranilic acid	3,3,4-benzophenon tetracarboxylic dianhydride	brown	>300	4.5	69

Synthesis of Poly (ester –imide-1)

(Poly ester –imide -2) was prepared by the condensation of one mole (1.1gm) (phenol -1) prepared with one mole(1.2gm) of (imide -2) were mixed at 120 ºC under constant stirring after the dissolution, add the dibutyltine dilaurate catalyst (1ml) and the temperature increased to 160 ºC for one hour. Then the product was filtered and dried.

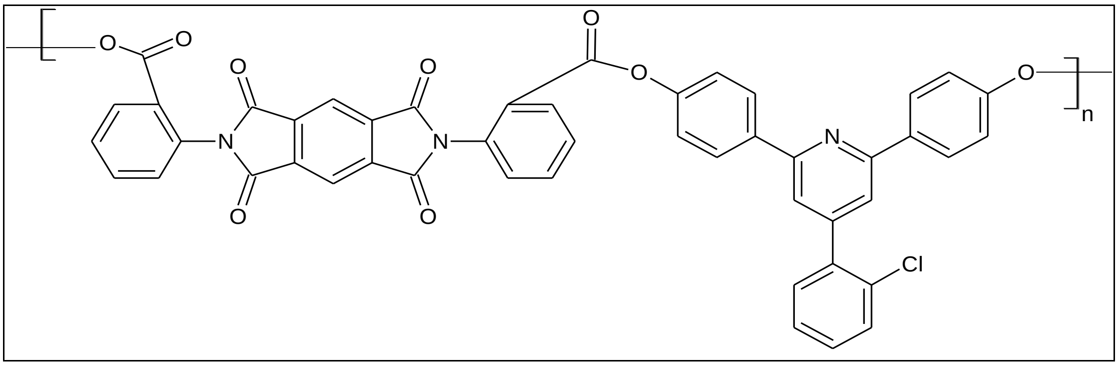


Figure 5- structure of (Poly ester –imide -1).

Polymer	***Formula***	***compounds***		***Color***	***Yield (%)***
Poly ester – imide -1	$C_{47}H_{24}ClN_3O_8[O]_n$	Phenol-2	imide monomer -2	Black	77

Synthesis of Poly (ester –imide-2)

(Poly ester –imide -3) was prepared by the condensation of one mole (1.1gm) (phenol -2) prepared with one mole (1.1gm) of (imide -2) were mixed at 120 ºC under constant stirring after the dissolution, add the dibutyltine dilaurate catalyst (1ml) and the temperature increased to 160 ºC for one hour. Then the product was filtered and dried.

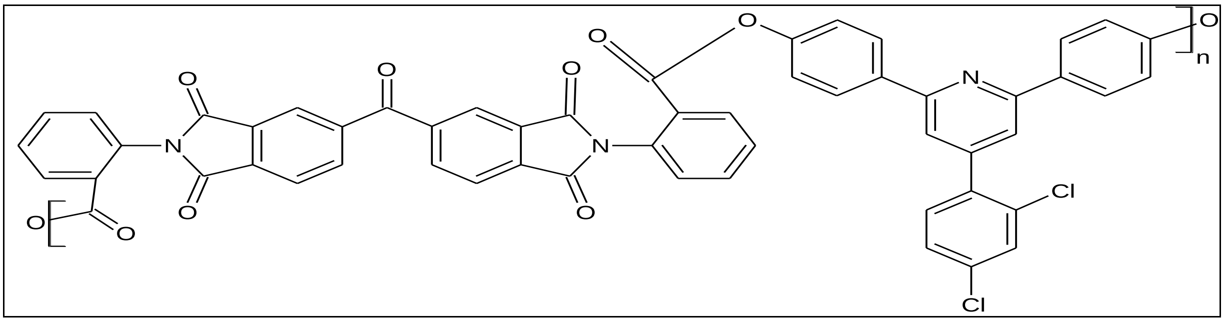
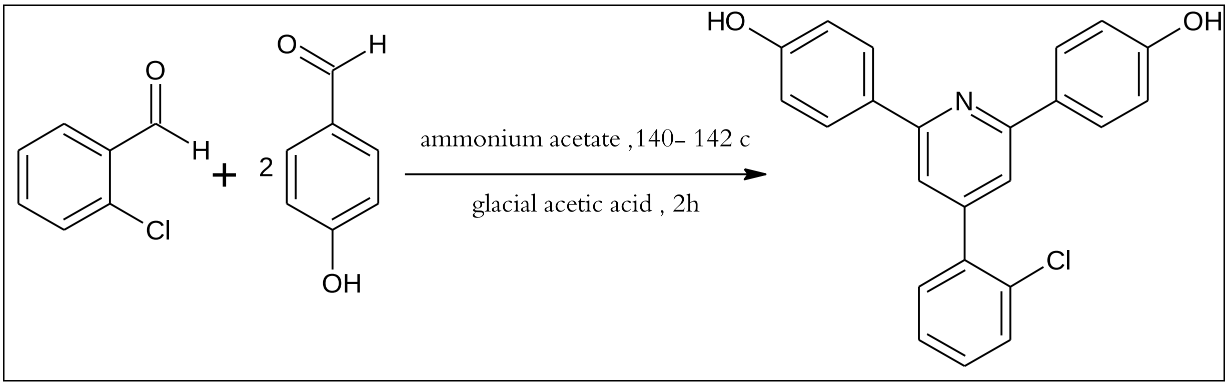


Figure 8- structure of (Poly ester –imide -2).

Polymer	Formula	Compounds		Color	Yield (%)
Poly ester –imide -2	$C_{54}H_{28}Cl_2N_3O_9[O]_n$	Phenol-3	imide monomer -3	Brown	70

Synthesis and characterization of (Phenol -1):

There are various ways to prepare pyridine rings, but the modified Chichibabin method is the best because it offers benefits like high yields, readily available starting materials, and the ability to incorporate other substances into the pyridine ring. This monomer (***Phenol -1***) was made by condensing Ortho chloro benzaldehyde with P-hydroxy acetophenone at 140–142 °C for two hours while in the presence of glacial acetic acid and ammonium acetate. The 1H-NMR and FTIR spectrum were used to describe this monomer.



Scheme 1-: Synthesis of (Phenol -1)

FTIR spectrum of (phenol-1):

FTIR spectrum of (phenol -1) as shown in figure (9) which indicates absorption broad band to (–OH) at (3300 cm^{-1}), absorption band at (600cm^{-1}) to (C-Cl), absorption band to C-O at 1164 cm^{-1}, (3150cm^{-1}), Absorption bands near (1590, 1400 cm^{-1}) for (aromatic -CH stretching) reveal (C=C) for aromatic rings, and (1610 cm^{-1}) of the heteroaromatic ring (C=N).

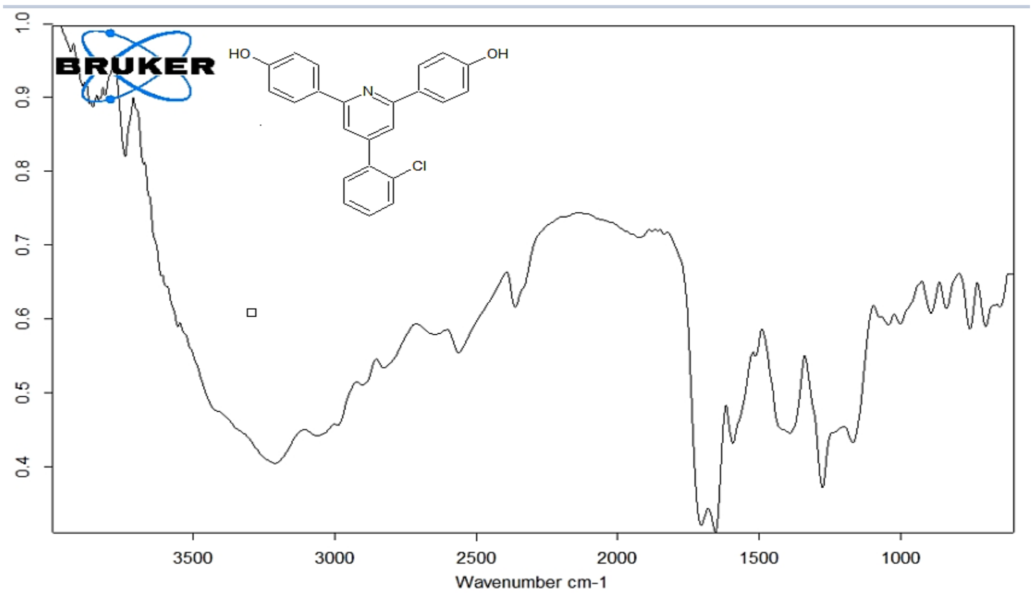
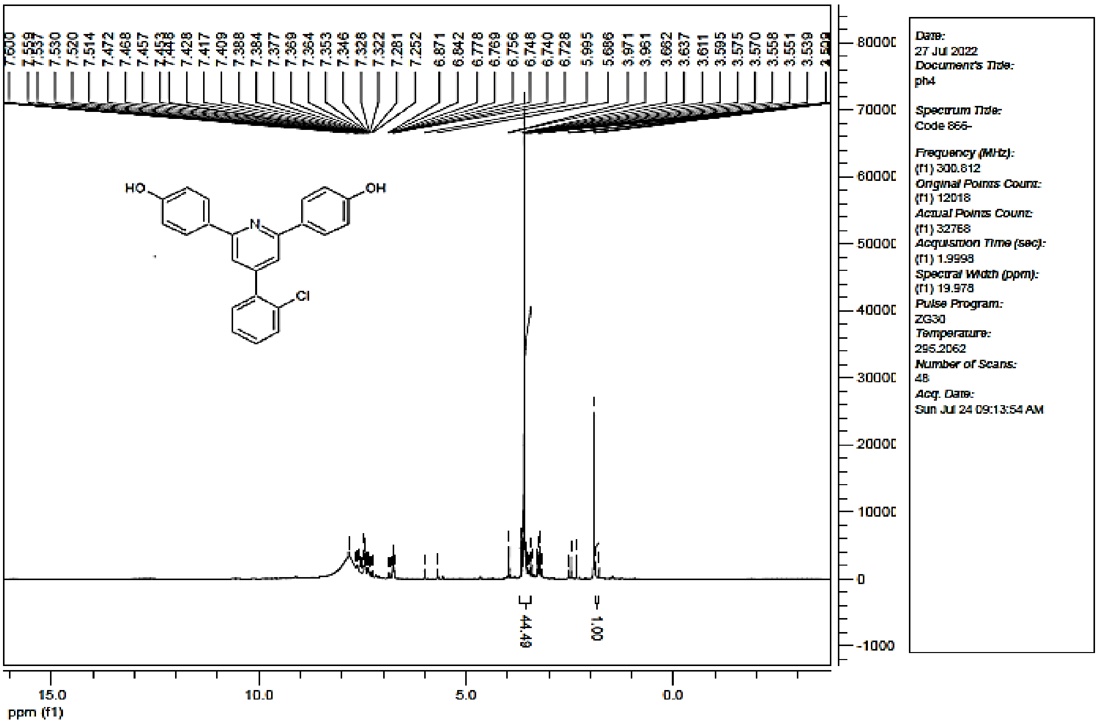


Figure 9- FTIR spectra for (Phenol -1).

^{1}HNMR spectrum of (Penol-1)

A multiplet to (14H, phenyl and hetero rings) at (7.7-9.0 ppm is visible in the 1HNMR spectrum of (Phenol -2) in Figure (14), as well as a doublet singlet to (2H, OH) at (8.1 ppm).



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Spectrum Title:
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Sun Jul 24 09:13:54 AM

Figure: 10 ^{1}H-NMR spectra of (Phenol -1).

^{13}CNMR spectra of (Phenol -1)

Olefin and aromatic carbon signals can be seen in the third zone, between 115.37 ppm and 133.9 ppm. At 163 ppm, a single linked to azomethine. The signals of hetero aromatic carbons appear in the third region between 138.4 ppm and 140ppm. Signal of carbon such as related to heteroatoms appear at 38-40 ppm of (C–OH).

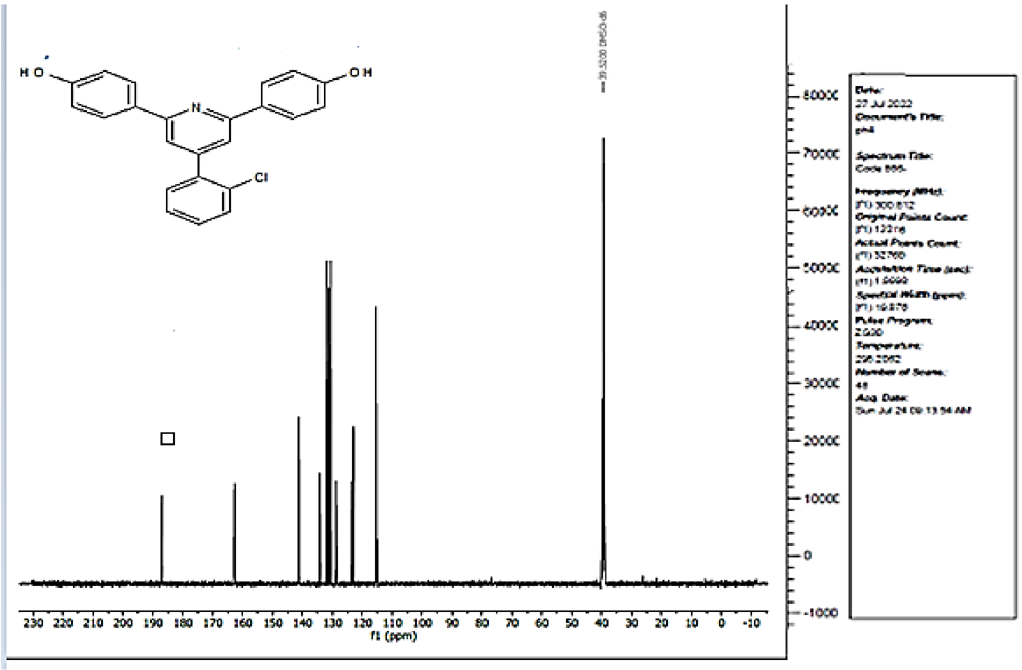
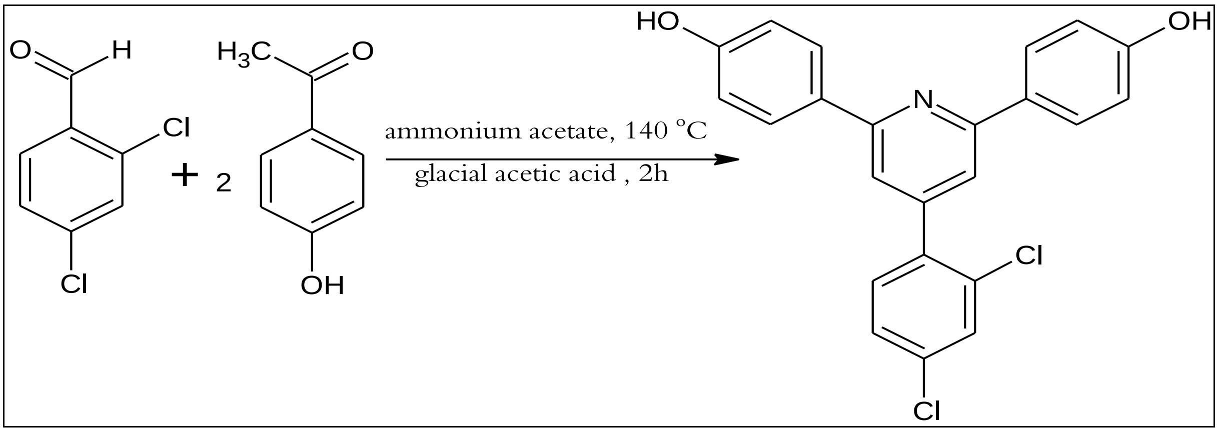


Figure: 11- ^{13}C-NMR spectra of (Phenol -1).

Synthesis and characterization of (Phenol- 2):

By condensing one mole of 2,4-dichlorobenzaldehyde with two moles of P-hydroxy acetophenone in the presence of glacial acetic acid and ammonium acetate at 140-142°C for two hours, this monomer (Phenol-2) was created. 1H-NMR and FTIR were used to characterize this monomer**.**



Scheme 2-: Synthesis of (Phenol -2).

FTIR spectrum of (phenol -2):

The FTIR spectrum of (phenol-2) is shown in Figure (12), where absorption bands to (-OH) are visible at (3300 cm^{-1}), (C-O) at (1200 cm^{-1}), (C=C) of the aromatic rings at (1400, 1550 cm^{-1}), (C=N) of heteroaromatic rings at (1650 cm^{-1}), (C-Cl) at (600 cm^{-1}), and (aromatic -CH stretching) at (3150) cm^{-1}, [18-20].

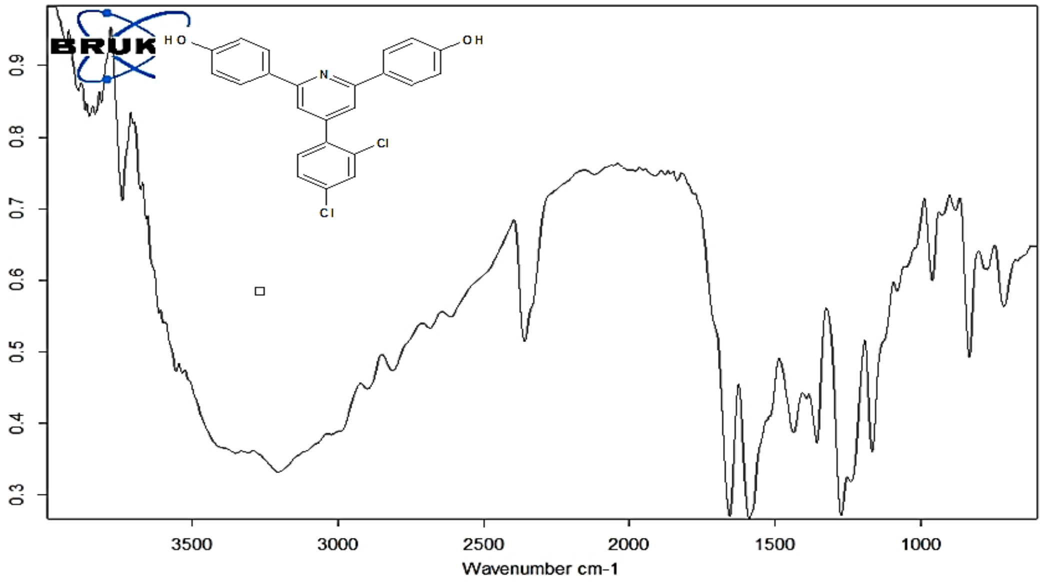


Figure: 12 FTIR spectra of (Phenol -3).

^{1}HNMR spectrum of (Phenol -3):

Figure (17) depicts the ^{1}HNMR spectrum of (Phenol-3) and reveals a multiple to (13H, phenyl and hetero rings) at (7.7-8.0 ppm and a singlet to (2H, OH) at (8.8 ppm, [18-20].

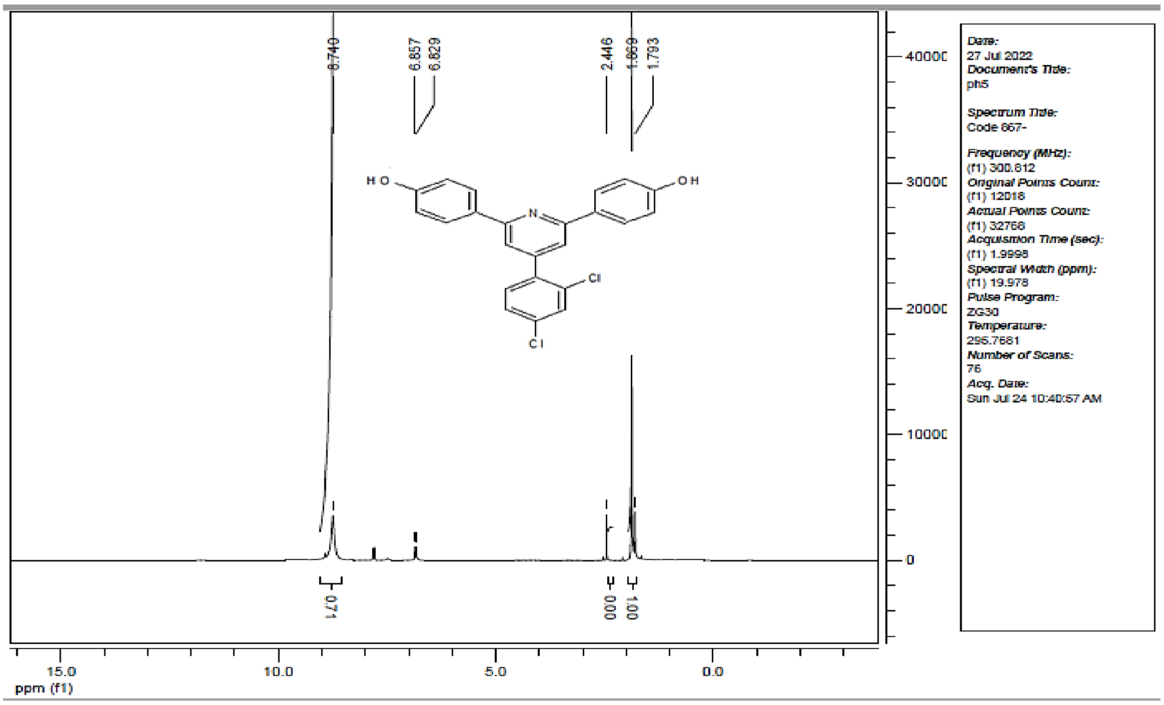
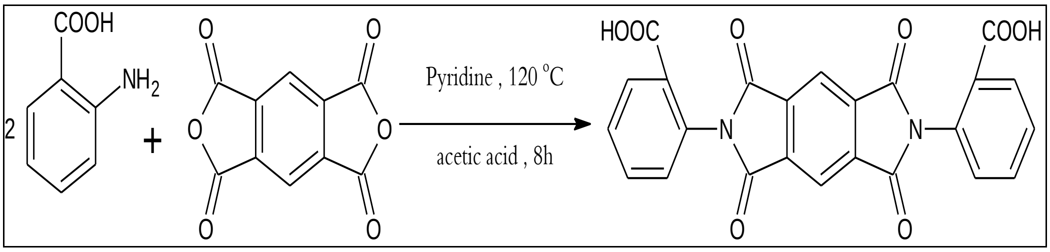


Figure: 13- ^{1}H-NMR spectra of (Phenol- 2).

Synthesis and characterization of (Imide- 1):

This monomer (Imide- 1) was made by condensing one mole of Pyromellitic di anhydride with two moles of anthracitic acid in the presence of pyridine and acetic acid (2:3), the mixture was then stirred for two days at room temperature, and stirring it at reflux temperature for eight hours at 120 °C. The 1H-NMR and FTIR spectrum were used to describe this monomer, [25,26,26].



Scheme 3- Synthesis of (Imide- 1).

FTIR spectrum of (Imide -1)

FTIR spectrum of (**imide – 1**) Figure (13) shows absorption a broad bands at (3250-2500 cm^{-1}) to (OH group), (1466,1590cm^{-1}) for (C=C) ring, (3850 cm^{-1}) to (aromatic C-H stretching) , (1700 cm^{-1}) to (C=O) and (1400cm $^{-1}$) for (C-N) , The characteristic absorption of (NH_2) group disappeared .

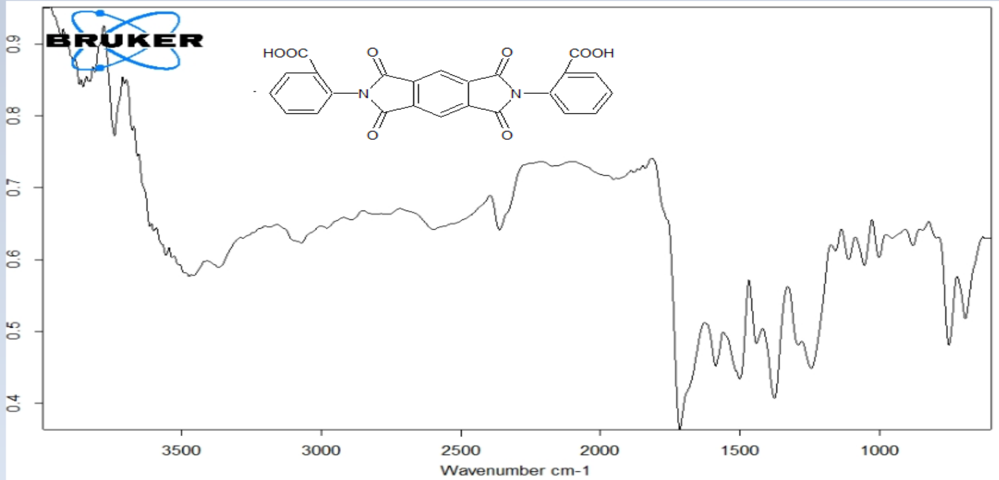
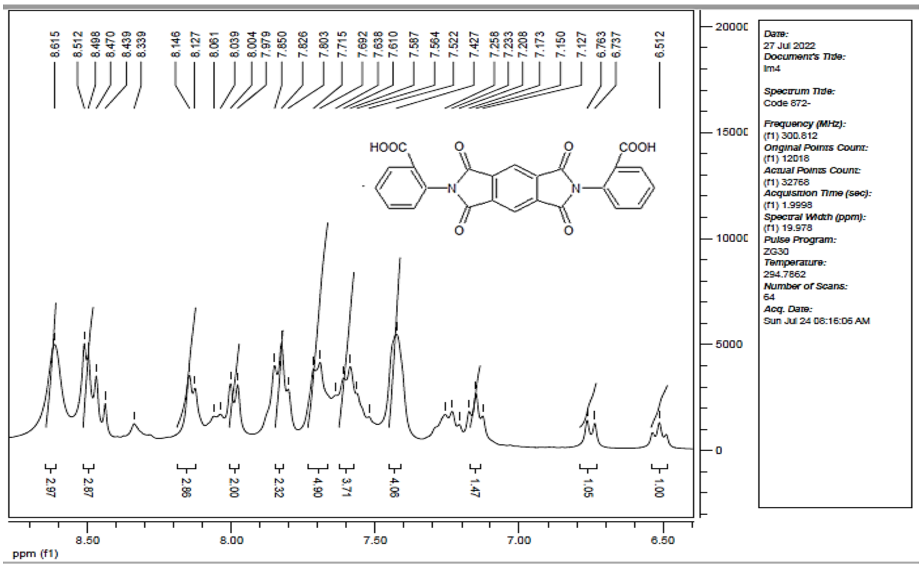


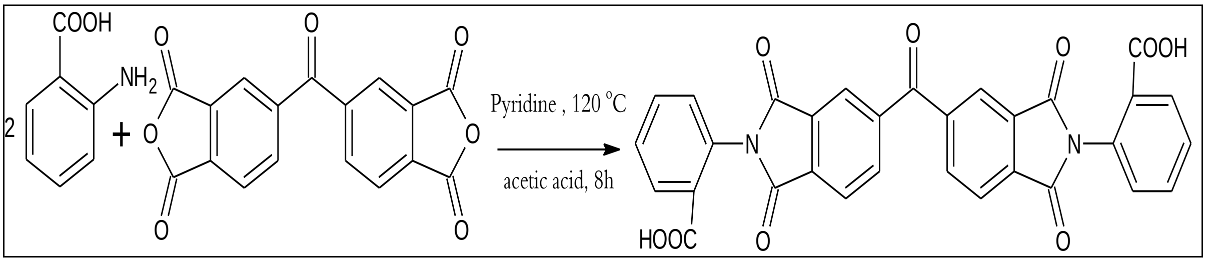
Figure: 13 -FTIR spectra of (Imide -1).

^{1}HNMR spectrum of (Imide - 1):

Figure (14), which depicts the ^{1}HNMR spectrum of imide 1, demonstrates that the chemical shifts at 2.5 ppm are typical of DMSO-d6 as a solvent, with a multiple at (7.9-8.1 ppm) to (8H, phenyl substituted rings). a multiple at (8.3-8.6 ppm) to (2H, phenyl unsubstituted rings) at (3.3-8.6 ppm) for the OH group, [26,27,28].



That monomer (Imide-2) was made by condensing one mole of 3,3,4-benzophenon tetracarboxylic dianhydride with two moles of anthracitic acid in the presence of acetic acid (2:3). The solution was stirred at room temperature for two pyridine and days before being stirred at reflux temperature for eight hours at 120 ºC. The 1H-NMR and FTIR spectrum were used to describe this monomer.



Scheme 4-: Synthesis of (Imide -2).

FTIR spectrum of (Imide -2)

Figure (15) FTIR spectrum for (imide-2) reveals large bands of absorption for the OH group at 3400 cm^{-1}, the C=C ring at 1466 and 1590 cm^{-1}, aromatic C-H stretching at 3850 cm^{-1}, C=O at 1700 cm^{-1}, and C-N at 1400 cm^{-1}. The (NH$_2$) group's distinctive absorption vanished.

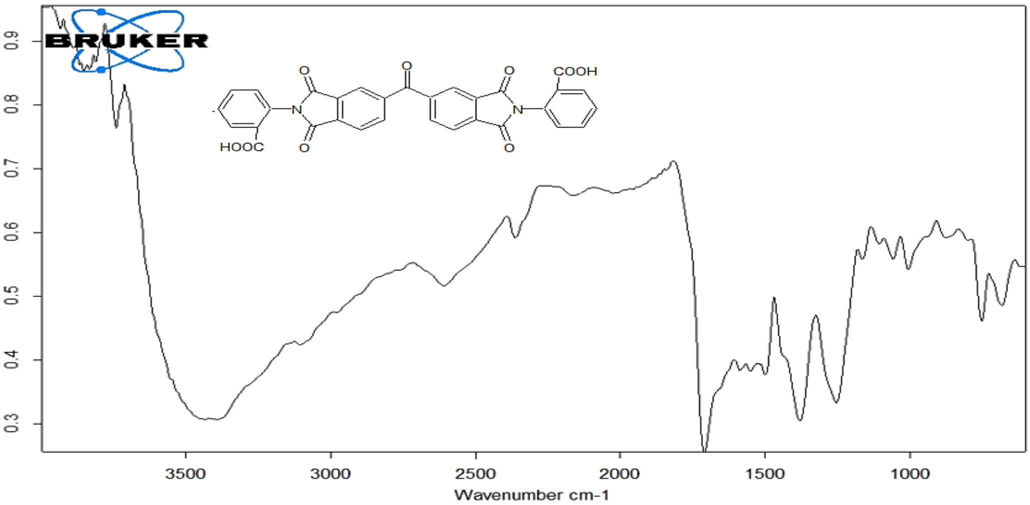
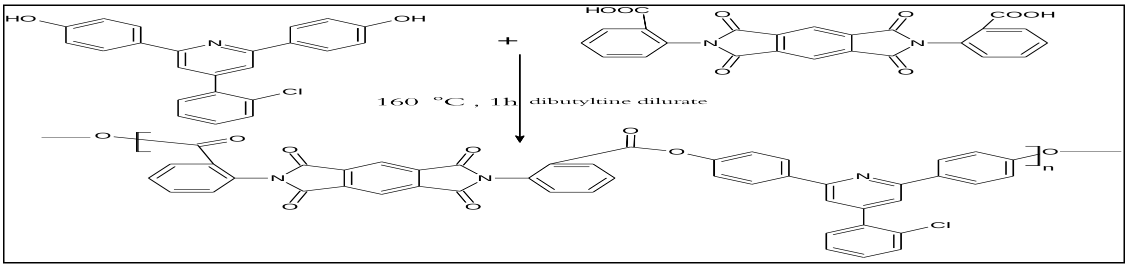


Figure: 15- FTIR spectra of (Imide -2).

Synthesis and characteristic of Poly (ester –imide -2)

(Poly ester –imide -2) was prepared by the condensation of one mole of (phenol -2 prepared) with one mole of (dicarboxylic acid) (imide-2) were combined at 120 ºC while being constantly stirred following the dissolution, add the dibutyltine dilaurate catalyst and the temperature increased to 160 ºC for one hour. This polyester-imide was characterized by ^{1}H-NMR and FTIR.



Scheme 5- Synthesis of poly (ester imide- 2).

FTIR spectrum of Poly (ester –imide - 1):

The FTIR spectrum of (Poly ester -imide - 2) is shown in figure 16. It reveals absorption bands at (2925 cm^{-1}) to (-OH group) and (3113 cm^{-1}) to (aromatic -CH stretching), absorption bands at (1625 cm^{-1}) indicating of the aromatic ring's C=C, and absorption band at (1020 cm^{-1}) indicating of C-N, the absorption band at (650 cm^{-1}) to C-Cl and absorption band at (1650 cm^{-1}) of (C=O aldehyde).

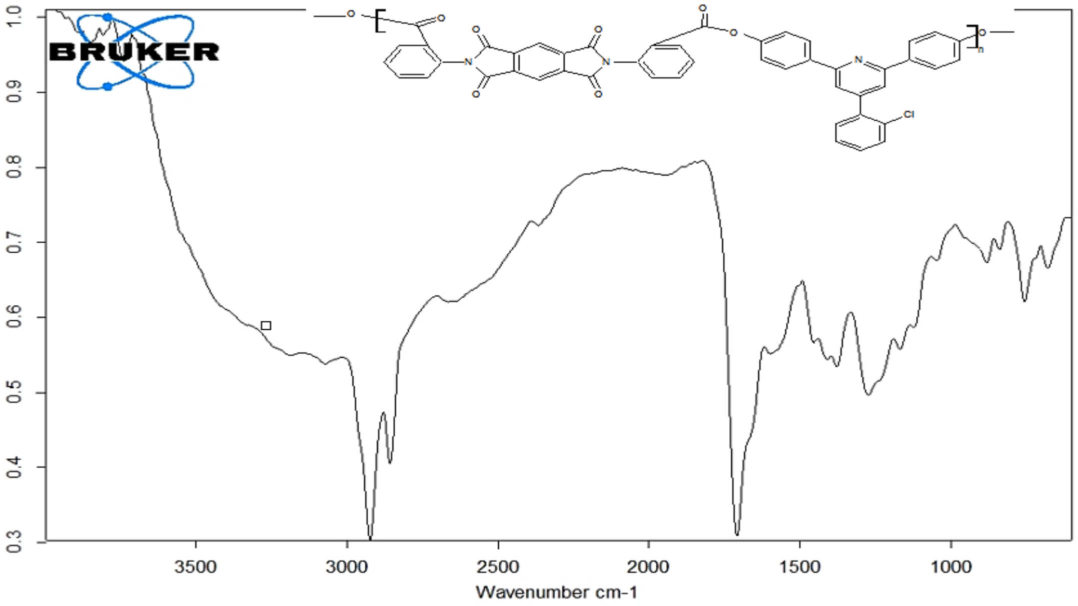
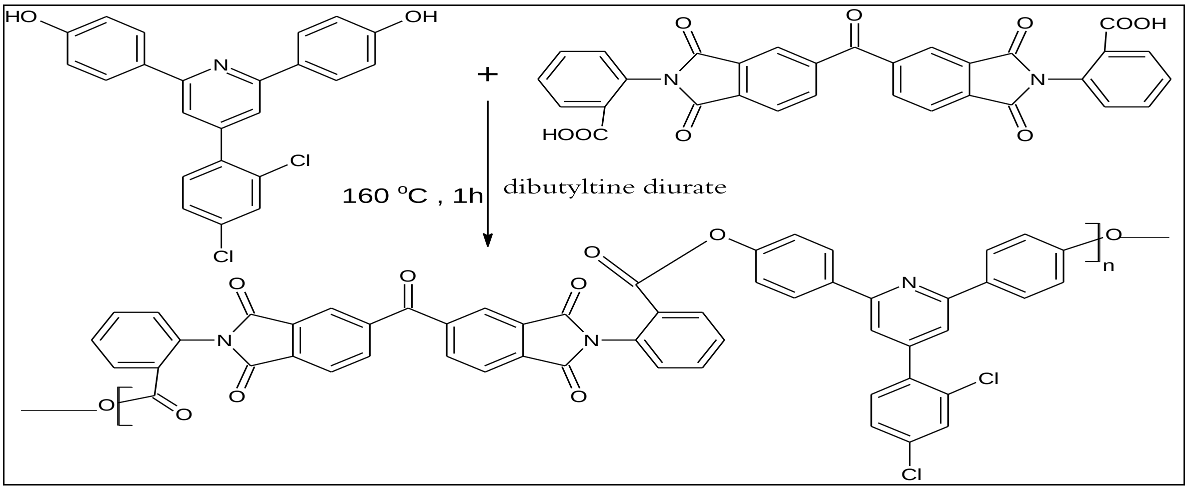


Figure: 16- FTIR spectra of (poly –ester imide- 2)

Synthesis and characteristic of (Poly ester –imide – 2):

(Poly ester –imide-2) was prepared by the condensation of one mole of (phenol -1 prepared) with one mole of (*imide-3)* were combined at 120 °C while being constantly stirred following the dissolution., add the dibutyltine dilaurate catalyst and the temperature increased to 160 ºC for one hour. This polyester-imide was characterized by ^{1}H-NMR and FTIR.



Scheme 6- Synthesis of (poly –ester imide- 3).

FTIR spectrum of (Poly ester –imide - 2):

Figure (17), which depicts the FTIR spectrum of poly ester-imide-3, shows absorption bands at (2925 cm^{-1}) for (-OH group), (3113 cm^{-1}) for (aromatic-CH stretching), absorption bands at (1625 cm^{-1}), which indicate the presence of C-C in the aromatic ring, and (1020 cm^{-1}), which indicates the presence of C-N. The absorption bands at (1650 cm^{-1}), (650 cm^{-1}), and (1650 cm^{-1}), all for the heteroaromatic ring (C=N).

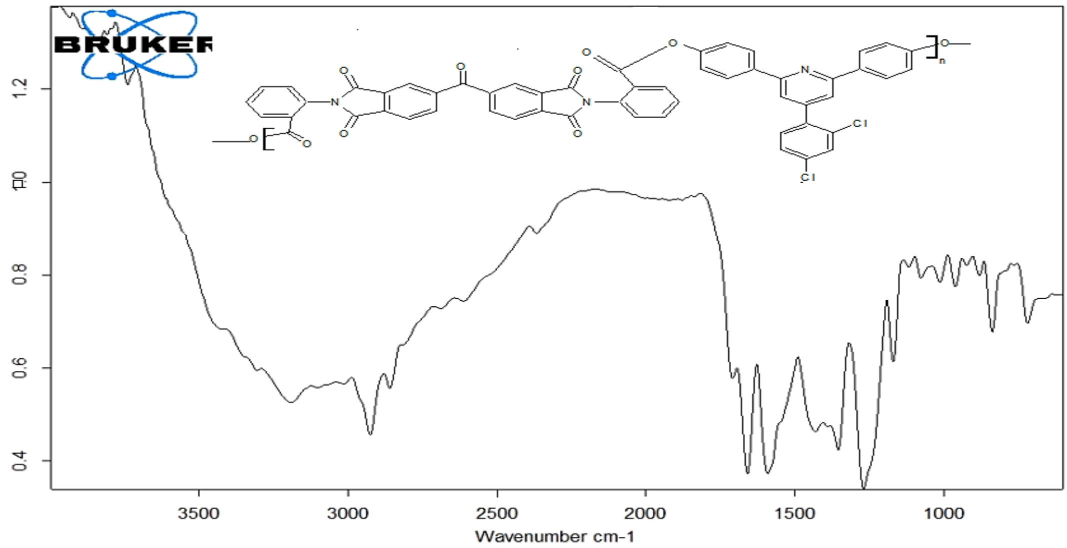


Figure: 17 -FTIR spectra for (poly –ester imide -3).

^{1}HNMR spectra for (poly –ester imide -2):

^{1}HNMR spectrum of (**poly –ester imide -2**) in Figure (18) appearances the chemical shifts at 0.9-1.8 ppm are characteristic of DMSO-d6 as solvent, a multiple at (δ 0.5-7.2 ppm) to (26H, phenyl rings and hetero rings). A singlet at δ (6.2-7.2) ppm (1H) for OH groups. because of the electron-withdrawing imide C=O group. The furthest downfield region (7.9–8.8 ppm) is where the aromatic protons-containing polymers are located. Between 2.1 and 2. 3 ppm is where the methyl proton can be found.

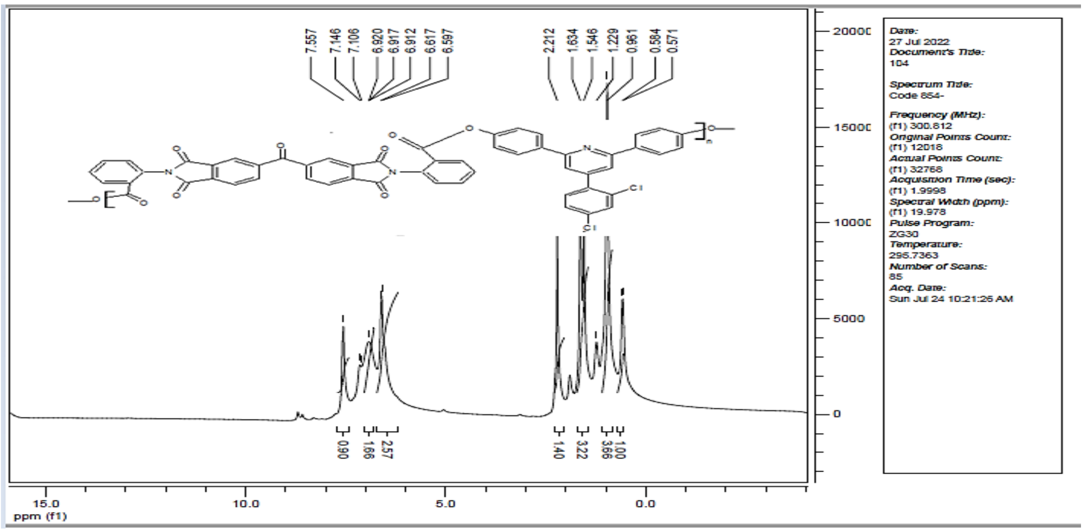


Figure: 18- ^{1}HNMR spectra of (poly –ester imide- 3).

CONCLUSIONS

In this research, aromatic poly (ester-imid)s were created via directly polycondensing imides that contained dicarboxylic acid with a variety of aromatic diols. FTIR and ^{1}H NMR were used to confirm the polymer and monomer structural details. The resultant poly (ester-imide) s can be employed as surface substances, film-forming substances, and substances for the electrical and electronic industries. The thermal stability has been significantly improved by the addition of a heterocyclic molecule to the polymer backbone. The newly created PEIs can therefore be employed as high-performance polymers. Because the polymers' chains contain ester groups, it is anticipated that they will be more soluble. These characteristics can make these (PEIs) appealing for real-world uses such processable high-performance engineering polymers, which could be the focus of more research.

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