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Synthesis and Characterization of New Aromatic Polyesters Derived from New Aromatic Di- and Tri Hydroxyl Monomers with 4-Phenylenediacrylic Acid and Malonic Acid

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In the present work, six new aromatic polyesters (PE1-PE6) have been synthesized in high yields from the polycondensation between di- and tri hydroxyl monomers containing methylene unit, Schiff-base linkages and pyridine heterocyclic ring with 4-phenylenediacrylic acid and malonic acid using dibutyltin dilaurate as catalyst. The structure analysis of the polymers has been carried out by using FT-IR and ^{1}H NMR spectroscopy. The monomers were characterized by FTIR and ^{1}H NMR. FT-IR technique confirmed the esterification of di and tri hydroxyl monomers by the acid in all the polymers.

Keywords: Synthesis, Aromatic polyesters, 4-Phenylenediacrylic acid, Malonic acid.

INTRODUCTION

The family of polyesters comprises all polymers with ester functional groups in the polymer backbone. The chemistry of the structural units connecting the ester group can be varied over an immensely broad range, making the polyesters a diverse group covering labile biomedical matrices to liquid crystals, fibers and temperature resistant performance materials, *etc*. Polyesters are the first family of synthetic condensation polymers[1-3]. Polyesters can typically be formed by a stepwise condensation reaction from difunctional monomers such as diols and acids[2].

Recently, Takasu *et al.*[4] and Liu *et al.*[5] reported that the $HfCl_4$ $(THF)_2$ complex more efficiently catalyzed the direct polycondensation of diols and dicarboxylic acid compounds, in which the procedure was a solution polycondensation in *o*-xylene with reflux (about 144 ºC) for 24 h. Ober *et al.*[6] synthesized polyesters from dihydroxy compounds by polymerizing diacid chlorides at 500 ºC for 24 h in inert atmosphere using pyridine as proton acceptor. Polyesters were prepared by Ramireddy and coworkers[7] by using pyridine as catalyst and HCl scavenger, which was produced as a byproduct of the esterification reaction with acid chlorides. The reaction was allowed to proceed for 48 h at room temperature in dry nitrogen. Polyesteramides with exact desired structure can be synthesized from monomers with proper structure and functional groups. Sek *et al.*[8] synthesized monomers and carried out the polymerization reactions in boiling chlorobenzene at 130 ºC in presence of pyridine in argon atmosphere .The reaction variables have strong influence on molecular weight of the polymers as observed by Economy[9].

Since the reaction parameters have prominent influence on the rate of reaction and molecular weight of the polymers, the polycondensation reaction was carried out at different temperature with varying monomer concentration in different solvent system over a range of reaction period and the yield and the molecular weight of the resulting polymers were studied. The polymers, synthesized by the condensation of aromatic diols and diacids through a low temperature procedure, were subjected to Fourier transform infrared (FTIR) spectroscopy to study the chemical constituents of the molecules and the molecular interaction among the polymer chains. The chemical composition of the polymers can be determined by the definite absorption bands in the spectrum.

The analyses of the thermal properties of the polyesters have been made by the help of the thermograms obtained from the DSC studies. Furthermore, polyesters are known to possess enhanced thermal stabilities[10].

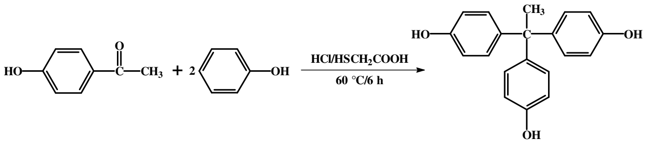
In the present work, a series of new aromatic polyesters containing both methylene unit, Schiff-base linkages and pyridine hetero cyclic ring have been synthesized in high yields from the polycondensation between di- and tri hydroxyl monomers with 4-phenylenediacrylic acid and malonic acid using dibutyltin dilaurate as catalyst.

EXPERIMENTAL

Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu-FTIR-8400S spectrometer (Japan) with KBr pellets in the optical range of 4000-400 cm^{-1}. ^{1}H NMR spectra were registered using a Bruker, 250Mhz, spectrometer, at polymer laboratories Co Iran using DMSO as a solvent. The solubility of the polymers was determined with (0.01 g) of polyester in (2 mL) of a solvent.

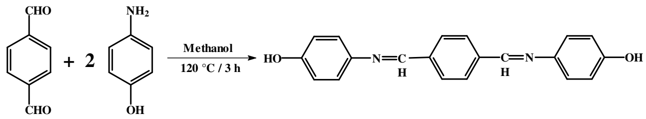
Absolute methanol, acetic acid, ammonium acetate, dibutyltin dilaurate, all from (BDH/England); dichloromethane, hexane, procured from (BIOSOLVE). Hydrochloric acid, salicylaldehyde, benzaldehyde all from (HiMedia); diethyl ether obtained from (IGCC/England) while phenol, *p*-aminophenol, 4-chlorobenzaldehyde, glacial acetic acid, piperidine, pyridine, terephthalaldehyde, dimethyl sulphoxide, *m*-cresol, N,N-dimethylacetamide, 4-(dimethyl amino)-benzaldehyde, *p*-hydroxyacetophenone, tetrahydrofurane obtained from Merck. Absolute ethanol from (Scharlab S.L), malonic acid and N,N-dimethylformamide from Aldrich.

Synthesis of 1,1,1-tris(4-hydroxyphenyl)ethane (M1): A mixture of 4-hydroxy acetophenone (2.72 g, 20 mmol), phenol (4 g, 42 mmol), HCl catalyst (37.5 g) and thioglycolic acid (0.5 g) promoter were placed in a three necked-round bottom flask equipped with a condenser, mechanical stirrer and thermometer and kept in a thermostat bath at 60 ºC for 6 h. After a definite period of time, the reaction mixture was transferred to cold water to quench the reaction. Then, the product was washed, dried[11] to yield 5 g (82 % wt) of brown powder (**Scheme-I**). The monomer has characterized by FTIR.



Scheme-I: Synthesis of M1

Synthesis of M2: This monomer was prepared by the condensation of terephthalaldehyde (1.34 g, 10 mmol) and *p*-aminophenol (2.2 g, 20 mmol) in 15 mL of methanol, by boiling the mixture under reflux at 120 ºC for 3 h. The precipitated was filtered and recrystallized from methanol and dried in a vacuum desiccators[12] to yielding 2.5 g (79 % wt) of very-light yellow crystals. m.p. 205-210 ºC (**Scheme-II**). This monomer was characterized by FTIR and ^{1}H NMR spectra.

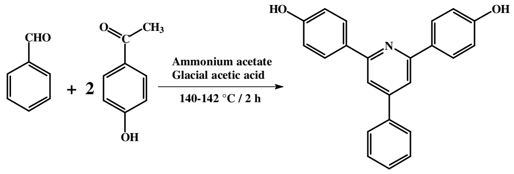


Scheme-II: Synthesis of M2

General synthesis of M3, M4, M5, M6: In a round-bottomed flask (150 mL) equipped with a reflux condenser, a mixture of aldehyde derivative (10 mmol), that showed in (Table-1), *p*-hydroxyacetophenone (2.72 g, 20 mmol), ammonium acetate (7.5 g) and glacial acetic acid (20 mL) was refluxed at 140-142 ºC for 2 h. Upon cooling, crystals separated, which were filtered and washed first with acetic acid (50 %) and then with cold ethanol. These product crystals were recrystallized from absolute ethanol and then dried at 60 ºC under vacuum[13,14].

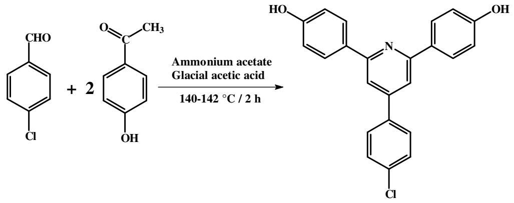
Synthesis of M3: There are several methods for preparation of the pyridine ring. Modified Chichibabin method is one of the best methods for the preparation of a pyridine ring[15,16], which offers advantages such as good yield, available starting material and potential for introducing different substituent's in the pyridine ring.

M3 is prepared by the condensation of one molecule of benzaldehyde with two molecules of *p*-hydroxyacetophenone in the presence of ammonium acetate and glacial acetic acid at 140-142 ºC for 2 h (**Scheme-III**). This monomer was characterized by FTIR.



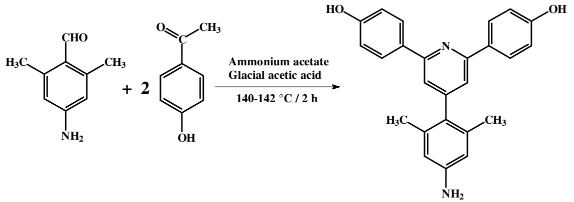
Scheme-III: Synthesis of M3

Synthesis of M4: M4 is prepared by the condensation of one molecule of 4-chlorobenzaldehyde with two molecules of *p*-hydroxyacetophenone in the presence of ammonium acetate and glacial acetic acid at 140-142 ºC for 2 h (**Scheme-IV**). This monomer was characterized by FTIR.



Scheme-IV: Synthesis of M4

Synthesis of M5: M5 is prepared by the condensation of one molecule of 4-(dimethylamino)benzaldehyde with two molecules of *p*-hydroxyacetophenone in the presence of ammonium acetate and glacial acetic acid at 140-142 ºC for 2 h (**Scheme-V**). This monomer was characterized by FTIR.



Scheme-V: Synthesis of (M5)

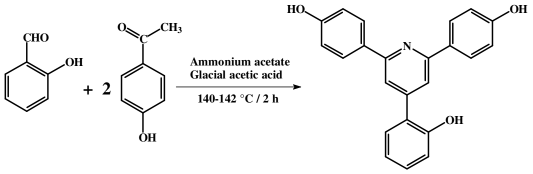
TABLE-1
SYNTHESIS OF MONOMERS (M3, M4, M5, M6)

Monomers	Substance		Weight of monomer (g)	Yield (% wt)	Colour	m.p. (ºC)
	Aldehyde derivative	Weight (g)				
M3	Benzaldehyde	1.06	2.6	77	Greenish yellow	278-282
M4	4-Chloro benzaldehyde	1.41	2.94	79	Blackish brown	Viscous liquid
M5	4-(Dimethylamino) benzaldehyde	1.49	2.97	78	Blackish red	Viscous liquid
M6	Salicylaldehyde	1.22	2.80	79	Reddish brown	205-210

TABLE-2
SYNTHESIS OF POLYESTERS (PE1-PE6)

Polyesters	Monomers		Diacid (g/mmol)	Dihydroxy (g/mmol)	Yield (% wt)	Colour
	Diacid	Dihydroxy				
PE1	Malonic acid	M1	2.08 / 20	3.06 / 10	76	Light brown
PE2	Malonic acid	M2	1.04 / 10	3.16 / 10	79	Light pink
PE3	*p*-Phenylenediacrylic acid	M3	2.18 / 10	3.39 / 10	77	Light yellow
PE4	*p*-Phenylenediacrylic acid	M4	2.18 / 10	3.72 / 10	78	Black
PE5	*p*-Phenylenediacrylic acid	M5	2.18 / 10	3.82 / 10	79	Brown
PE6	*p*-Phenylenediacrylic acid	M6	4.36 / 20	3.55 / 10	79	Deep brown

Synthesis of M6: M6 is prepared by the condensation of one molecule of salicylaldehyde with two molecules of *p*-hydroxyacetophenone in the presence of ammonium acetate and glacial acetic acid at 140-142 ºC for 2 h. This monomer was characterized by FTIR and ^{1}H NMR spectra.



Scheme-VI: Synthesis of M6

Synthesis of polyesters (PE1- PE6): In this section, we used polycondensation method for synthesis of a series of two new polyesters from the direct polycondensation reaction of malonic acid with two new different aromatic dihydroxy monomers (M1, M2), respectively and four new polyesters from the direct polycondensation reaction of *p*-phenylenediacrylic acid with four new different aromatic dihydroxy monomers (M3, M4, M5 and M6), respectively, by using the dibutyltin dilaurate catalyst [0.15 wt. (%)] (**Scheme-VII**) (Table-2). The materials were dried under vacuum at 50 ºC giving rise to the PE series. The materials were obtained as powders[17]. These polymers have a soft segment such as methylene unit, vinyl moiety and Schiff-base groups and pyridine heterocyclic ring in main chain for improving solubility in organic solvents. These polyesters were characterized by FTIR and ^{1}H NMR spectra.

RESULTS AND DISCUSSION

The FTIR spectrum of M1 as shown in (Fig. 1) which indicates absorption band at (3271 cm^{-1}) to (-OH group), (3062 cm^{-1}) to (aromatic -CH Str), (2985 cm^{-1}) to (aliphatic -CH Str) and absorption bands around (1666-1512 cm^{-1}) show the presence of the aromatic ring.

The FTIR spectrum of (M2 Schiff-Base) is shown in (Fig. 2) which indicates absorption bands at (3311 cm^{-1}) to (-OH group), (3078 cm^{-1}) to (aromatic -CH stretching), (2922 cm^{-1}) to (aliphatic -CH stretching) and absorption bands around (1612-1546 cm^{-1}) show the presence of the aromatic ring.

^{1}H NMR spectrum of M2, is shown in Fig. 3 assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ (3.5) ppm (s, 2H) for C-H, δ (3.4) (s ,2H) for OH group, δ (6.8 -8.2) ppm(s, 12H) for Ar-H group.

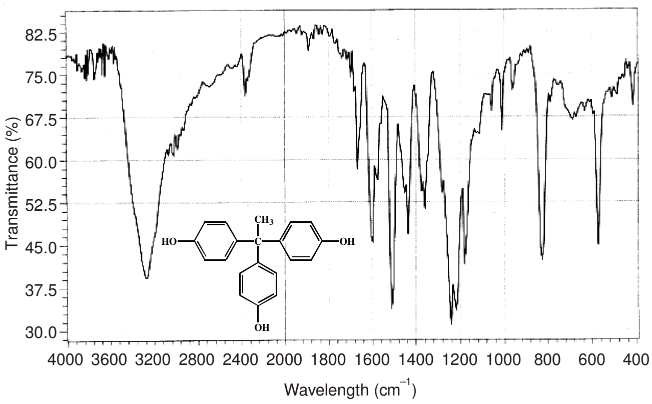


Fig. 1. FTIR spectrum of M1

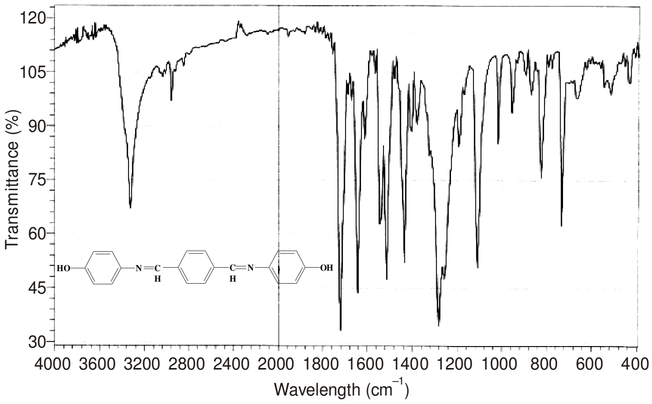


Fig. 2. FTIR spectrum of M2

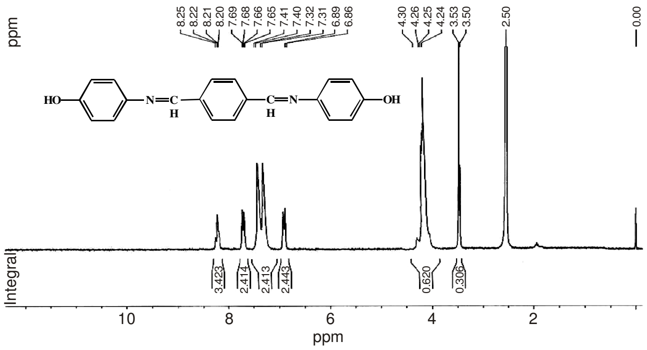
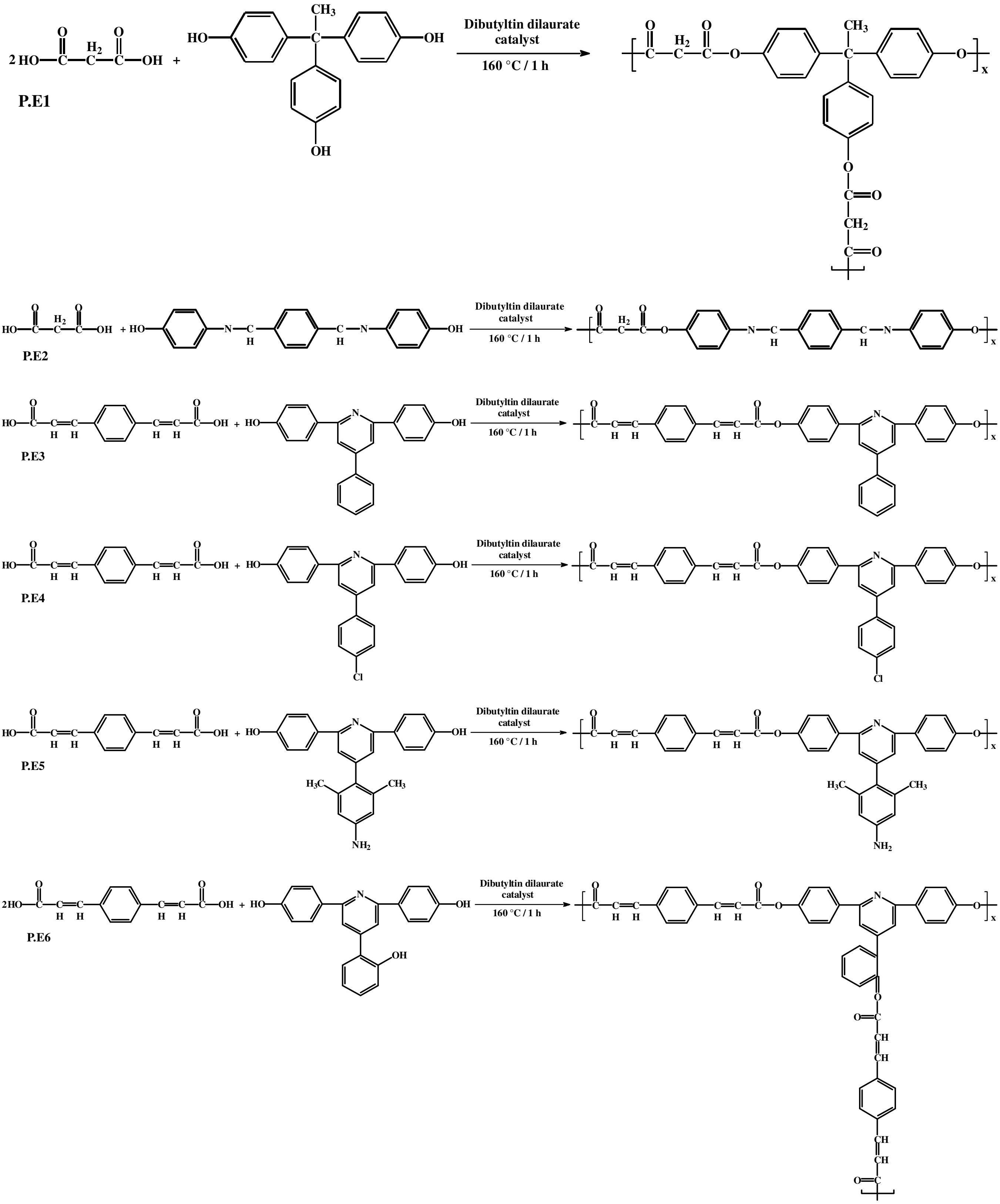


Fig. 3. ^{1}H NMR spectrum of M2

The FTIR spectrum of M3 as shown in (Fig. 4) which indicates absorption band at (3366 cm^{-1}) to (-OH group), (3148 cm^{-1}) to (aromatic -CH stretching), absorption bands around (1671-1656 cm^{-1}) show the presence of the aromatic ring and (1590-1523 cm^{-1}) to heteroaromatic ring (C=N).

The FTIR spectrum of M4 as shown in (Fig. 5) which indicates absorption band at (3377cm^{-1}) to (-OH group), (3138 cm^{-1}) to (aromatic -CH stretching), absorption bands around



Scheme-VII: Synthesis of PE1-PE6

($1670-1654\ cm^{-1}$) show the presence of the aromatic ring, ($1592-1521\ cm^{-1}$) to heteroaromatic ring (C=N) and ($811\ cm^{-1}$) to (C-Cl).

The FTIR spectrum of M5 as shown in (Fig. 6) which indicates absorption bands at ($3366\ cm^{-1}$) to ($-NH_2$ group), ($3311\ cm^{-1}$) to (-OH group), ($3044\ cm^{-1}$) to (aromatic -CH stretching), ($2806\ cm^{-1}$) to (aliphatic -CH stretching), absorption bands around ($1668-1648\ cm^{-1}$) show the presence of the aromatic rings and ($1587-1517\ cm^{-1}$) to heteroaromatic ring (C=N).

The FTIR spectrum of M6 as shown in (Fig. 7) which indicates absorption band at ($3356\ cm^{-1}$) to (-OH group), ($3138\ cm^{-1}$) to (aromatic -CH stretching), absorption bands around

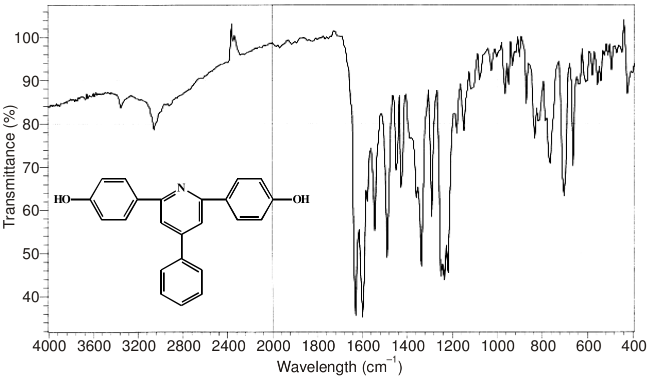


Fig. 4. FTIR spectrum of M3

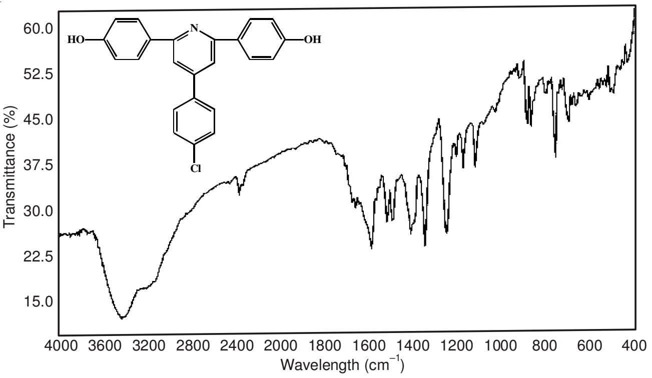


Fig. 5. FTIR spectrum of M4

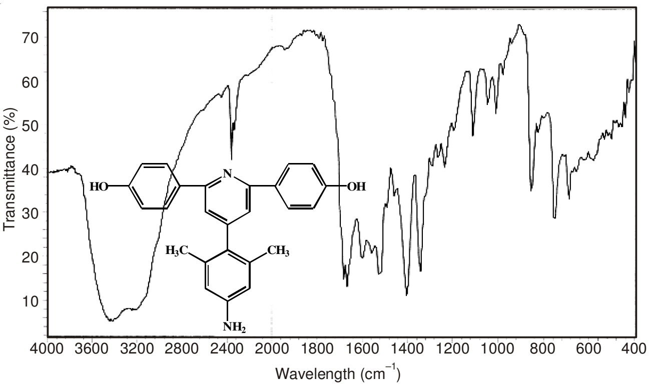


Fig. 6. FTIR spectrum of M5

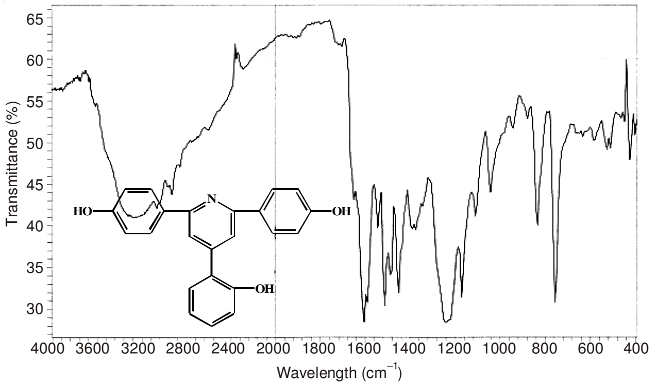


Fig. 7. FTIR spectrum of M6

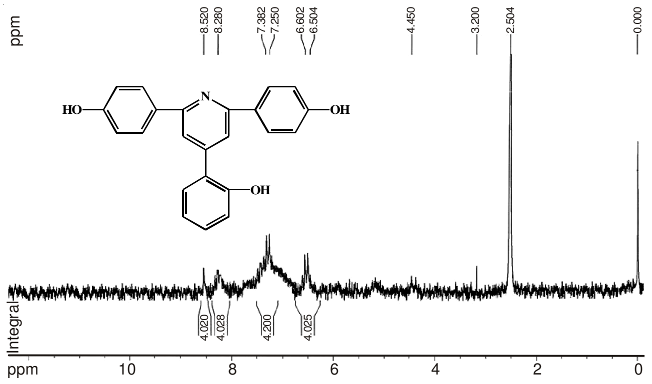


Fig. 8. ^{1}H NMR spectrum of M6

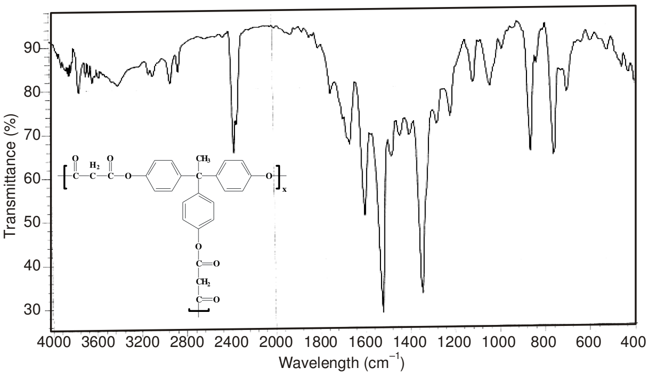


Fig. 9. FTIR spectrum of PE1

(1679-1658 cm^{-1}) show the presence of the aromatic ring and (1599-1527 cm^{-1}) to heteroaromatic ring (C=N).

^{1}H NMR spectrum of M6, is shown in Fig. 8 assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ (4.5) ppm (s, 3H) for OH, δ (5.7), δ (6.5 -8.5) ppm (s, 14H) for Ar-H group.

Characterization of polyesters (PE1-PE6)

FTIR spectrum of PE1: The FTIR spectrum of PE1 as shown in (Fig. 9) which indicates absorption band at (3070 cm^{-1}) to (aromatic -CH str), (2989 cm^{-1}) to (aliphatic -CH str), (1789-1766 cm^{-1}) to (-C=O str, ester), (1100 cm^{-1} -C-O str, ester) and absorption bands around (1646-1532 cm^{-1}) show the presence of the aromatic ring.

FTIR spectrum of PE2: The FTIR spectrum of PE2 as shown in (Fig. 10) which indicates absorption band at (3066 cm^{-1}) to (aromatic -CH Str), (2988 cm^{-1}) to (aliphatic -CH Str), (1779-1756 cm^{-1}) to (-C=O Str, ester), (1108 cm^{-1} -C-O Str, ester) and absorption bands around (1635-1530 cm^{-1}) show the presence of the aromatic ring.

FTIR spectrum of PE3: The FTIR spectrum of PE3 as shown in (Fig. 11) which indicates absorption band at (3135 cm^{-1}) to (aromatic –CH stretching), absorption bands around (1673-1650 cm^{-1}) show the presence of the aromatic ring, (1533 cm^{-1}) to vinyl segment, (1762-1752 cm^{-1}) to (-C=O str, ester), (1102 cm^{-1} -C-O str, ester) and (1588-1522 cm^{-1}) to heteroaromatic ring (C=N).

FTIR spectrum of PE4: The FTIR spectrum of (PE4) as shown in (Fig. 12) which indicates absorption band at (3119 cm^{-1}) to (aromatic –CH stretching), absorption bands around (1669-1649 cm^{-1}) show the presence of the aromatic ring, (1537 cm^{-1}) to vinyl segment, (1781-1749 cm^{-1}) to (-C=O str, ester), (1155 cm^{-1} -C-O str, ester), (1583-1524 cm^{-1}) to heteroaromatic ring (C=N) and (796 cm^{-1}) to (C-Cl).

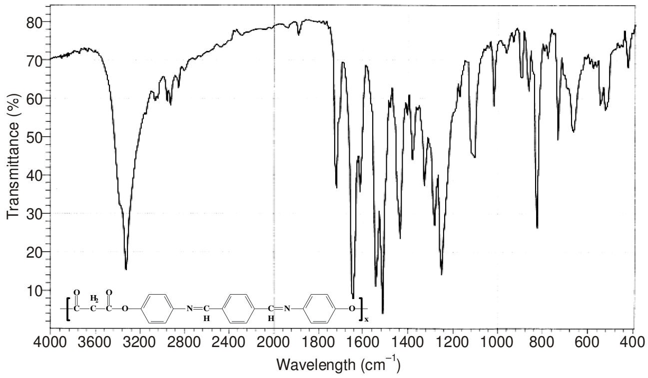


Fig. 10. FTIR spectrum of PE2

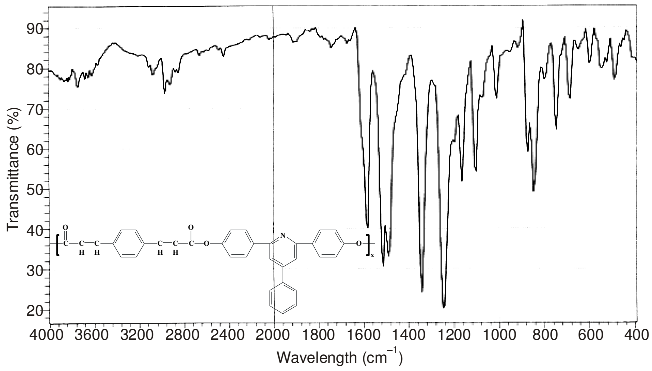


Fig. 11. FTIR spectrum of PE3

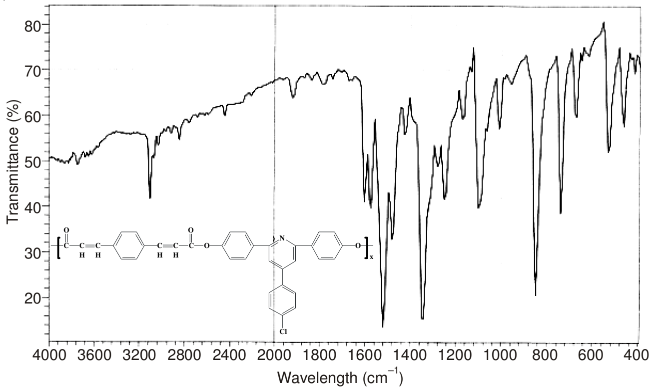


Fig. 12. FTIR spectrum of PE4

FTIR spectrum of PE5: The FTIR spectrum of PE5 as shown in (Fig. 13) which indicates absorption band at (3362 cm^{-1}) to (-NH$_2$ group), (3112 cm^{-1}) to (aromatic -CH stretching), (2812 cm^{-1}) to (aliphatic -CH stretching), absorption bands around (1642-1659 cm^{-1}) show the presence of the aromatic ring, (1532 cm^{-1}) to vinyl segment, (1743-1788 cm^{-1}) to (-C=O str, ester), (1163 cm^{-1} -C-O str, ester) and (1581-1529 cm^{-1}) to heteroaromatic ring (C=N).

FTIR spectrum of PE6: The FTIR spectrum of PE6 as shown in (Fig. 14) which indicates absorption band at (3122 cm^{-1}) to (aromatic –CH stretching), absorption bands around (1651-1638 cm^{-1}) show the presence of the aromatic ring, (1529 cm^{-1}) to vinyl segment, (1782-1747 cm^{-1}) to (-C=O str, ester), (1178 cm^{-1} -C-O str, ester) and (1579-1527 cm^{-1}) to heteroaromatic ring (C=N).

^{1}H NMR spectrum of PE6, is shown in Fig. 15 assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ (5.7), δ (6.7 -8.0) ppm (s, H) for Ar-H group.

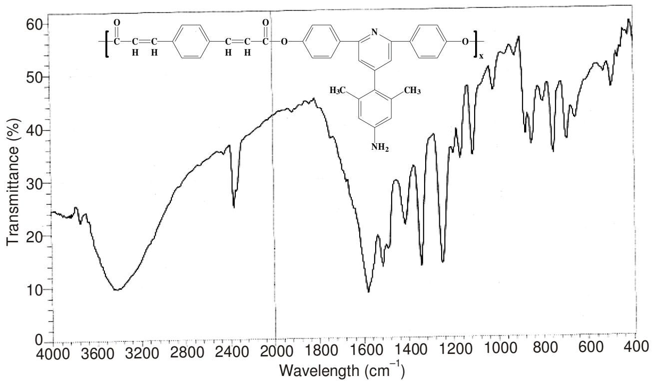


Fig. 13. FTIR spectrum of PE5

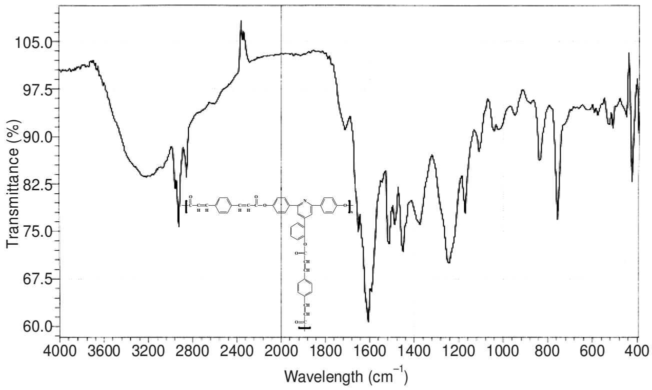


Fig. 14. FTIR spectrum of PE6

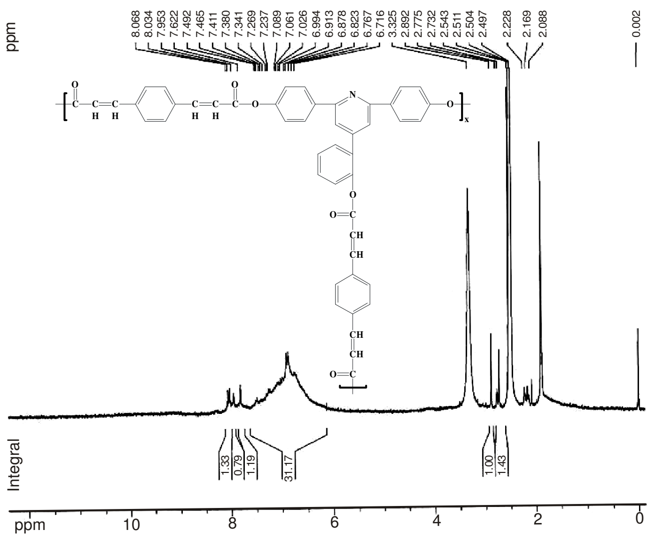


Fig. 15. ^{1}H NMR spectrum of PE6

Solubility of polyesters: Solubility of polyesters PE1-PE6 was qualitatively tested in organic solvents and the results are summarized in Table-3. The method that attempt to enhance their process abilities and solubilities were either by introducing bulky groups, flexible linkages, or molecular asymmetry into the polymer backbones. In this work, the attachment of bulky pendant groups in polymer backbone not only could provide an enhanced solubility because of decreased packing density and crystallinity, but also could impart an increase in T$_g$ by restricting the segmental mobility[18].

One of the major objectives of this work was producing polyesters with improved solubility. The solubility was investi-

TABLE-3
SOLUBILITY OF POLYESTERS: PE1-PE6

Solvent	Polyesters					
	PE1	PE2	PE3	PE4	PE5	PE6
DMAc	+ –	+ +	+ +	+ +	+ +	+ –
DMF	+ –	+ +	+ +	+ –	+ +	+ +
NMP	+ +	+ –	+ –	++	+ –	+ +
Pyridine	+ –	+ +	+ –	+ +	+ +	+ –
m-Cresol	+ +	+ –	+ + +	+ + +	+ –	+ +
THF	+ –	+ –	+ –	+ –	+ –	+ –
$CHCl_3$	+ –	+ +	+ +	+ +	+ +	+ –
CH_2Cl_2	+ +	+ +	+ –	+ –	+ –	+ +
DMSO	+ +	+ + +	+ +	+ –	+ +	+ +
Conc. H_2SO_4	+ –	+ +	+ +	+ –	+ –	+ +

Full Soluble. +++ Soluble at room.T. ++ Partially Soluble. + –.

gated as (0.03 g) of polymeric sample in (3 mL) of a solvent. All of the newly synthesized polyesters have good soluble in common polar and dipolar aprotic solvents without need for heating.

Conclusion

Polycondensation polymerization between di- and tri hydroxyl monomers was possible with dibutyltin dilaurate as catalysts for synthesis of polyesters containing methylene unit, Schiff-base linkages and pyridine hetero cyclic ring with 4-phenylenediacrylic acid and malonic acid, respectively at 160 ºC for 1 h. The polymers were characterized by proton nuclear magnetic resonance spectroscopy and infrared spectroscopy confirmed the molecular composition of four strictly alter-nating, highly ordered polyesters having methylene chains as flexible spacers and phenylene or pyridine heterocyclic groups as the rigid segments. In this work, the attachment of bulky pendant groups in polymer backbone not only could provide an enhanced solubility because of decreased packing density and crystallinity, but also could impart an increase in T_g by restricting the segmental mobility.

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