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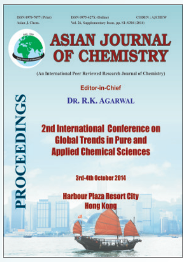

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Synthesis and Characterization of New Aromatic Co-Polyamides

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Six new aromatic Co-polyamides CoP_1-CoP_6 were prepared by direct Yamazaki's polycondensation reaction of various aliphatic and aromatic dicarboxylic acid (adipic acid, phthalic acid, terephthalic acid and 4-phenylenediacrylic acid) with new various types of aromatic diamine monomers: monomers containing flexible linkages (methylene group), Schiff-base diamine monomer and diamine monomer containing pyridine heterocyclic group and bearing bulky aromatic pendant groups in the 4-position of the pyridine ring, in the presence of LiCl in pyridine and triphenyl phosphite as condensing agents in N-methyl-2-pyrrolidinone as solvent. 4-Phenylenediacrylic acid (PPDAA) was prepared by the condensation reaction of terephthalaldehyde with malonic acid in the presence of pyridine. The monomers were characterized by FTIR and ^{1}H NMR. The resulting polyamides were characterized by FTIR and ^{1}H NMR and their physical properties including solubility, thermal stability and thermal behaviour were studied as well. All of these new polymers show good solubility in polar aprotic solvents and very good thermal stability.

Keywords: Co-polyamides, Aromatic Co-polyamides, Aromatic diamine monomers.

INTRODUCTION

Thermal characteristics are very important for all polymers processed by moulding, injection or spinning. This applies not only to the melting temperature, but also the temperature of decomposition, the crystallization temperature and other characteristics. In addition, the enthalpies of melting and crystallization are important for semi-crystalline polymers as well. The DSC study of all components of blends (used for any product prepared *via* melting) therefore gives basic information about the components' future behaviour in the blend and during processing[1].

Some properties of homopolymers are not always satisfying for their application in certain fields. Copolymer monomer based on a certain monomer with some amount of another, functional co-monomer may have specific characteristics which predestine this copolymer as raw material for products with better properties, or as an additive for homopolymer and may thus improve the properties of the product. Copolymers are able to improve many properties, including thermal properties[2,3].

Copolymer has one great advantage, good compatibility with relevant homopolymers and from this point of view the deterioration of the blend properties is lower. Semi-crystalline (block) copolymers can co-crystallize with homopolymers, several type of crystals with various sizes and levels of perfection can be formed and blocks of copolymer can create their own crystallites[4,5].

During the copolyamide formation both mechanisms are applicable, but different to such an extent that there are formed block rather than statistic copolyamides[6].

In the present paper the synthesis of a new types of aromatic Co-polyamides from various aliphatic and aromatic dicarboxylic acid (*e.g.*, adipic acid, phthalic acid, terephthalic acid and 4-phenylenediacrylic acid) with new aromatic diamines, has been reported whose light scattering and dilute solution behavior have been published elsewhere[7,8]. The polycondensation is carried out in the presence of triphenyl phosphite (TPP) in *N*-methyl-2-pyrrolidinone (NMP), pyridine mixture, containing 3 wt. % LiCl by the method of Yamazaki *et al.*[9]. Because of the low solubility of Co-polyamides, the polycondensation reaction terminates quickly and results in low molecular weight products. In order to do away with this problem, the polycondensation is carried out in the presence of LiCl[10,11].

EXPERIMENTAL

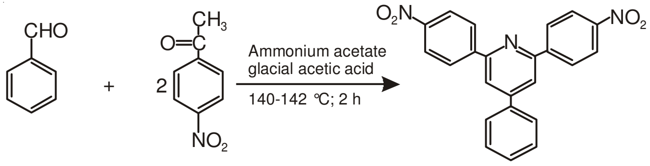
Fourier transform infrared (FTIR) spectra were recorded on a SHIMADZU-FTIR-8400S spectrometer (Japan) with KBr pellets in the optical range of 4000-400 cm^{-1}. ^{1}H NMR spectra were registered using a Bruker, 250 MHz, spectrometer, at Polymer Laboratories Co. Iran using DMSO as a solvent.

Differential scanning calorimetry (DSC) were measurements by DSC 131 Evo, Setaram, (France) using a heating rate of 10 °C/min in N$_2$ atmosphere within the temperature range of (30-600 °C). The sample weight used approximately (10 mg) mg. The peaks are used to determine the thermal properties of the samples. The solubility of the polymers was determined with (0.01 g) of a Co-polymer in (2 mL) of a solvent.

N-Methyl-2-pyrrolydinone (NMP) from (ALFA-PRODUCTS); absolute methanol, acetic acid, lithium chloride, palladium on charcoal 10 %, from (BDH, England); dichloromethane from (Biosolve); ammonium acetate, malonic acid and adipic acid from (Chem-supply). Hydrochloric acid, salicylaldehyde, from (HiMedia); diethyl ether from (IGCC, England); aniline, 3-chloroaniline, 2-bromoaniline, calcium chloride, benzaldehyde, 2,6-diamino pyridine, dimethyl sulphoxide (DMSO), glacial acetic acid, *m*-cresol, *N*,*N*-dimethylacetamide, 1,4-phenylene diamine, phthalic acid, terephthalic acid, piperidine, pyridine, terephthalaldehyde, triphenyl phosphite (TPP), tetrahydrofurane (THF), all from (MERCK); absolute ethanol from (Scharlab S.L); acetone, *p*-nitroacetophenone, all from (ALDRICH); *N*,*N*-dimethylformamide (DMF) from (Sinopharm Chemical Reagent); and hydrazine monohydrate from (THOMAS-BAKER).

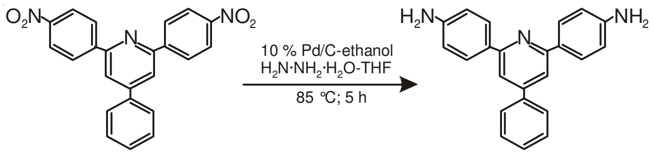
Synthesis of monomers

Synthesis of 4-phenyl-2,6-*bis*(4-nitrophenyl)pyridine (PNPP): In a round-bottomed flask (150 mL) equipped with a reflux condenser, a mixture of benzaldehyde (1.6 g, 15 mmol), *p*-nitro acetophenone (5 g, 30 mmol), ammonium acetate (15 g) and glacial acetic acid (37.5 mL) was refluxed at 140-142 °C for 2 h. Upon cooling, crystals separated, which were filtered and washed first with acetic acid (50 %) and then with cold ethanol. These dark yellow crystals were recrystallized from absolute ethanol and then dried at 60 °C under vacuum[12,13] to produce 4.88 g (82 % wt.) of very-deep yellow crystals: m.p. 240-244 °C (**Scheme-I**):



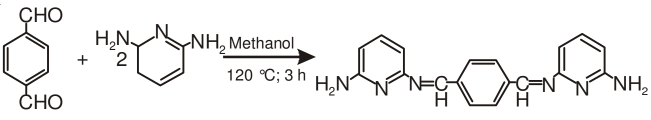
Scheme-I: Synthesis of [PNPP]

Synthesis of 4-phenyl-2,6-*bis*(4-aminophenyl)pyridine (PAPP) [M1]: (2 g, 5 mmol) of the (PNPP), 0.2 g of 10 % Pd/C and 100 mL of ethanol were introduced into a three-necked flask to which 20 mL of hydrazine monohydrate was added dropwise over a period of 1 h at 85 °C. After completing the addition, the reaction was continued at reflux temperature for another 4 h. To the suspension, 40 mL of THF was added to re-dissolve the precipitated product and refluxing was continued for 1 h. The mixture was filtered to remove the Pd-C and the filtrate was poured into water. The product was filtered off, washed with hot water and dried in vacuum[14,15] to yielding 1.45 g (85 % wt.) of light brown crystals: m.p. 105 °C (**Scheme-II**).



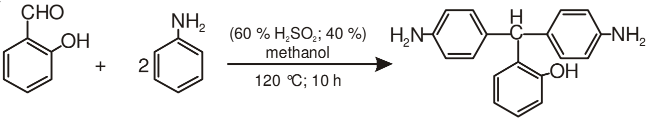
Scheme-II: Synthesis of M1

Synthesis of 1,4-*Bis*(6-aminopyridin-2-ylimino)-dimethylene benzene [M2]: This monomer was prepared by the condensation of terephthalaldehyde (3 g, 22 mmol) and 2,6-diamino pyridine (5 g, 46 mmol) in 15 mL of methanol, by boiling the mixture under reflux at 120 °C for 3 h. The precipitate was filtered and recrystallized from methanol and dried in a vacuum desiccators[16] to yielding 6.8 g (98 % wt) of white crystals; m.p. 71-74 °C (**Scheme-III**).



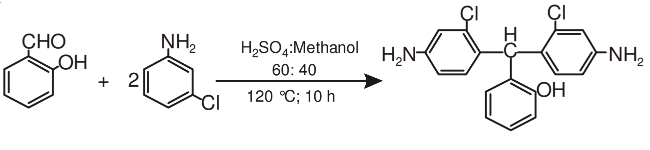
Scheme-III: Synthesis of M2

Synthesis of 2-[*bis*(4-aminophenyl)methyl]phenol [M3]: To a 0.1 M solution of H$_2$SO$_4$ in methanol (60 %: 40 %), aniline (2 g, 21 mmol) and salicylaldehyde (1.2 g, 10 mmol) were added and the mixture was refluxed at 120 °C for 10 h with constant stirring. Upon completion of the reaction, the solvent was removed under vacuum and to the residue water (2 × 25 mL) and then CH$_2$Cl$_2$ (50 mL) were added. The organic extract was dried over anhydrous[17] Na$_2$SO$_4$ to yielding 2.3 g (79 % wt.) of deep yellow crystals: m.p. 75-95 °C (**Scheme-IV**).

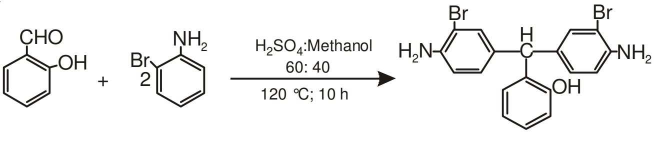


Scheme-IV: Synthesis of M3

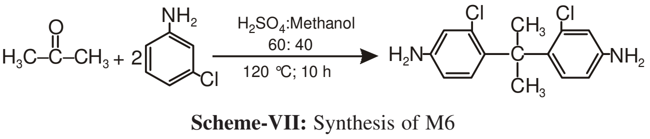
The other diamino compounds were prepared by the same procedure as above using 3-chloro aniline with salicylaldehyde (M5), 2-bromo aniline with salicylaldehyde (M6), 3-chloro aniline with acetone (M7), 2-bromo aniline with acetone (M8), respectively, are shown in (Table-1) (**Schemes V** to **VIII**).



Scheme-V: Synthesis of M4



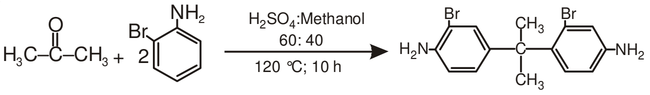
Scheme-VI: Synthesis of M5



Scheme-VII: Synthesis of M6

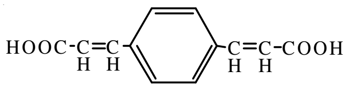
TABLE-1
SYNTHESIS AND PHYSICAL PROPERTIES OF MONOMERS (M4, M5, M6, M7)

Monomers	Substance		Weight (g)	Yield (% wt)	Color	m.p. (°C)
	Aniline or derived	Benzaldehyde derived or acetone				
M4 [2-(*bis*(4-amino-3-chlorophenyl)methyl)phenol]	2.69 g (21 mmol)	1.22 g (10 mmol)	2.6	72	Deep green	240 Decomp.
M5 [2-(*bis*(4-amino-3-bromophenyl)methyl)phenol]	3.6 g (21 mmol)	1.22 g (10 mmol)	3.36	75	Deep brown	130 Decomp.
M6 [4,4'-(propane2,2-diyl)*bis*(2-chloroaniline)]	2.69 g (21 mmol)	0.58 g (10 mmol)	2.3	78	Black	Viscous
M7 [4,4'-(propane2,2-diyl)*bis*(2-bromoaniline)]	3.6 g (21 mmol)	0.58 g (10 mmol)	2.9	76	Black	Viscous



Scheme-VIII: Synthesis of [M7]

Synthesis of 4-phenylenediacrylic acid [PPDAA]: In a 100 mL round-bottomed flask were added terephth-alaldehyde (3.48 g, 26 mmol), malonic acid (8.27 g, 94 mmol) to 30 mL of pyridine containing small amount of piperidine. The reaction mixture was stirred for 2 h at 45 °C, 4 h at 80 °C and 3 h at 110 °C, respectively. The solution was poured into large amount of distilled water and neutralized with 10 % HCl to obtain white precipitate. The precipitate was filtered, washed with water, acetic acid and acetone and then dried in a vacuum oven at room temperature[18] to give 5.1 g (90 % wt) of white crystals; m.p. 222-225 °C (**Scheme-IX**).



Scheme-IX: Structure of PPDAA

Synthesis of Co-polyamides [CoP$_1$-CoP$_6$]: A typical procedure was described as follows. In a three-necked flask equipped with a reflux condenser and N_2 inlet, dicarboxylic acid and diamines (Table-2) were added. Then (2 g) dried lithium chloride, (14 mL) N-methyl-2-pyrrolidinone, (2.8 mL) pyridine and (2.8 mL) triphenyl phosphite were charged. The resulting mixture was reacted at 120 °C for 2 h under the nitrogen atmosphere. After the polymerization, the viscous mixture was poured into (200 mL) methanol. The Co-polymer was filtered and washed by methanol and hot water and then dried at 100 °C for 12 h in vacuum[19] **(Scheme-X and XI)**.

RESULTS AND DISCUSSION

The FTIR spectrum of (PNPP) indicated absorption band at (1500 cm^{-1}), (1340 cm^{-1}) to (-NO_2) asymmetric and symmetric stretching, respectively, absorption bands around (1676-1622 cm^{-1}) show the presence of the aromatic ring and (1550-1520 cm^{-1}) to heteroaromatic ring (C=N).

In the FTIR spectrum of (M1), the characteristic absorptions of the nitro group disappeared and (-NH_2) stretching absorption bands of the amino group appeared at (3380 cm^{-1}).

^{1}H NMR spectrum of (M1), is assigns the following chemical shifts; δ(2.5) ppm for DMSO, 5.6 (s, 4H) for NH_2 group, δ(6.1-8.5) ppm (s, 15H) for ArH group.

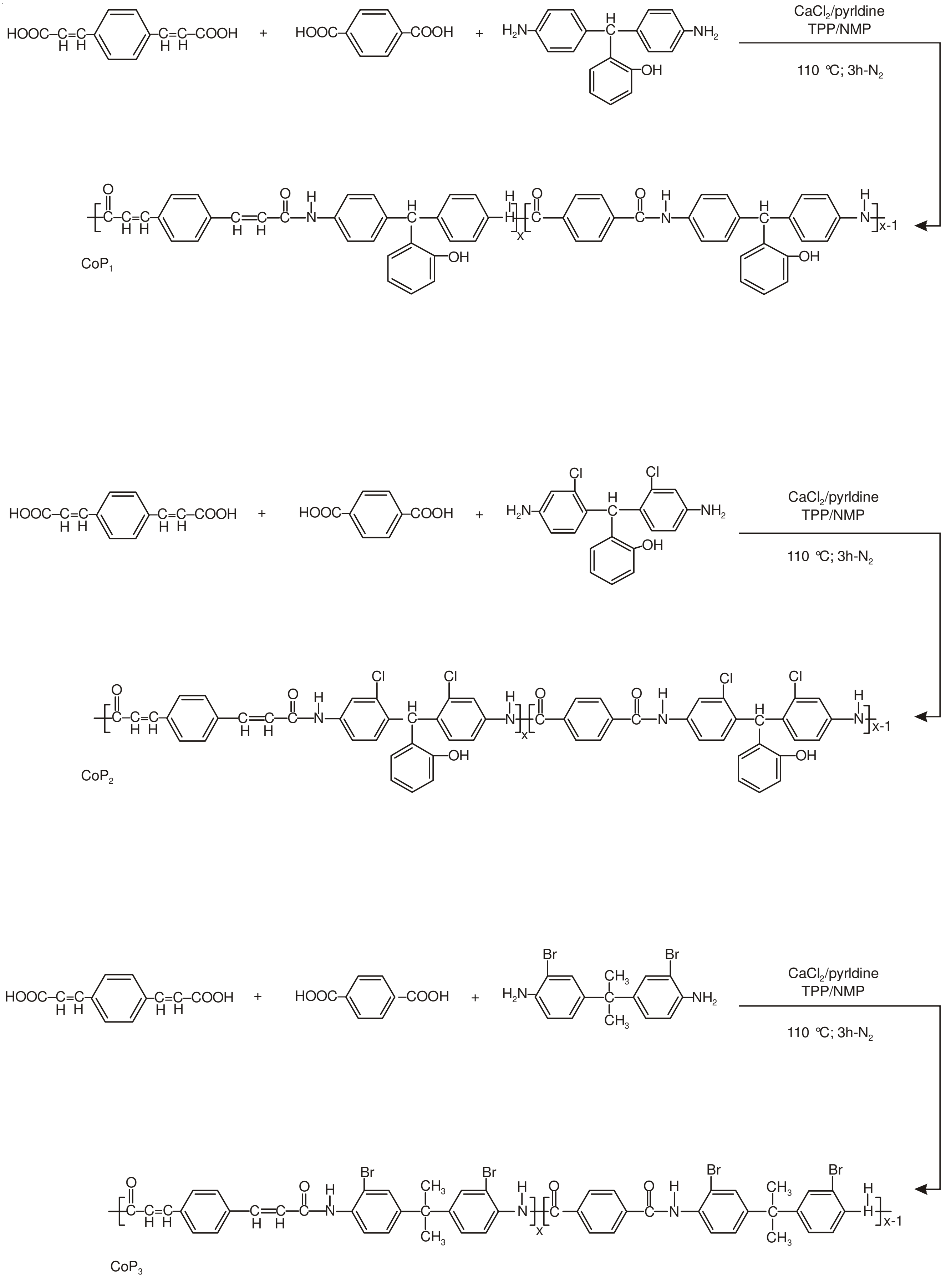
The FTIR spectrum of (M2 Schiff-base) which indicates absorption bands at (3625 cm^{-1}) to (-NH_2 group), (3070 cm^{-1}) to (aromatic -CH stretching), (2916 cm^{-1}) to (aliphatic -CH stretching), absorption bands around (1610-1542 cm^{-1}) show the presence of the aromatic ring and (1519-1504 cm^{-1}) to heteroaromatic ring (C=N).

The FTIR spectrum of (M3) indicated absorption bands at (3440 cm^{-1}) to (-NH_2 group), absorption band at (3370 cm^{-1}) to (-OH group), (3108 cm^{-1}) to (aromatic -CH stretching), (2905 cm^{-1}) to (aliphatic -CH stretching) and absorption bands around (1606-1540 cm^{-1}) show the presence of the aromatic ring. The characteristic absorption of (C=O aldehyde) disappeared.

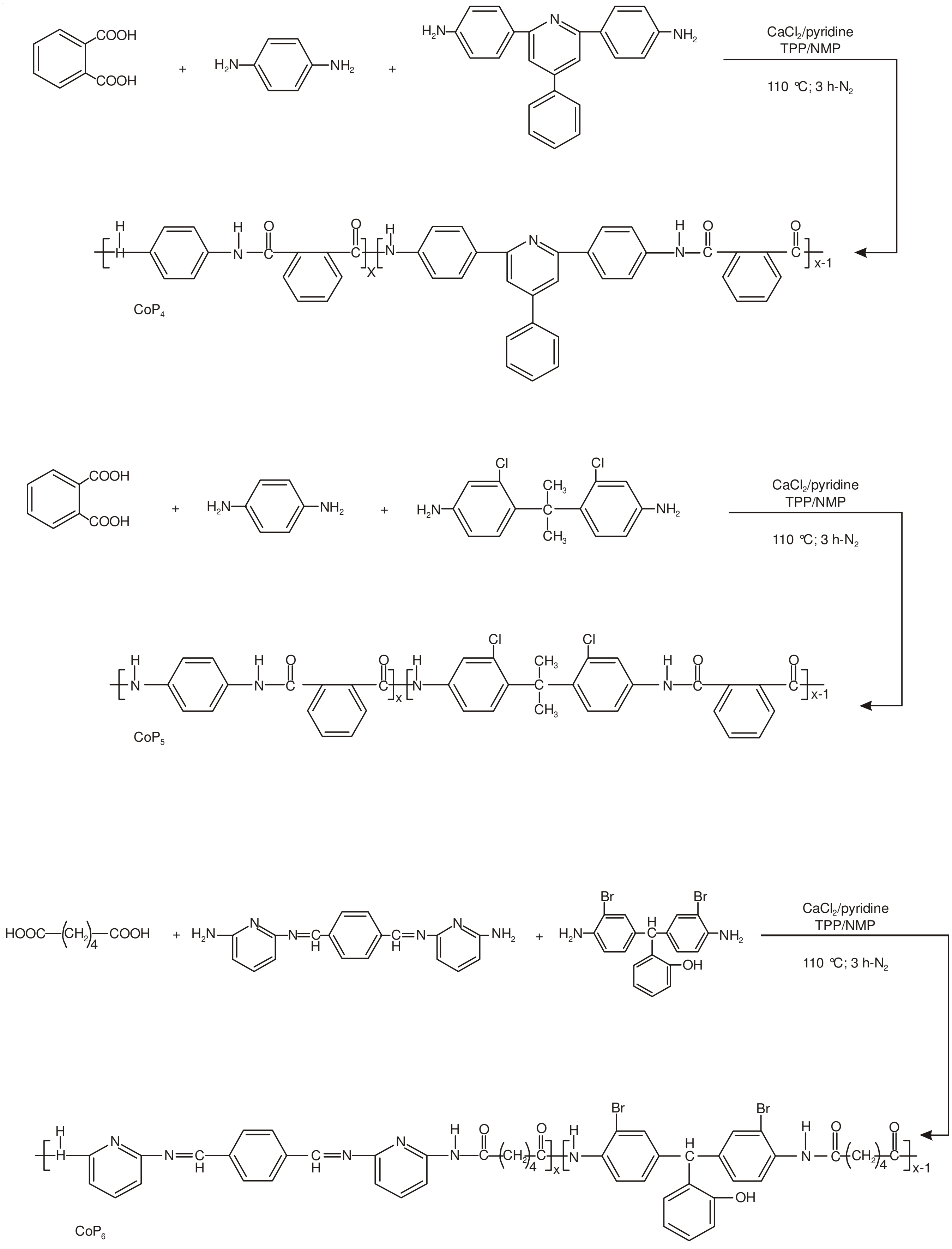
The FTIR spectrum of (M4) indicated absorption bands at (3415 cm^{-1}) to (-NH_2 group), absorption band at (3388 cm^{-1})

TABLE-2
SYNTHESIS OF CO-POLYAMIDES (CoP^1-CoP^6)

Co-polyamides	Monomers		Diacid (g/mmol)	Diamine (g/mmol)	Yield (% wt)	Color
	Diacid	Diamine				
CoP$_1$	PPDAA Terephthalic acid	M3 /	0.654 / 3 0.332 / 2	1.450 / 5 /	80	Light green
CoP$_2$	PPDAA Terephthalic acid	M4 /	0.654 / 3 0.332 / 2	1.800 / 5 /	79	Brown
CoP$_3$	PPDAA Terephthalic acid	M7 /	0.654 / 3 0.332 / 2	1.920 / 5 /	80	Light brown
CoP$_4$	Phthalic acid /	1,4-Phenylene diamine M1	0.830 / 5 /	0.324 / 3 0.710 / 2	82	Yellow
CoP$_5$	Phthalic acid /	1,4-Phenylene diamine M6	0.830 / 5 /	0.324 / 3 0.600 / 2	81	Brown
CoP$_6$	Adipic acid /	M2 M5	0.730 / 5 /	0.948 / 3 0.896 / 2	79	Brown



Scheme-X: Synthesis of CoP_1-CoP_3



Scheme-XI: Synthesis of CoP_4-CoP_6

to (-OH group), (3107 cm^{-1}) to (aromatic -CH stretching), (2918 cm^{-1}) to (aliphatic -CH stretching) and absorption bands around (1608-1510 cm^{-1}) show the presence of the aromatic ring and (721 cm^{-1}) to (C-Cl). The characteristic absorption of (C=O aldehyde) disappeared.

^{1}H NMR spectrum of (M4), assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ(5.8) ppm (s, 1H) for C-H group, 6.2 (s, 4H) for NH_2 group, δ(6.3-8.6) ppm (s, 10H) for ArH group, 6.01 (s, 1H, OH) δ (2.135) ppm (s, 2H) for N-OH group.

The FTIR spectrum of (M5) indicated absorption bands at (3415 cm^{-1}) to (-NH_2 group), absorption band at (3376 cm^{-1}) to (-OH group), (3103 cm^{-1}) to (aromatic -CH stretching), (2932 cm^{-1}) to (aliphatic -CH stretching) and absorption bands around (1614-1521 cm^{-1}) show the presence of the aromatic ring and (552 cm^{-1}) to (C-Br). The characteristic absorption of (C=O aldehyde) disappeared.

^{1}H NMR spectrum of (M5), assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ(6.2) ppm (s, 1H) for C-H group, 6.0 (s, 4H) for NH_2 group, δ(6.2 -8.9) ppm (s, 10H) for ArH group, 5.7 (s, 1H, OH) group.

The FTIR spectrum of (M6) indicated absorption bands at (3425 cm^{-1}) to (-NH_2 group), absorption band at (3100 cm^{-1}) to (-OH group), (3107 cm^{-1}) to (aromatic -CH stretching), (2918 cm^{-1}) to (aliphatic -CH stretching) and absorption bands around (1608-1510 cm^{-1}) show the presence of the aromatic ring and (725 cm^{-1}) to (C-Cl). The characteristic absorption of (C=O aldehyde) disappeared.

The FTIR spectrum of (M7) indicated absorption bands at (3415 cm^{-1}) to (-NH_2 group), absorption band at (3300 cm^{-1}) to (-OH group), (3100 cm^{-1}) to (aromatic -CH stretching), (2932 cm^{-1}) to (aliphatic -CH stretching) and absorption bands around (1614-1523 cm^{-1}) show the presence of the aromatic ring and (554 cm^{-1}) to (C-Br). The characteristic absorption of (C=O aldehyde) disappeared.

The FTIR spectrum of (CoP_1) indicated absorption bands at (3378 cm^{-1}) to (-OH group), (3208 cm^{-1}) to (aromatic -CH stretching), (2901 cm^{-1}) to (aliphatic -CH stretching), absorption bands around (1610-1536 cm^{-1}) show the presence of the aromatic ring, the sharp band at (1616 cm^{-1}) to (C=O amide) and (1544 cm^{-1}) to vinyl segment.

^{1}H NMR spectrum of (CoP_1), assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ (8.5) ppm for HC=CH δ (6.3-8.6) ppm (s, 10H) for ArH group, 5.7 (s, N-H) group.

The FTIR spectrum of (CoP_2) which indicated absorption bands at (3335 cm^{-1}) to (-OH group), (3123 cm^{-1}) to (aromatic -CH stretching), (2915 cm^{-1}) to (aliphatic -CH stretching), absorption bands around (1603-1511 cm^{-1}) show the presence of the aromatic ring, the sharp band at (1621 cm^{-1}) to (C=O amide), (1524 cm^{-1}) to vinyl segment and (808 cm^{-1}) to (C-Cl).

^{1}H NMR spectrum of (CoP_2), assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ (6.2) ppm (s, 1H) for C-H group, 6.0 (s, 4H) for NH_2 group, δ (6.2 -8.9) ppm (s, 10H) for ArH group, 5.7 (s, 1H, OH) group.

The FTIR spectrum of (CoP_3) which indicated absorption bands at (3200 cm^{-1}) to (aromatic -CH stretching), (2923 cm^{-1}) to (aliphatic -CH stretching), absorption bands around (1610-1549 cm^{-1}) show the presence of the aromatic ring, the sharp band at (1619 cm^{-1}) to (C=O amide), (1537 cm^{-1}) to vinyl segment and (748 cm^{-1}) to (C-Br).

The FTIR spectrum of (CoP_4) which indicated absorption band at (3210 cm^{-1}) to (aromatic-CH stretching), absorption bands around (1654-1633 cm^{-1}) show the presence of the aromatic ring, (1570-1511 cm^{-1}) to heteroaromatic ring (C=N) and the sharp band at (1588 cm^{-1}) to (C=O amide).

^{1}H NMR spectrum of (CoP_4), assigns the following chemical shifts; δ (2.5) ppm for DMSO, δ (6.1) ppm (s,1H) for N-H group, δ (6.7 -8.5) ppm for Ar-H group.

The FTIR spectrum of (CoP_5) which indicated absorption bands at (3213 cm^{-1}) to (aromatic -CH stretching), (2943 cm^{-1}) to (aliphatic -CH stretching), absorption bands around (1608-1538 cm^{-1}) show the presence of the aromatic ring, the sharp band at (1630 cm^{-1}) to (C=O amide) and (818 cm^{-1}) to (C-Cl).

The FTIR spectrum of (CoP_6) which indicated absorption band at (3315 cm^{-1}) to (-OH group), (3207 cm^{-1}) to (aromatic -CH stretching), absorption bands around (1645-1627 cm^{-1}) show the presence of the aromatic ring, (1547-1498 cm^{-1}) to heteroaromatic ring (C=N), the band at (1634 cm^{-1}) to (C=O amide) and (687 cm^{-1}) to (C-Br).

Differential scanning calorimetry study: From the DSC curves, the glass transition temperature (T_g), the crystallization temperature (T_c) and the melting temperature (T_m) were measured. The endothermic peaks of copolyamides are related to melting temperature. This increased in T_m is assigned to the linear terephthalic acid and *p*-phennylenediacrylic acid moieties incorporated into the polymer back bone during synthesis of co-polyamide. Hence , T_m is higher fore CoP_1, CoP_2, CoP_4 and CoP_5 as the polymer chain more rigid parts and/or a polymer contains less free volume. Samples usually showed multiple endotherms which are explained as due to the fusion of different population of crystallites with different sizes. As expected , T_m values are lower for CoP_3 and CoP_6) due to the higher chain flexibility of the formers afforded with increasing the amount of methylene of polymeric back bone and steric hindrance of terminal functional groups can influence T_m of resultant polymers. In addition, the polymer CoP_6, has the lowest thermal stability than the other polymers containing rigid pyridine and phenylene moieties. This behaviour can be explained by the presence of methylene units which are more vulnerable to thermo-oxidative processes[21-23].

Glass transition temperature (T_g) of all co-polyamides were in the range (236-254 °C), in case of copolyamides (CoP_1, CoP_2, CoP_3, CoP_4, CoP_5 and CoP_6) it is interesting to note that the change of the diacids had a noticeable T_g difference. In addition, endothermic peaks above their glass transition temperatures were observed in DSC scans, which may be attributed to the crystalline molecular structure for all co-polamides. The higher in T_g of (CoP_1, CoP_2, CoP_4 and CoP_5) compared to that analogous co-polyamides might be endorsed to the existence of hetroaromatic pyridine rings and phenylene moieties. This increased in T_g is assigned to the linear terephthalic and *p*-phennylenediacrylic acids moieties incorporated into the polymer back bone during synthesis of co-polyamide. Particularly, the end group contribution becomes significant[24]. Thus it will be interesting to introduce different chain ends using substitution reaction since end group modification in (CoP_1, CoP$_2$, CoP$_3$ and CoP$_5$) had a strong effect on T$_g$ as observed in previous studies[24-26]. Usually, amore polar functional group causes T$_g$ to be higher. T$_g$ of co-polyamides may be strongly dependent on the inter-association of functional groups with the neighboring molecule as well as the volume fraction occupied by terminal groups[26]. It seems that several factors such as the rigidity, polarity, length and steric hindrance of terminal functional groups can influence T$_g$ of resultant polymers. DSC data indicated that the CoP$_3$ containing symmetric dimethyl substituted resulted in lower T$_g$ value than that of unsubstituted co-polyamides. The consideration of segmental symmetry is useful in explaining this behavior. The dimethyl substitution leads to an symmetric segment which can result in less efficient chain packing and hence more free volume that led to relatively easier chain mobility of polymer segments in comparison with asymmetrical substituted and unsubstituted Co-polyamides, ultimately leading to decrease in glass transition temperature. The T$_g$, T$_m$ and T$_c$ obtained from DSC are reported in Table-3.

TABLE-3
THE GLASS TRANSITION, MELTING TEMPERATURE AND CRYSTALLIZATION TEMPERATURE OBTAINED FROM DSC

Samples	T$_m$ (°C)	T$_g$ (°C)	T$_c$ (°C)
CoP$_1$	510	248	272
CoP$_2$	531	254	288
CoP$_3$	461	236	272
CoP$_4$	502	240	264
CoP$_5$	510	250	290
CoP$_6$	416	238	290

Solubility of Co-polyamides: Solubility of Co-polyamides CoP$_1$-CoP$_6$ was qualitatively tested in organic solvents and the results are summarized in (Table-4). The method that attempt to enhance their processabilities 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[27].

One of the major objectives of this work was producing Co-polyamides with improved solubility. The solubility was investigated as 0.02 g of polymeric sample in 5 mL of solvent. All of the newly synthesized Co-polyamides have good soluble in common polar and dipolar aprotic solvents without need for heating.

TABLE-4
SOLUBILITY OF CO-POLYAMIDES: CoP$_1$-CoP$_6$

Solvent	Co-Polyamides					
	CoP$_1$	CoP$_2$	CoP$_3$	CoP$_4$	CoP$_5$	CoP$_6$
DMAc	++	++	++	+++	+ -	+ -
DMF	++	++	++	+ -	++	+ -
NMP	+ -	+ -	+ -	++	+ -	++
Pyridine	+ -	++	++	++	++	+ -
m-Cresol	+++	+++	+++	+++	+ -	++
THF	++	++	+ -	+ -	+ -	+ -
CHCl$_3$	+ -	+ -	++	++	++	+ -
CH$_2$Cl$_2$	++	+++	++	+ -	+ -	++
DMSO	+++	+++	++	++	++	++
Conc. H$_2$SO$_4$	++	++	+ -	++	+ -	++

Full soluble +++; Soluble at room temp. ++; Partially soluble + -

Conclusion

Six new aromatic Co-polyamides have been synthesized. For this purpose, a typical polycondensation process has been followed under mild conditions. The reaction variables, such as temperature, time, monomer concentration, solvent system *etc*. have been found to have strong influence on the molecular weight of the polymers. Synthesis of Co-polyamides containing methylene unit, Schiff-base linkages and pyridine hetero cyclic ring with adipic acid, phthalic acid, terephthalic acid and 4-phenylenediacrylic acid, respectively at 120 °C for 2 h under the nitrogen atmosphere. The polymers were characterized by proton nuclear magnetic resonance spectroscopy and infrared spectroscopy confirmed the molecular composition of six strictly alternating, highly ordered Co-polyamides having methylene chains as flexible spacers and phenylene or pyridine hetryclic groups as the rigid segments. From the DSC curves, the glass transition temperature, the crystallization temperature and the melting temperature were measured. All the polymers showed a glass transition temperature, in the range of 236-256 °C. The higher in T$_g$ of (CoP$_1$, CoP$_2$, CoP$_4$ and CoP$_5$) compared to that analogous Co-polyamides might be endorsed to the existence of hetroaromatic pyridine rings and phenylene moieties. This increased in T$_g$ is assigned to the linear terephthalic and *p*-phennylenediacrylic acids moieties incorporated into the polymer back bone during synthesis of Co-polyamide. In the same time, the presence of symmetric dimethyl substituted together with ether linkages brings much more flexibility to the macromolecular chain and decreases the glass transition of the polymers CoP$_3$ and CoP$_6$. The melting temperatures of the CoP$_3$ and CoP$_6$ decrease with increasing the amount of methylene of polymeric backbone and steric hindrance of terminal functional groups. The CoP$_6$ has the lowest melting point among the series of the result and Co-polyamides . T$_m$ is higher fore CoP$_1$, CoP$_2$, CoP$_4$ and CoP$_5$ as the polymer chain more rigid parts and/or a polymer contains less free volume. All of these new polymers show good solubility in polar aprotic solvents and good thermal stability.

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