

New Derivative Benzothiazole Suspend Diphenylamine Based Aromatic Polyamides as Electrochromic Light Emitting Devices

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In this work, a set of some substituted aromatic polyamides containing (benzothiazole)diphenylamine moieties (**P1-P5**) was prepared via the phosphorylation polycondensation technique from the reaction of several aromatic dicarboxylic acids with synthesized N,N-bis(4-aminophenyl)-2-amine-6-methoxybenzothiazole (**M**). It was prepared from the cesium fluoride-mediated double N-arylation reaction of 6-methoxybenzothiazole (**a**) with *p*-fluoronitrobenzene to form dinitro intermediate (**I**) followed by palladium-catalyzed hydrazine reduction. FTIR, ¹H and ¹³C NMR spectra techniques were utilized to characterize the chemical structures of all the resultant intermediates and polyamides. Thermal analysis revealed that the synthesized polyamides showed perfect thermal stability and superior glass transition temperatures (*T_g*). Dilute solutions of these polyamides in N-methyl pyrrolidone (10⁻⁵ M) showed good optical properties where exhibited intensive photoluminescence in the region of blue colour. Cyclic voltammograms of the synthesized polymers membrane molding onto the basis of ITO-plated glass in the special electrolyte contains 10⁻¹ M of tetrabutylammonium perchlorate (TBAP) in dry CH₃CN which exhibited one oxidation redox wave couples.

Keywords: Polyamides, Photoreceptor, Electrochromic, Photoluminescence.

INTRODUCTION

Most of the aromatic polyamides are a type of high active polymers because of their perfect mechanical behaviour, high chemical resistance and high thermal stability [1-3]. Many attempts have been done to enhance the solubility and process ability of these polymers through constitutional improvement of their monomers [4-6].

In modern studies, polyamides materials have been quite used in organic electronic-devices like light-emitting diodes, transistors [7,8]. Aromatic amines always used in structure of hole-emitting polymers in the electronic diodes as electro-acceptor diodes [9] and organic light emitting devices (OLEDs) [10,11]. All electro-acceptor polyamides gave reversible visible changes in absorption or transmittance upon electrochemically oxidized or reduced like conjugated polymers, inorganic coordination and transition-metal oxides complexes [12,13].

Triphenylamine (TPA) and diphenylamine (DPA) are recognized for their electro and photoactive behaviours lead to operate as photo electronic applications in electro-

photography, electro-luminescent devices, electronic transistors, photo cells and electrochromic or electrofluorochromic diodes [14-18].

Triphenylamines are known readily oxidized to product stable radical cations provided that the *para*-position of the phenyl group with the oxidation process are still kept and are always done with a strong different in colours. During the late years, a large number of excellent-application of aromatic polyamides and its polyimides with strong and active redox groups (DPA and TPA), have been synthesized to use for electrochromic purpose [19,20].

EXPERIMENTAL

2-Amino-6-methoxybenzothiazole (Merck, 98 %), 4-fluorobenzonitrile (Acros, 98.7 %), cesium fluoride, (Acros, 98 %), dimethylsulfoxide (DMSO) (Merck, 98 %), 10 % palladium on charcoal (Pd/C), (Fluka), ethanol (Merck, 99.7 %), triphenylphosphite (Merck, 97 %), CaCl₂ (Merck, 99 %), N-methyl pyrrolidone (NMP) (Aldrich, 98 %), terephthalic

acid (Aldrich, 97 %), isophthalic acid (Aldrich, 97 %), 1,4-dicarboxylic naphthalene acid (Aldrich, 94 %), biphenyl-4,4'-dicarboxylic acid (Aldrich, 97 %), 4,4'-oxydibenzoic acid (Aldrich, 98 %).

Characterization technique: The spectrum of FT-IR for all compounds was performed by a Spotlight 400 Perkin-Elmer spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) data are recorded by a JEOL spectrometer. UV-visible absorption and photoluminescence spectrum were performed in (10^{-5} M) N-methyl pyrrolidone on a Cary 60 UV-visible spectrophotometer.

The measurements of X-ray were recorded by $\text{CuK}\alpha$ radiation beam (1 $\frac{1}{4}$ 1.541_A) with Max Flax (CMF) mirror. Thermal and decomposition measurements were performed on a Perkin Elmer DSC6 instrument under N_2 atmosphere with a scan rate of $20^\circ\text{C}/\text{min}$ and an SDT Q600 thermogravimetric analyzer.

Synthesis of diphenylamine-diamine monomer (M)

Synthesis of 4,4-dinitro-6-methoxybenzothiazole-diphenylamine (I): In a round bottom flask 250 mL with a magnetic bar, 5.4 g (0.03 mol) (2-amino, 6-methoxybenzothiazol) (**a**), 8.46 g (0.06 mol) *p*-fluoronitrobenzene and 9.20 g (0.06 mol) of CsF in 80 mL (DMSO) were refluxed to 120°C for 20 h. The final solution was stream into 200 mL solution $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1) to get precipitate after filtration washed with methanol and water several times and recrystallized from (DMF)/methanol to give dark yellow solid crystals 10.38 g (yield 82 %) of dinitro compound (**I**) m.p. $292-294^\circ\text{C}$. Anal. calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_5\text{S}$ (422.42): C, 56.87; H, 3.34; N, 13.26; O, 18.94; S, 7.59. Found: C, 56.62 %; H, 2.96 %; N, 13.46 %; O, 18.77 %. FT-IR: 1576, 1344 ($-\text{NO}_2$), 1234, 1194, 1139, 1060 (benzothiazole). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.05-7.98 (d, 4H, Ha), 7.58-7.47 (d, 2H, Hc), 7.47-7.38 (d, 4H, Hb), 7.05-6.97 (d, 1H, Hd), 3.83 (s, 3H, H_{OCH_3}). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ , ppm): 174.55 (C_4), 156.76 (C_9), 148.62 (C_3), 145.52 (C_6), 137.43 (C_{10}), 131.92 (C_5), 124.84 (C_1), 122.93 (C_2), 118.21 (C_8), 114.64 (C_{11}), 104.92 (C_7), 55.81 (C_{CH_3}).

Synthesis of 4,4-diamino-6-methoxybenzothiazole-diphenylamine monomer (M): In a 250 mL stirred round flask, 10 g (0.024 mol) dinitro intermediate, 0.20 g 10 wt % Pd/C, 10 mL $\text{NH}_2\text{-NH}_2$ hydrate in 120 mL Et-OH are refluxed at 130°C for 12 h. Then the Pd/C powder was separated by filtration of the hot crude and cooled to form a pale white precipitate crystal after filtration and dried *in vacuo* at 80°C to give 8.15

g (yield 75 %) of diamine (**M**) as pale white crystals **Scheme-I**. mp: $262-264^\circ\text{C}$. FT-IR: 3326, 3272 cm^{-1} ($-\text{NH}_2$ stretch.). Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{OS}$ (362.45): C, 66.28; H, 5.01; N, 15.46; O, 4.41; S, 8.85. Found: C, 66.56 %; H, 5.21 %; N, 15.63 %. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.58-7.50 (d, 2H, Hc), 7.11-7.06 (d, 4H, Ha), 7.02-6.96 (d, 1H, Hd), 6.12-6.05 (d, 4H, Hb), 4.53 (s, 2H, H_{NH_2}), 3.82 (s, 3H, H_{OCH_3}). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, δ , ppm): 174.53 (C_4), 156.72 (C_9), 145.54 (C_6), 137.91 (C_{10}), 132.51 (C_3), 131.91 (C_5), 131.22 (C_2), 118.20 (C_8), 117.22 (C_1), 114.62 (C_{11}), 104.91 (C_7).

Synthesis of polyamides (P1-P5)

Synthesis of polyamide(P1): Synthesized polyamide (**P1**) was the example to explain the main synthetic path which used to prepare all the polymers. In a 50 mL stirred round-bottom flask, 1.10 g (0.002 mol) diamine monomer (**M**), 0.50 g (0.002 mol) of terephthalic acid **R1**, 3.0 mL triphenylphosphite (TPP), 4.0 mL NMP, 1.0 mL pyridine and 0.30 g CaCl_2 . The flask was refluxed at 120°C for 3 h. The solution of polyamide product was poured into 200 mL of CH_3OH with stirring gave a fibrous, dark brown precipitate after filtration and washed completely by methanol and hot water and dried [21], (1.15 g (78 % yield) m.p. $331-334^\circ\text{C}$ **Scheme-II**. FT-IR (film): 3320 (amide N-H stretch), 1664 cm^{-1} (amide $\text{C}=\text{O}$ stretch). All polyamides were synthesized by same method.

Synthesis of polyamide (P2): This polyamide was synthesized by the same route as explained in method of **P1**. Pale brown (72 % yield), m.p. $321-323^\circ\text{C}$. FT-IR (film): 3332 (N-H stretch for amide part), 1667 cm^{-1} (amide $\text{C}=\text{O}$ stretch group).

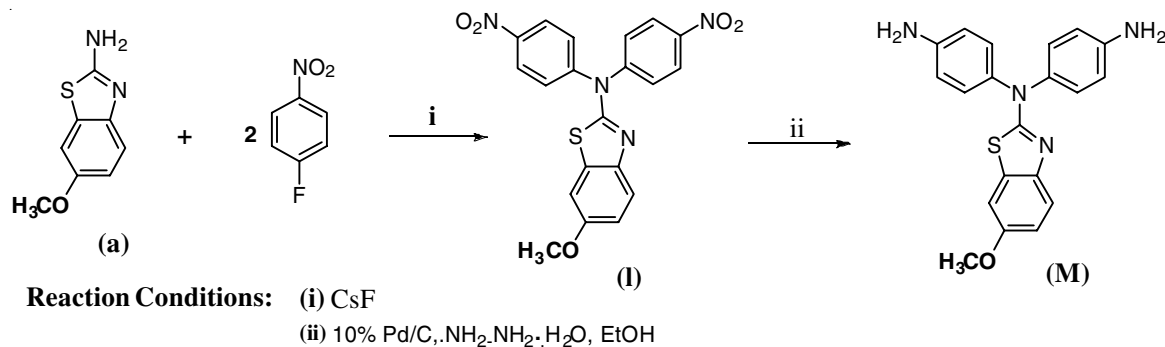
Synthesis of polyamide (P3): This polyamide was synthesized by the same route as explained in method of **P1**. Pale brown, (81 % yield), m.p. $332-334^\circ\text{C}$. FT-IR (film): 3336 (N-H stretch for amide part), 1662 cm^{-1} (amide $\text{C}=\text{O}$ stretch).

Synthesis of polyamide (P4): This polyamide was synthesized by the same route as explained in method of **P1**. Black brown, (68 % yield), m.p. $322-324^\circ\text{C}$. FT-IR (film): 3330 (N-H stretch for amide part), 1665 cm^{-1} (amide $\text{C}=\text{O}$ stretch).

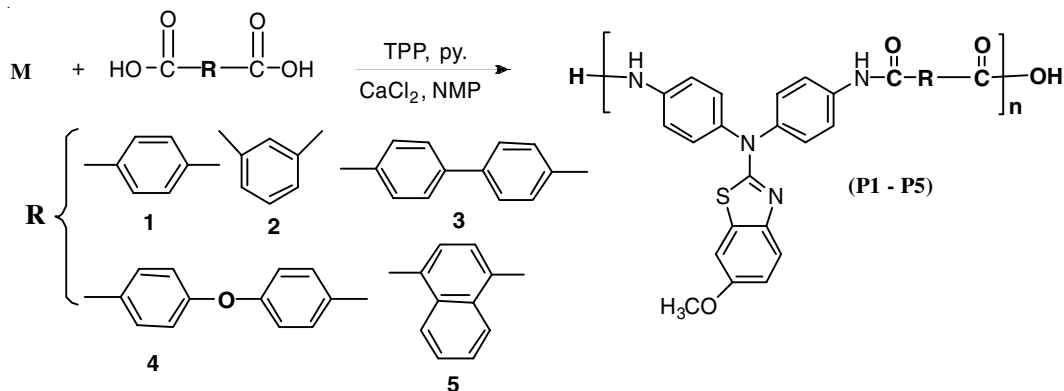
Synthesis of polyamide (P5): This polyamide was synthesized by the same route as explained in method of **P1**. Dark yellow, (75 % yield), m.p. $325-327^\circ\text{C}$. FT-IR (film): 3338 (N-H stretch for amide part), 1661 cm^{-1} (amide $\text{C}=\text{O}$ stretch).

RESULTS AND DISCUSSION

Monomer synthesis: Intermediate diphenylamine monomer 4,4-diamino-6-methoxybenzothiazole-diphenylamine (**M**) was synthesized *via* double N-arylation nucleo-



Scheme-I: Synthetic path for the monomer (**M**)



Scheme-II: Synthetic route for polyamides (P1-P5)

philic aromatic fluoro-displacement reaction of two equivalent 4-fluoronitrobenzene with compound (a), then by catalytic reduction using Pd/C and $\text{NH}_2\text{-NH}_2$ in EtOH of the intermediate dinitro compound (I). The structure of (I) and (M) was characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR spectroscopic techniques. The NO_2 part of (I) showed two characteristic bands 1576 and 1344 cm^{-1} which pass away after reduction. The monomer with di- NH_2 (M) gave characteristic- NH_2 absorptions in the regions of 3326 , 3272 cm^{-1} (Fig. 1).

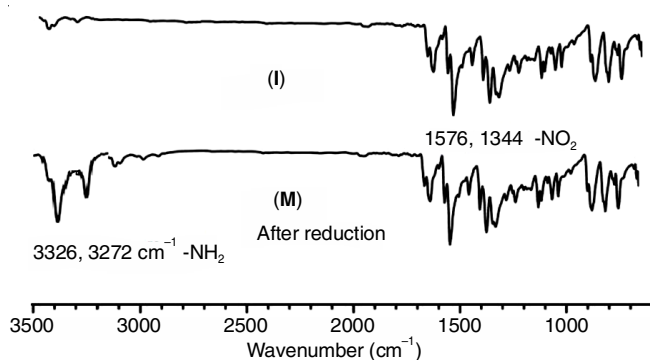


Fig. 1. FTIR spectra of (I), (M)

The ^1H and ^{13}C NMR spectrum of compounds (I), (M) are expressed in the Figs. 2 and 3, respectively. The spectra in the figures agreed well with the suggested unit structures. The complete reduction of nitro groups of the intermediate compounds to the amino groups monomers are confirmed by the strong field shift of aromatic hydrogens and by the resonance indicators 3.82 ppm assignable to the amino hydrogens.

Poly(amine-amide) synthesis: Scheme-II shows that polyamides (P1-P5) were synthesized by poly-condensation reactions from the diamines monomer (M) by different aromatic di-carboxylic acids by the Yamazaki reaction conditions. The yield products showed highly viscous solutions with high inherent viscosities in the range $0.62\text{--}0.87\text{ dL/g}$ (Table-1).

FTIR spectra of these polyamides were in the range $3338\text{--}3320\text{ cm}^{-1}$ (N-H stretch amide group) and $1664\text{--}1661\text{ cm}^{-1}$ (C=O stretch for amide for group) (Fig. 4).

Polyamides properties

Solubility and inherent viscosity: The resultant polyamides in 10% (w/v) different solvents exhibited excellent solubility because of the presence of diphenylamine unit (DPA)

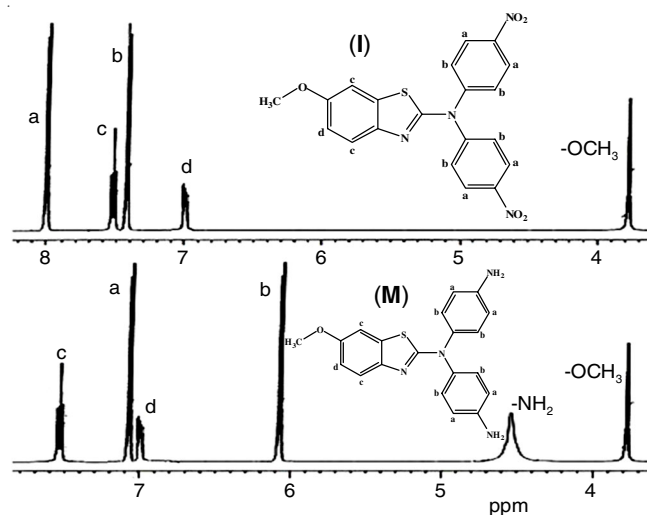
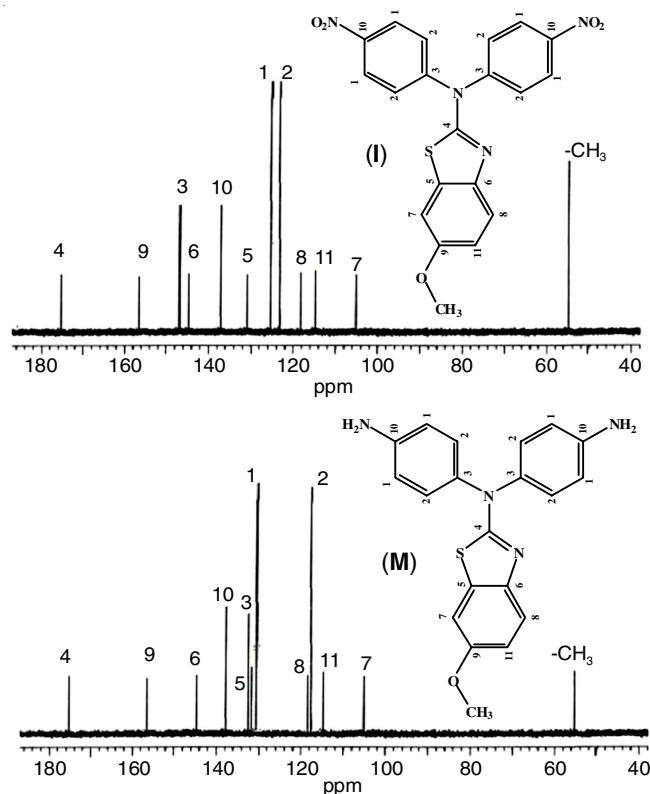
Fig. 2. ^1H NMR spectra of (I) and (M)Fig. 3. ^{13}C NMR spectra of (I) and (M)

TABLE-1
INHERENT VISCOSITY (η_{inh}) AND SOLUBILITY BEHAVIOUR OF SYNTHESIZED POLYAMIDES

Polyamide codes	η_{inh}^a (dL/g)	Solubility in the solvents ^b					
		DMSO	DMF	NMP	DMAc	<i>m</i> -Cresol	THF
P1	0.62	++	++	++	++	–	–
P2	0.65	++	++	++	++	–	–
P3	0.76	++	++	++	++	+	–
P4	0.84	++	++	++	++	+	–
P5	0.87	++	++	++	++	+	–

^aMeasured at a concentration of 10^{-5} M in DMSO; ^bSolubility was tested with 10 % (w/v) of stirred solvent; ++: High solubility at room temperature; +: Low solubility at room temperature; –: Non solubility

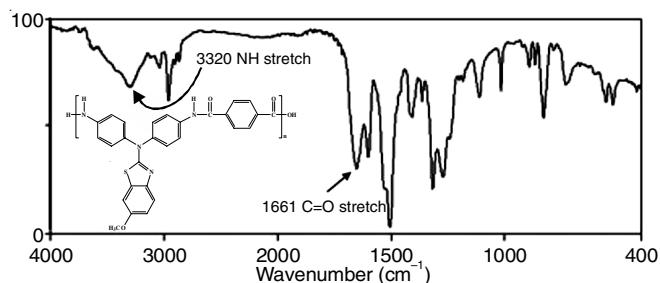


Fig. 4. FTIR spectra of **P1**

so polyamides **P3**, **P4**, **P5** have more solubility than others because of bigger at pending phenyl unit chromophores in the recurrent unity, which lead to increase the open bulky in the polyamide chains to let the insertion of additional solvent in. The inherent viscosity of synthesized polyamides was measured at a concentration of (10^{-5} M) in DMSO solvent. The polyamides solubility and inherent viscosity was summarized in Table-1.

X-ray diffraction data: The diffraction patterns appear in Fig. 5 explain that the polyamides X-ray diffraction measurements exhibited that all the polyamides were ultimately amorphous.

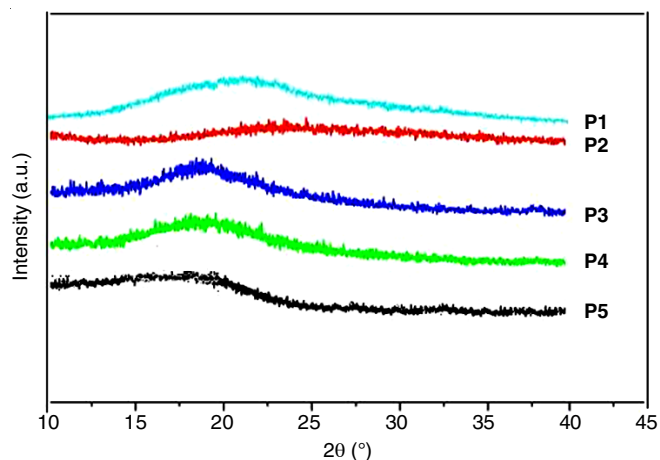


Fig. 5. WAXD patterns of polyamides (**P1-P5**)

Thermal properties: DSC and TGA technique was applied to evaluate the thermal behaviour of the synthesized polymers and the results are outline in Table-2. These polyamides recorded glass transition T_g values between (322-306) °C in the scan rate at 20 °C/min in N_2 atmosphere. The highest T_g value were of polyamides **P1** and **P3** because of the rigidity and low turning of its diacid groups, in other side the lower T_g values of polyamides **P2**, **P4** and **P5** can be illustrated in high elasticity and high turning of its diacid groups [22] (Fig. 6).

TABLE-2
THERMAL PROPERTIES OF POLYAMIDES

Polymer code	T_g^a (°C) in N_2	10 % T_d^b (°C) in air	Char (wt. %)	Yield ^c (%)
P1	322	600	561	63
P2	306	550	510	55
P3	320	590	560	60
P4	306	550	510	55
P5	307	352	549	59

^a°C Midpoint of baseline DSC trace in nitrogen; ^b°C Decomposition at which a 10^d wt % at a rate of 20 °C/min; ^cChar yield percent at 800 °C in N_2 .

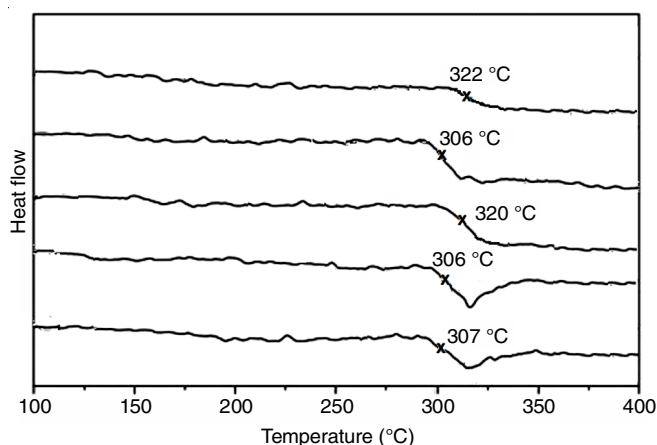
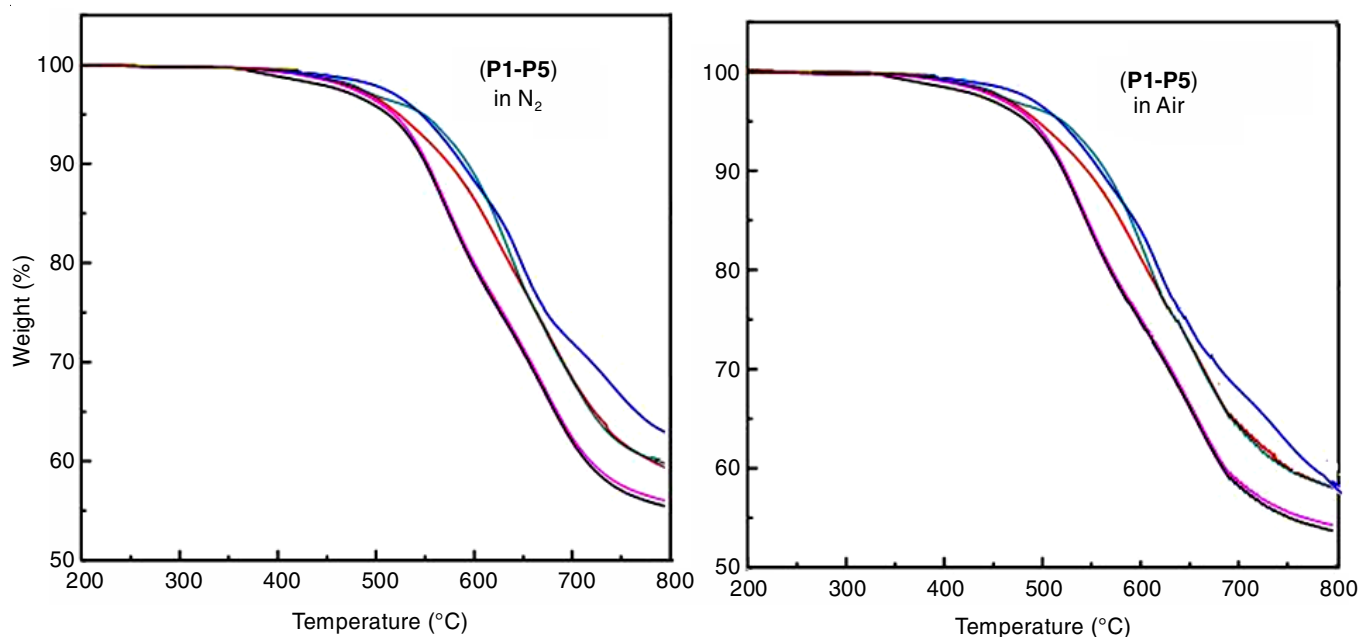
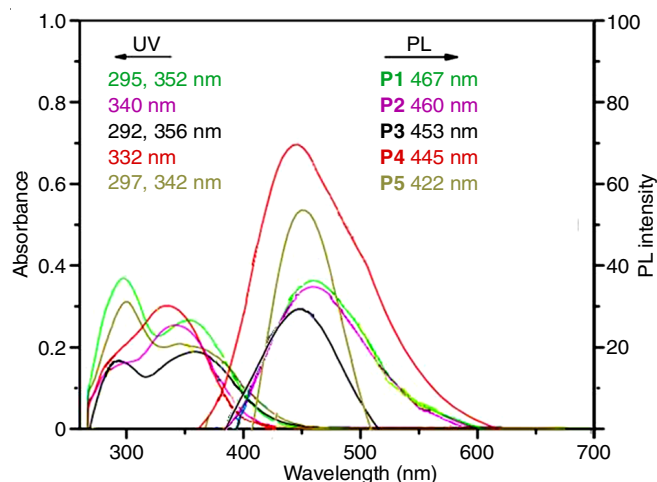
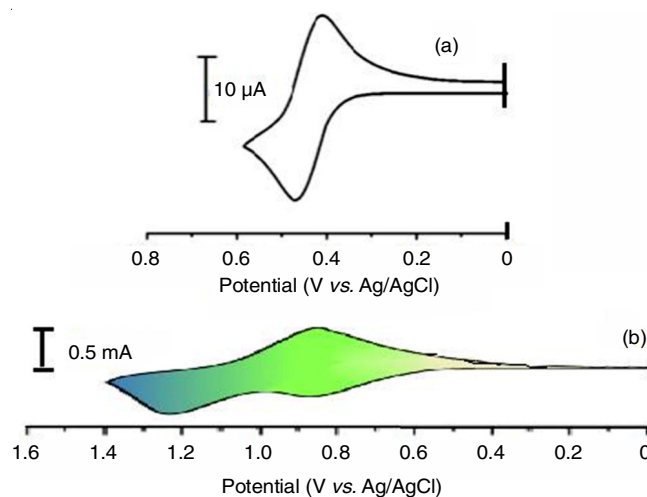


Fig. 6. DSC of polyamides (**P1- P5**) in N_2 atmosphere

Synthesized polyamides exhibited excellent thermal stability. They have onset decomposition after about 450 °C. The polyamides 10 % T_g were in the range of 550-600 °C in nitrogen and 510-561 °C in the air with char yield at 800 °C in N_2 of 55-63 wt % and 53-57 wt % in air. The high amount of the polymers char can be illustrated that they have high aromatic rings (Fig. 7).

Electrochemical and optical behaviours: The electrochemical and optical behaviours of all the synthesized polyamides were studied by UV-visible, photoluminescence spectroscopy (PL) and cyclic voltammetry (CV) (Table-3). Polyamides (**P1-P5**) in DMSO solution gave strong UV-visible absorption bands at the range 332-356 nm. The absorption bands are resulting from the π - π^* transition between the nitrogen atoms and aromatic rings. The solutions of these polyamides in DMSO gave photoluminescence emission spectra maxima at the range 422-467 nm in the blue region. Fig. 8 shows the UV-visible absorption and photoluminescence spectra of polyamides (**P1-P5**). The (**P5**) PL spectra showed a slightly shorter emission wavelength λ_{PL} than others due to

Fig. 7. TGA of polyamides (**P1-P5**) in N₂ and air atmosphereFig. 8. UV-visible and (PL) spectroscopy of (**P1-P5**)Fig. 9. Cyclic voltammogram of (a) (Fc/Fc⁺), (b) (**P1**) sheet onto an ITO-plated glass substrate in CH₃CN with 0.1 M TBAP at scan rate of 0.2 V/s

the disturbed chain-chain packing caused by the incorporate the bulky 1,4-naphthalene group in the repeat unit.

The red-ox action of polyamides (**P1-P5**) was studied by cyclic voltammetry for the molding sheet over ITO-plated glass base as a working electrode in CH₃CN with 0.1 M of TBAP as an electrolyte, under nitrogen atmosphere.

Each of these polyamides showed one reversible redox wave (Fig. 9). Cyclic voltammograms of polyamides (**P1-P5**)

performed at scan rate of 0.2 V/s. The polyamides recorded one reversible oxidation wave *versus* Ag/AgCl. The polyamides exhibited good reversible electrochromic properties by continuous 7 scans 0.0-1.40 V leading to change the original pale yellowish colour to blue. The HOMO and LUMO energy levels of all polyamides are calculated from the onset absorp-

TABLE-3
OPTICAL AND ELECTROCHEMICAL PROPERTIES FOR THE POLYAMIDES

Polyamide code	$\lambda_{\text{abs,max}}$ (nm) ^a	$\lambda_{\text{abs,Onset}}$ (nm) ^b	λ_{PL} (nm) ^c	Oxidation (V) (vs. Ag/AgCl) (gap) ^d	(HOMO-LUMO) (eV)	HOMO ^e (eV)	LUMO ^f (eV)
P1	295, 352	425	467	1.05	2.92	5.45	2.53
P2	340	422	460	1.06	2.94	5.46	2.52
P3	292, 356	462	453	1.08	2.68	5.48	2.80
P4	332	423	445	1.07	2.93	5.47	2.54
P5	297, 342	460	422	1.04	2.61	5.45	2.83

^aUV-visible absorption in (10⁻⁵ M) DMSO; ^bUV-visible absorption in (NMP 1 mg/mL); ^cPL spectra in (10⁻⁵ M) DMSO; ^dgap = 1240/ λ_{onset} of polymer films; ^eThe HOMO energy levels respect to (Fc/Fc⁺) (4.8 eV); ^fLUMO energy levels.

tion of the UV-visible absorption of thin films and oxidation half-wave potentials and [23]. The standard external redox of (Fc/Fc⁺) E1/2 is 0.41 V vs. Ag/AgCl and its HOMO energy is 4.80 eV with consideration to the zero vacuum scale.

Conclusion

In this work, it has been successfully prepared a new (benzothiazole) diphenylamine-containing diamine monomer (**M**). New aromatic amorphous polyamides with excellent thermal properties were synthesized *via* the phosphorylation polycondensation technique from the reaction of several aromatic dicarboxylic acids with this monomer. These polyamides showed perfect electrochromic properties stability with the electrochemical to change the colour from yellow to green and then blue so all the synthesized polyamides may be available for applications in electroluminescent devices as hole-transporting sheet and electrochromic materials due to their proper HOMO values.

CONFLICT OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this article.

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