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Synthesis, characterization, and properties of novel polyamides containing triaryl imidazole moiety

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ABSTRACT

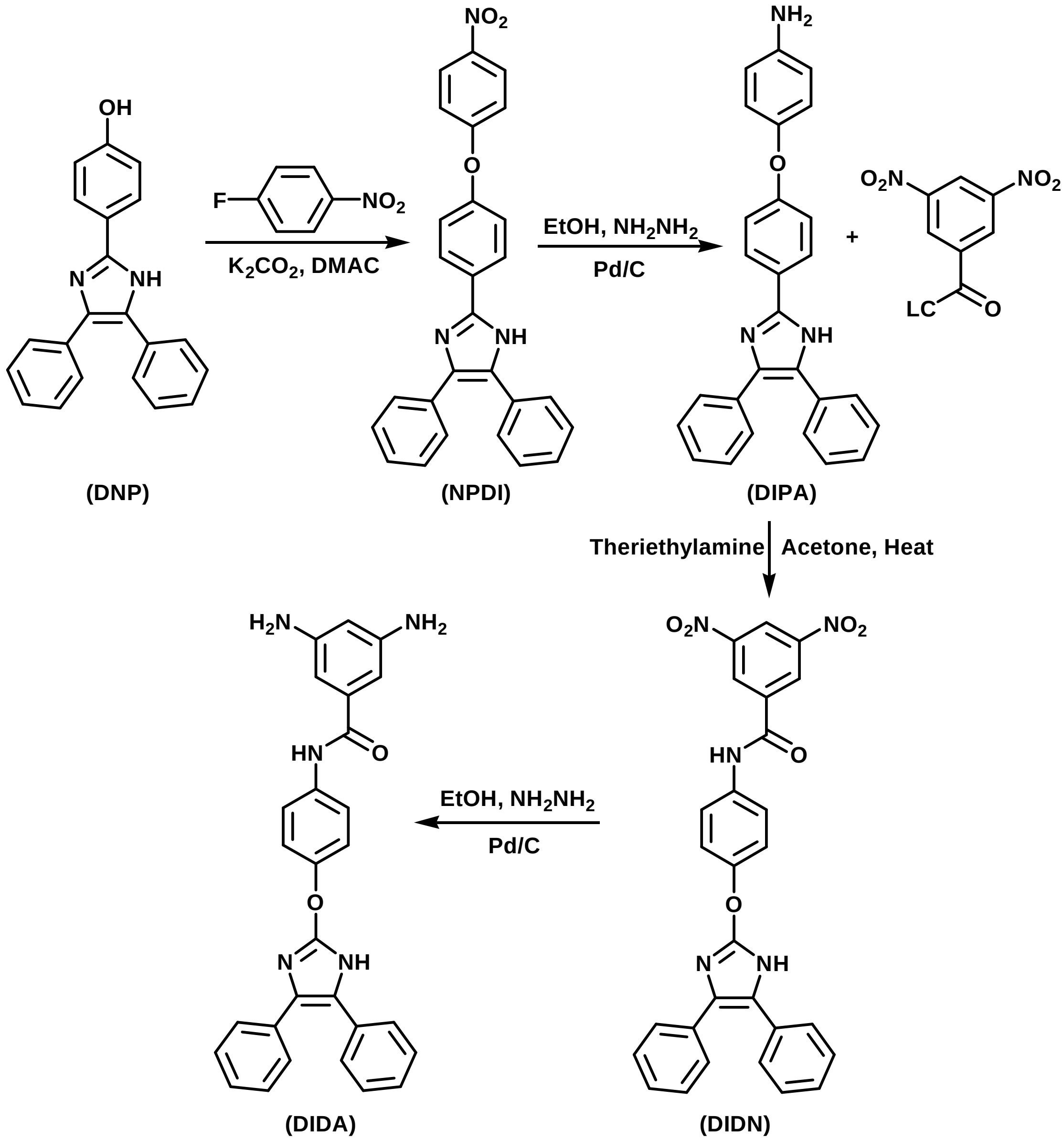
A series of novel polyamides containing triaryl imidazole pendent group was successfully synthesized by direct polycondensation of a new diamine monomer, N-(4-(4-(4,5-diphenyl-1H-imidazole-2-yl)phenoxy)phenyl)-3,5-diaminobenzamide (DIDA), with various aromatic and aliphatic dicarboxylic diacids. These polyamides were characterized by elemental analysis, FT-IR and ^{1}H NMR spectroscopy techniques, and their physical properties such as solubility, viscosity, and thermal properties by means of differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA) were investigated. These polyamides with inherent viscosities of 0.37 to 0.51 dL/g were readily soluble in many organic solvents and gave tough and flexible films by solution casting. These polyamides exhibited glass transition temperatures (T_gs) between 194 and 296°C, and their initial decomposition temperature varied from 250 to 380°C and for a total weight loss of 10% (T_{10}) from 360°C to 510°C in nitrogen.

KEYWORDS

Polyamides;
Polycondensation;
Solubility;
Synthesis;
Thermal properties.

INTRODUCTION

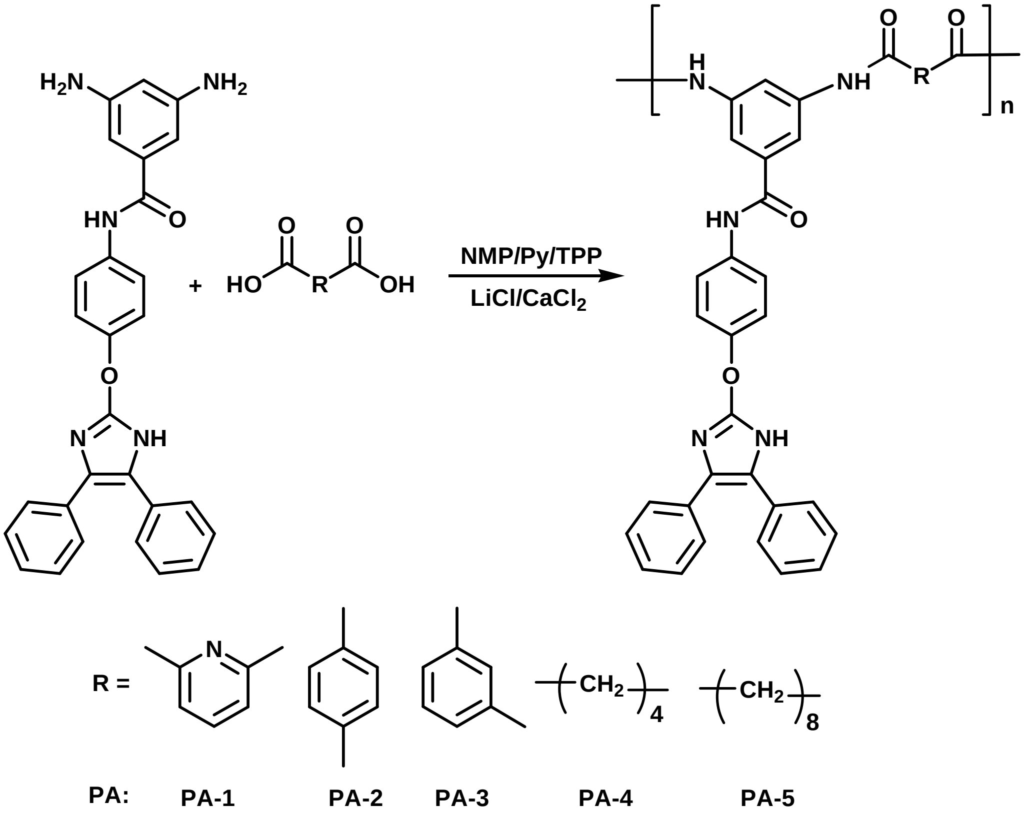
Aromatic polyamides are difficult to process as high performance polymers due to their high softening temperatures and/or insolubility in most organic solvents[1-3]. There has been, therefore, an increased interest in the preparation of polyamides with different substituents or structural irregularities to improve their processability without compromising their other desired properties. Different approaches such as introducing flexible and mixed linkages such as -O-, -S-, CO-, -SO_2-, -$C(CF_3)_2$- into the polymer chain[4-8], replacing symmetrical aromatic rings by the unsymmetrical ones[9-12], introducing noncoplanar and alicyclic monomers into the polymerization system[13-15], were taken by the researchers to improve the solubility of polyamides in organic solvents. Generally, one of the successful approaches to increase the solubility and processability of polymers without sacrificing high thermal stability is the introduction of bulky pendent groups into polymer backbone[16-22]. On the other hand, some reports have concerned the incorporation of imidazole and its derivatives into polymeric frameworks[23,24]. The rigidity, symmetry and aromaticity of the imidazole ring would contribute to the thermal and chemical stability and retention of mechanical properties of the resulting polymer



Scheme 1 : Synthetic route to the target diamine monomer (DIDA)

at elevated temperatures, in addition, increased polarizability resulting from the nitrogen atom in imidazole ring improves the solubility of the polymer in organic solvents[25]. Moreover, lophine, 2,4,5-triphjenylimidazole, and its derivatives are well-known potential chemiluminescence compounds and have significant analytical applications utilizing their fluorescence and chemiluminescence properties[26,27].

Our synthetic research effort was directed towards structural modifications designed to disturb regularity and chain packing, thus providing better process ability to the polymers. The present investigation deals with the synthesis and characterization of five polyamides from direct polycondensation of a new diamine monomer, N-(4-(4-(4,5-diphenyl-1H-imidazole-2-yl)phenoxy)phenyl)-3,5-diaminobenzamide (DIDA), and various aliphatic and aromatic dicarboxylic acids. These polyamides contain bulky triaryl imidazole pendent groups with flexible aryl-ether and amide linkages that create functionalities to the side chain which impart their properties to the polymers. The synthesized polyamides have been characterized by means of elemental analysis, FT-IR and ^{1}H NMR spectroscopy and tested for different physical properties such as measurements of viscosity, solubility, and thermal stability.



Scheme 2 : Synthesis of the polyamides

EXPERIMENTAL

Materials and measurements

All materials and solvents were purchased either from Merck or from Fluka Chemical Co. Benzil, 4-hydroxybenzaldehyde, 3,5-dinitrobenzoylchloride, ammonium acetate, p-fluoronitrobenzene, hydrazine monohydrate, Pd/C, potassium carbonate, triphenyl phosphite (TPP), triethylamine (NEt_3), acetic anhydride, and reagent-grade aromatic dicarboxylic acids such as pyridine-2,6-dicarboxylic acid (PDA), terephthalic acid (TPA), isophthalic acid (IPA), sebacic acid (SA), adipic acid (AA), and solvents such as DMF, DMSO, m-cresol, ethanol, methanol, acetone, hexamethylphosphoramide (HMPA) and tetrahydrofuran (THF) were used without further purification. N-methyl-2-pyrrolidone (NMP), N, N-dimethylacetamide (DMAc), and pyridine were purified by distillation over calcium hydride under reduced pressure. LiCl and $CaCl_2$ were dried at 180 °C in vacuum for 14 h.

FT-IR measurements were performed on a Bruker-IFS 48 spectrometer (Ettlingen, Germany). ^1H NMR and ^{13}C NMR spectra were recorded in dimethyl sulfoxide-d_6 (DMSO-d_6) solution using a Bruker Avance 500 MHz instrument (Germany). Elemental analysis was performed by a CHN Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric (TGA) analyses were recorded on a Stanton Redcraft STA-780 (London, UK) at heating rate of 10 °C/min under nitrogen atmosphere. The dynamic mechanical measurements were recorded on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) over a temperature range of 25-300°C at 1 Hz and at a heating rate of 5°C/min. Inherent viscosity was measured by using an Ubbelohde viscometer in a concentration of 0.6 dL/g in NMP at 25°C. UV-visible and fluorescence emission spectra were recorded on a Cecil 5503 and Perkin-Elmer LS-3B spectrophotometers, respectively.

Monomer synthesis

4-(4,5-diphenyl-1H-imidazol-2-yl)phenol (DIP)

In a 500 mL round-bottomed, two-necked flask equipped with a condenser, magnetic stirrer bar and a nitrogen gas inlet tube, a mixture of (12.21 g, 0.10 mol) of 4-hydroxy benzaldehyde, (21.02 g, 0.10 mol) of benzil, (53.09 g, 0.70 mol) of ammonium acetate and 300 mL of glacial acetic acid was refluxed for 24 h. Upon cooling, the precipitated white solid was collected by filtration and washed with ethanol. The yield of the crude product was 27.42 g (87%). The crude product was recrystallized from ethanol to afford white solid with mp= 278-280°C. FT-IR (KBr disk) at cm-1: 3423 (NH), 3031(OH), 1612 (C=C), and 1545 (C=N).

2-(4-(4-nitrophenoxy) phenyl)-4,5-diphenyl-1H-imidazole (NPDI)

In a 100 mL round-bottomed two-necked flask equipped with a reflux condenser and a magnetic stirrer bar, a mixture of 3.12 g (0.01 mol) DIP, 1.37 g (0.01mol) p-fluoronitrobenzene, and 1.50 g (0.01 mol) potassium carbonate was refluxed for 2 h in 40 mL DMAc. During this time, the progress of the reaction was followed by thin layer chromatography (TLC). Then the mixture was cooled and poured into 100 mL water. The precipitated solid was collected by filtration, washed with water and dried in a vacuum oven at 80 ºC for 12 h. The yield of the reaction was 96% and mp = 208-210 °C. FT-IR (KBr, cm^{-1}): 1522, 1346 (NO2), 1254 (C-O-C stretching) and 1588 (C=N). Anal. Calcd. For $C_{27}H_{19}N_3O_3$:C, 74.82%; H, 4.38%; N, 9.69%. Found, C, 74.93%; H, 4.44%; N, 9.59%.

4-(4-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy)aniline (DIPA)

In a 100 mL two necked round-bottomed flask equipped with a reflux condenser, a magnetic stirrer bar and a dropping funnel, a mixture of 4 g (9.20 mmol) NPDI, 0.50 g of 10% Pd/C and 20 mL ethanol was charged. 3.50 mL hydrazine monohydrate was added drop-by-drop over a 30 min period through dropping funnel. The reaction mixture was refluxed for 1 h, and then filtered while hot to remove Pd/C and heated to reduce the volume of solvent. After cooling, the precipitated crystals were isolated by filtration and recrystallised from acetonitrile and dried in a vacuum oven at 80 °C. The yield of the reaction was 85%, mp=198-200°C. FT-IR (KBr, cm^{-1}): 3443-3464 (NH_2), 1267 (C-O-C), 1520 (C=N), and 1492 (C=C). Anal. Calcd. for $C_{27}H_{21}N_3O$:C, 80.39%; H, 5.21%; N, 10.42%. Found, C, 80.48%; H, 5.35%; N, 10.52%.

N-(4-(4-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy) phenyl)-3,5-dinitrobenzamide (DIDN)

In a 100 mL two necked round-bottomed flask equipped with a reflux condenser, a magnetic stirrer bar and a dropping funnel, 3 g (7.40 mmol) DIPA was dissolved in 50 mL acetone. 4 mL triethylamine (Et_3N) was added to the solution and 4.30 g (18 mmol) 3,5-dinitrobenzoyl chloride in 5 mL of dry acetone was charged into the mixture through dropping funnel. Then the reaction mixture was refluxed for 24 h. The progress of the reaction was followed by thin layer chromatography. After cooling at room temperature, the reaction mixture was poured into large volume of water. The orange powder was collected by filtration, washed and dried overnight in a vacuum oven at 70 °C. The yield of the reaction was 95%, mp=187-190 °C. FT-IR (KBr, cm^{-1}): 1542-1345 (NO_2), 1664 (C=O), 1244 (C-O-C), 1608 (C=N), and 1502 (C=C). Anal. Calcd. for $C_{34}H_{23}N_5O_6$:C, 68.34%,; H, 3.85%; N, 11.72%. Found, C, 68.22% H, 3.92%; N, 11.80%.

N-(4-(4-(4,5-diphenyl-1H-imidazol-2-yl) phenoxy) phenyl)-3,5-diaminobenzamide (DIDA)

In a 100 mL two necked round-bottomed flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer bar, 1 g (1.67 mmol) DIDN was refluxed in 20 mL of absolute ethanol in the presence of 0.5 g of 10% Pd/C catalyst. 1.5 mL hydrazine monohydrate was added drop-by-drop over a 30 min period through dropping funnel. The reaction mixture was further refluxed for 1 h, and then filtered while hot to remove the catalyst and heated to reduce volume of the solvent. Upon cooling, a white powder precipitated, it was isolated by filtration and then recrystallized from ethanol and dried in a vacuum oven at 70°C overnight. The yield of the reaction was 81%, mp = 176-178°C. FT-IR (KBr, cm^{-1}): 3458 and 3367 (NH_2), 3347 (NH, amide), 3408 (NH, imidazole), 1658 (C=O), 1259 (C-O-C), 1593 (C=N), 1512 (C=C). ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 4.96 (s, 4H, NH_2), aromatic protons at δ: 6.0 (t, 1H, J=2Hz), 6.29 (d, 2H, J=2Hz), 7.06 (d, 2H, J=8Hz), 7.08 (d, 2H, J=8 Hz), 7.31-7.51 (m, 10H), 7.82 (d, 2H, J=7.5Hz), 8.07 (d, 2H, J=7.5Hz), 10.03 (s, 1H, N-H amide), 12.63 (s, 1H, N-H imidazole). ^{13}C-NMR (500 MHz, DMSO-d_6, ppm) δ: 167.2, 157.7, 152.9, 151.1, 149.1, 145.2, 136.9, 136.8, 135.9, 135.2, 131.1, 128.6, 128.4, 128.2, 127.9, 127.7, 127.0, 126.9, 126.4, 125.1, 121.8, 121.6, 119.7 and 117.6. Anal. Calcd for $C_{34}H_{27}N_5O_2$: C, 75.97%; H, 5.02%; N, 13.03%. Found, C, 76.10%; H, 4.97%; N, 12.98%.

Polyamides synthesis

The polyamides were prepared by the following general procedure

In a 50 mL two necked round-bottomed flak equipped with a reflux condenser, a magnetic stirrer bar and a nitrogen gas inlet tube, a mixture of 1 mmol dicarboxylic acid, 0.53 g (1 mmol) DIDA, 1.20 mL (5 mmol) triphenyl phosphite (TPP), 0.60 g (14.15 mmol) lithium chloride (LiCl), 0.60 g (6.21 mmol) $CaCl_2$, 1mL pyridine and 5.0 mL NMP was refluxed at 100 °C for 12 h under a blanket of N_2. After cooling, the reaction mixture was poured into a large volume of methanol and the precipitate was collected on a filter paper and washed thoroughly with hot water, then dried in a vacuum oven at 80 ° C for 24 h. The inherent viscosities of the polymers were in the range of 0.37-0.51 dLg^{-1}. The yields of reaction were in the range of 94-98%.

PA-1

FT-IR (KBr, cm^{-1}): 3450 (N-H), 1663 (C=O), 1229(C-O-C). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 12.63 (1H, imidazole ring), 11.45 (2H, N-H amide), 10.61 (1H, N-H amide), 6.85-8.99 (24H, aromatic protons). Anal. Calcd. for $C_{41}H_{28}N_6O_4$: C, 73.65%; H, 4.19%; N, 12.57%. Found: C, 73.55%; H, 4.26%; N, 12.49%.

PA-2

FT-IR (KBr, cm^{-1}): 3358 (N-H), 1642 (C=O), 1233(C-O-C). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 12.60 (1H, imidazole ring), 10.72 (2H, N-H amide), 10.48 (1H, N-H amide), 7.09-8.65 (25H, aromatic protons). Anal. Calcd. for $C_{42}H_{29}N_5O_4$: C, 75.56%; H, 4.34%; N, 10.49%. Found: C, 75.66%; H, 4.47%; N, 10.58%.

PA-3

FT-IR (KBr, cm^{-1}): 3402 (N-H), 1657 (C=O), 1247(C-O-C). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 12.64 (1H, imidazole ring), 10.81 (2H, N-H amide), 10.50 (1H, N-H amide), 7.05-8.70 (25 H, aromatic protons). Anal. Calcd. for $C_{42}H_{29}N_5O_4$: C, 75.56%; H, 4.34%; N, 10.49%. Found: C, 75.68%; H, 4.46%; N, 10.57%.

PA-4

FT-IR (KBr, cm^{-1}): 3418 (N-H), 1664 (C=O), 1244(C-O-C). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 12.49 (1H, imidazole ring), 10.38 (1H, N-H amide), 10.16 (2H, N-H amide), 7.08-8.13 (21H, aromatic protons), 1.65-2.49 (8H, aliphatic protons). Anal. Calcd. for $C_{40}H_{33}N_5O_4$: C, 74.18%; H, 5.10%; N, 10.81%. Found: C, 74.29%; H, 5.21%; N, 10.96%.

PA-5

FT-IR (KBr, cm^{-1}): 3415 (N-H), 1627 (C=O), 1228(C-O-C). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 12.51 (1H, imidazole ring), 10.38 (1H, N-H amide), 10.22 (2H, N-H amide), 6.78-8.15 (21H, aromatic protons), 1.29-3.54 (16H, aliphatic protons). Anal. Calcd. for $C_{44}H_{41}N_5O_4$: C, 75.10%; H, 5.83%; N, 9.95%. Found: C, 75.23%; H, 5.92%; N, 10.07%.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

A new aromatic diamine bearing a pendent triaryl imidazole group with an ether linkage was synthesized according to the synthetic route depicted in Scheme 1. Condensation of benzil with an aromatic aldehyde and ammonium acetate is a convenient synthetic method for preparation of triaryl imidazole. This reaction was applied for the synthesis of DIP, as was reported in the previous publication[28]. The diamine DIDA was synthesized by two nucleophilic aromatic substitution reactions. First, nucleophilic substitution of p-fluoronitrobenzene with DIP in the presence of K_2CO_3 in DMAc to give the mononitro compound NPDI, which was followed by the reduction of nitro group into amine group by means of Pd/C-catalyzed hydrazine monohydrate in ethanol to afford the monoamine compound DIPA. Second, nucleophilic substitution of 3,5-dinitrobenzoyl chloride with DIPA in the presence of triethylamine to give the dinitro compound DIDN, which was followed by the catalytic hydrogenation of the nitro groups to afford the target diamine DIDA. FT-IR spectrum of the dinitro compound DIDN showed absorption bands at 1542 cm^{-1} and 1345 cm^{-1} which are related to -NO$_2$ symmetric and asymmetric stretching. FT-IR spectrum of the diamine DIDA showed the characteristic absorption bands of the primary amine at 3458 and 3367 cm^{-1} due to N-H stretching. The ^{1}H NMR spectrum of the diamine DIDA in figure 1 shows signals at 12.63 and 10.03 which are related to the protons of NH group in imidazole ring and amide linkage, respectively. The ^{1}H NMR spectrum also confirmed that the nitro groups have been completely transformed into the amino groups by the high field shift of the aromatic protons and by the signal at 4.96 ppm. The assignments of each proton and carbon shown in these figures agree well with the proposed molecular structure of the diamine DIDA.

Polyamide synthesis and characterization

The synthesis methodology for these new polyamides (PA1-5) by Yamazaki and Higashi reaction conditions[29,30] is outlined in scheme 2. The PAs were prepared in good yields by direct polycondensation of the diamine DIDA with five different aromatic and aliphatic dicarboxylic diacids (PDA, TPA, IPA, SA, AA) in the presence of TPP and pyridine as condensing agent. This method is an efficient way to form amide bonds and to obtain polyamides of moderate to high degree of polymerization on the laboratory scale. The reaction readily proceeded within a homogeneous solution in NMP and in the presence of LiCl and CaCl$_2$. The precipitates formed when the viscous polyamide solutions were trickled into stirring methanol. The PAs were obtained in almost quantitive yields and their inherent viscosities were between 0.37 and 0.51 dL/g, indicative of the formation of moderate molecular weights. The structures of these polyamides were confirmed by means of elemental analysis, and FT-IR and ^{1}H-NMR spectroscopy. The data from FT-IR spectra of polyamides are presented in the experimental section. In general, FT-IR spectra of the polyamides showed the characteristic absorptions of amide group occurred around 3350 cm^{-1} and 1660 cm^{-1}, peculiar to N-H stretching and carbonyl stretching, respectively. The ^{1}H-NMR spectrum of the polyamide PA-4 is shown in figure 2. As it can be seen, the absorption peaks at 10.16 and 10.38 ppm were assigned to the N-H protons of the amide groups in the backbone and in the pendent unit, respectively. The N-H proton of the imidazole group was assigned at 12.49 ppm. The resonance of aromatic protons appeared in the range of 7.08-8.13 ppm, and the aliphatic protons in the range of 1.65-2.49 ppm. The total protons in the spectrum are consistent with the proposed chemical structure of polyamide PA-4.

Solubility

The solubility behavior of these new polyamides was determined at concentration of 5% (w/v) in a number of solvents, and the obtained results are tabulated in TABLE 1. All of the prepared polyamides exhibited excellent solubility in polar aprotic solvents such as NMP, DMAc, DMF, DMSO, HMPA and pyridine at room temperature and in m-cresol upon heating at 60°C. The polyamide PA-5 with longer aliphatic chain in the backbone dissolved in m-cresol at room temperature. The solubility behavior of the synthesized polyamides was almost identical which can be due to presence of bulky-flexible pendent group in the diamine monomer. This could be because the bulk of the pendent group in the diamine residue is sufficient to override the effect of the interchain interactions superimposed by the backbone. Comparison of the solubility of the previously reported polyamides[17,20,30] with these polyamides indicates that the presence of bulky polar pendent groups in the polymers backbone display an enhanced solubility in organic solvents. The bulky pendent groups increase the chain distance and decrease the interaction of the polymer chains; consequently, the solvents molecules are able to penetrate easily. We believe, however, that the presence of ether linkages and polar amide groups in the pendent units can also contribute effectively in the solubility of these polyamides by interacting with the polar molecules of solvents. All the polyamides films could be obtained by casting their NMP solutions. In general, the films were transparent, flexible, and tough at room temperature.

Thermal properties

Thermal behavior of the polyamides was assessed by using DSC, DMTA, and TGA analyses. The T$_g$ values of the polyamides were taken as the midpoint of the change in slope of the baseline in DSC curve and the maximum of tanδ curve in DMTA experiments. DSC thermograms and the representative DMTA results are

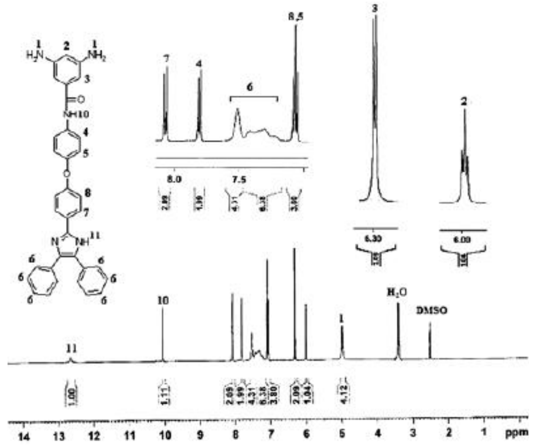


Figure 1 : ¹H NMR spectrum of diamine DIDA

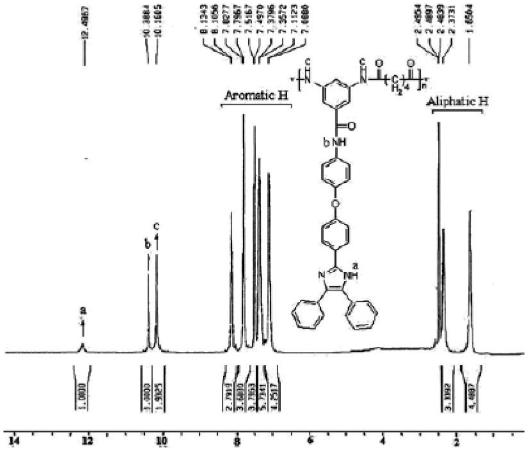


Figure 2 : ¹H NMR spectrum of polyamide PA-4

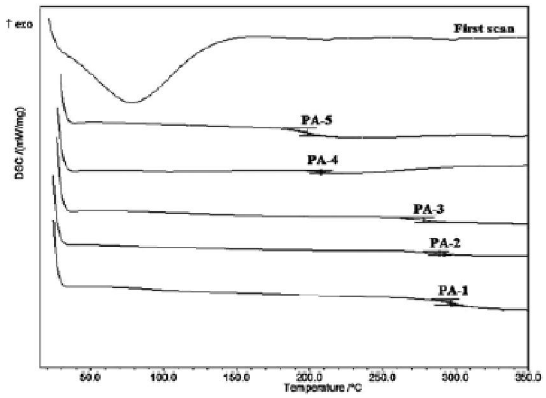


Figure 3 : DSC curves of the polyamides

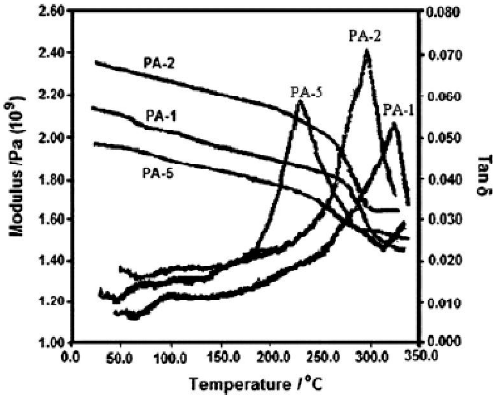


Figure 4 : DMTA curves of polyamides PA-1, PA-2 and PA-5

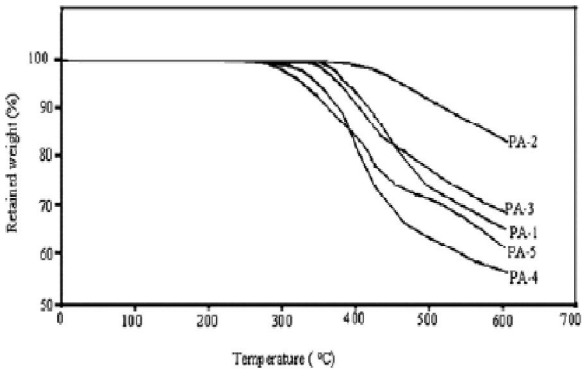


Figure 5 : TGA curves of the polyamides

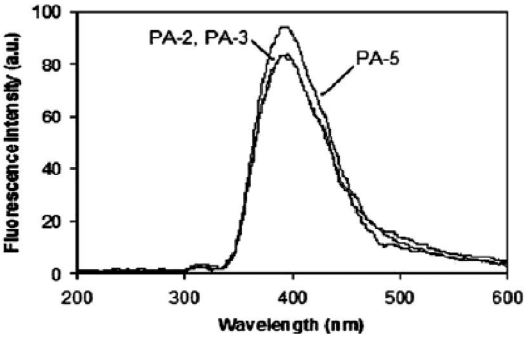


Figure 6 : Photoluminescence emission of polyamides PA-2, PA-3 and PA5

shown in figure 3 and 4, respectively. The first DSC scan of all polyamides showed an endothermic peak around 100°C which is related to the loss of moisture, as revealed in figure 3 (top curve). Quenching from temperature of 350°C to room temperature yielded amorphous samples so that in most cases the T_gs could easily be observed in the second heating traces of DSC. The DSC curves did not exhibit endothermic peak up to 350 °C which can be associated to the amorphous nature of the polyamides. The bulky pendent group increases the steric hindrance for close-chain packing, thus increasing the fractional free volume between the polymer chains and reduces attraction between molecules. The T_g was taken as the midpoint temperature of baseline shift on the second DSC heating trace. The T_g values of the polyamides were in the range of 194-

TABLE 1 : Inherent viscosity and solubility of the polyamides

Polyamide code	η_{inh}(dl/g)	DMA$_c$	DMF	NMP	DMSO	Py	THF	Methanol	HMPA	m-cresol
PA-1	0.51	++	++	++	++	++	-	-	++	+
PA-2	0.49	++	++	++	++	++	-	-	++	+
PA-3	0.46	++	++	++	++	++	-	-	++	+
PA-4	0.40	++	++	++	++	++	-	-	++	+
PA-5	0.37	++	++	++	++	++	-	-	++	++

The solubility was determined by using 5 g sample in 100 mL of solvent. (DMAC: N, N-dimethylacetamide; DMF: N, N-dimethylformamide; NMP: N-methyl-2-pyrrolidone; DMSO: dimethyl solfoxide; THF: tetrahyro furan; PY: pyridine). (++: Soluble at room temperature; +: Soluble after heating at 60°C; +– : partially soluble after heating at 60°C; -: insoluble after heating at 60°C)

TABLE 2 : Thermal properties of the polyamides

Polymer	Tg(°C)^a	Tg(°C)^b	Ti(°C)	T5(°C)	T10(°C)	Char yield^c (%)
PA-1	298	320	330	395	410	58
PA-2	291	300	380	460	510	82
PA-3	275	-	320	380	400	68
PA-4	204	-	280	340	380	56
PA-5	198	225	250	320	360	61

^{a}Midpoint temperature of baseline shift on the second DSC heating trace (10 °C/min, in nitrogen) of the sample after quenching from 350°C. ^{b}DMTA was run from room temperature to 350 °C at 1 Hz at a heating rate of 5 °C/min, and relaxation temperatures were determined from corresponding peak top temperatures seen on the damping (tanδ). T_{10}: temperature for a total of 10% weight loss. ^{c}Residual weight percentage at 600 °C in nitrogen

296°C and are tabulated in TABLE 2. As it is anticipated, the T_g values of these polyamides pertained to the structure of the diacid component and increased with increasing rigidity of diacid employed. The aromatic polyamides PA-1, PA-2, and PA-3 showed the highest T_gs (275-296°C) due to the highest rigidity of the diacids used, which inhibited the molecular motion. The polyamides PA-4 and PA-5 which have been prepared from aliphatic diacids show lower T_gs (194-204°C) because of the flexibility of the aliphatic units in their backbones. Viscoelastic relaxation behaviors of these polymers were subjected to DMTA experiments. The DMTA results displayed the dynamic storage modulus and tanδ as a function of temperature. DMTA was run from room temperature to 350°C at 1 Hz at a heating rate of 5°C/min, and relaxation temperatures were determined from corresponding peak top temperatures seen on the damping (tanδ) curves. Two relaxation processes were observed above room temperature. The β-relaxation processes were observed from room temperature to 200°C, possibly due to the local molecular motions related to the diamine constituents of the polymer chain. The high temperature relaxation is an α-relaxation process; the peak temperatures in the tanδ curves were regarded as the T_gs of these polymers. In general, DMTA curves showed T_gs of the polyamides higher than those were obtained from DSC curves. The T_g value of PA-5 measured by DMTA was exceptionally 50°C higher than that obtained by DSC method which is unexplainable. The high T_gs of these polyamides can be due to the high barrier for segmental mobility as a result of bulkiness of the pendent groups and also due to interactions of side chains and side chains with the main chain through H- bonding. Thermal stability of the polyamides was evaluated by means of TGA at a heating rate of 10°C/min under nitrogen atmosphere. Figure 5 shows TGA curves of the polyamides. The thermo-analysis data of these polymers are summarized in TABLE 2. The initial decomposition temperatures (T_i) of these polymers were in the range of 250-380°C depended on the dicarboxylic acid component in the polyamide backbone. The TGA data indicated good thermal stability for the aromatic polyamide PA-2 up to 500°C with a weight loss of 10% in comparison with the polyamides PA-4 and PA-5 containing aliphatic unit in the backbone which lost 30-40% weight at this temperature. The aliphatic polyamides (PA-4 and PA-5) are thermally stable up to ~320°C, and they showed almost two-step decomposition path. The first step could be assigned to decomposition of the aliphatic chain while the second one could be associated to generalize polymer degradation. Also char yields of the polyamides at 600°C in nitrogen were in the range of 56-82% implying that these polyamides possess relatively good thermal stability. The high thermal stability of these polyamides can be attributed to inter and intra molecular interactions between side chains-side chains and side chains-main chains, resulting in restriction of segmental mobility.

Photophysical properties

The photoluminescence (PL) spectra PA-2, PA-3 and PA-5 in dilute (0.2 g/dL) NMP solution are shown in Figure 6. The polymers exhibited strong absorption at 315-319 nm, which was assigned to a π- π* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. The UV–vis absorption of polyamide films also showed similar absorbance. An excitation wavelength of 315 nm was used in all cases. The PL spectra of PA-2, PA-3 and PA-5 in NMP solutions exhibited broad emission from 393 nm to 397 nm. The higher fluorescence intensity of the aliphatic polyamide (PA-5) compared with the aromatic polyamides (PA-2, PA-3) could be attributed to reduced conjugation and capability of charge-transfer complex formation by the aliphatic diacid with the electron-donating diamine moiety in comparison to the stronger electron-accepting aromatic diacids[31].

CONCLUSIONS

A new diamine bearing a pendent group containing bulky triaryl imidazole (lophine), flexible ether and amide linkages was synthesized and used for the preparation of a series of novel organosoluble polyamides via direct phosphorylation polycondensation with various aromatic and aliphatic dicarboxylic acids. The attachment of a bulky packing-disruptive pendent group into these polymers backbone increased T_g by restricting the segmental mobility, while providing an enhanced solubility because of decreased packing density without sacrificing their high thermal stability and imparted photoluminescence activity because of the presence of lophine group in the pendent moiety. The aryl-ether linkage in the side chains can also impart properties such as better solubility and improve toughness as compared with polymers without an aryl-ether linkage. These polyamides exhibited excellent solubility in common aprotic solvents, with comparable T_gs and 10% weight-loss temperatures to the ordinary aromatic polyamide, which are insoluble in organic solvents.

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