

# Synthesis and characterization of heat-resistant and soluble poly(amide-imide)s from unsymmetrical dicarboxylic acid containing 2-(triphenyl phosphoranylidene) moiety and various aromatic diamines

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**Abstract.** An unsymmetrical and non-coplaner heterocyclic phosphorus containing dicarboxylic acid monomer, (**DCA-3**) is successfully synthesized with high purity. A series of novel aromatic poly(amide-imide)s having ether or/sulphur or/fluorine or/phosphorus containing phenyl moieties in their backbone are then prepared via a direct phosphorylation polycondensation of synthesized dicarboxylic acid with various aromatic diamines. Chemical structures of **DCA-3** as well as resulting polymers are confirmed by FT-IR, NMR spectroscopic techniques and elemental analysis. These polymers are readily soluble in a variety of aprotic polar solvents such as NMP, DMSO, DMAc and DMF, etc. UV spectra showed that all poly(amide-imide)s films exhibit high optical transparency. In addition, the glass transition temperatures ( $T_g$ ) of these polymers were determined by differential scanning calorimetry and found in the range 271–346°C. Furthermore, thermogravimetric analysis of these polymers showed good thermal stability, 10% weight loss at temperature in excess of 538°C and char yield at 700°C in nitrogen ranging from 68 to 79%. From wide-angle X-ray diffraction experiments, all polymers showed amorphous behaviour.

**Keywords.** Poly(amide-imide)s; pendent phosphorus; thermal stability; optical transparency; solubility.

## 1. Introduction

Aromatic polyimides are well known as high performance polymers which possess outstanding thermal stability, chemical resistance and excellent mechanical and electrical properties as well as low flammability.<sup>1–6</sup> However, some applications of polyimides are limited due to their poor solubility in common organic solvents, high glass transition temperature and high processing temperature, which are due to molecular stiffness and high level intermolecular packing of this polymeric system. In order to overcome these limitations, various synthetic efforts have been exercised in order to improve processability of polyimides without sacrificing the above mentioned excellent properties. It is observed that the incorporation of flexible linkage or pendent groups or molecular symmetry can impart many of these desirable properties to the polymers, making them suitable for a much wider range of applications.<sup>7–15</sup> However, the problem of processability of polyimides is still a big problem and

there is a need of further improvement. It has been demonstrated that the insertion of amide groups in imide containing macromolecular chains can enhance the organo-solubility and thermal stability. Among others, heterocycles are interesting chemical structures to modify the properties of aramides and thermally stable polymers because they usually impart excellent thermal stability with improved solubility and decrease the  $T_g$  of materials. As a consequence, research on aromatic polyimides with heterocycles in the main chain is widespread in scientific literature.<sup>16–20</sup> The incorporation of thermally stable groups such as aromatic or heterocyclic rings into polymer main chain is an effective approach to improve the thermal properties of polymers. The combination of above effective factors i.e., incorporation of heteroaromatic rings, pendent substituent and flexible linkages, with each other may be proposed as suitable choice for increasing the processability of aromatic polymers without extreme loss of thermal resistance.<sup>21–23</sup> On the other hand, depending upon applications, optical transparency of polymer films is of special importance, such as oriented films in liquid crystal display devices, flexible solar radiation

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protectors and optical half wave plates for light wave circuits.<sup>24–28</sup>

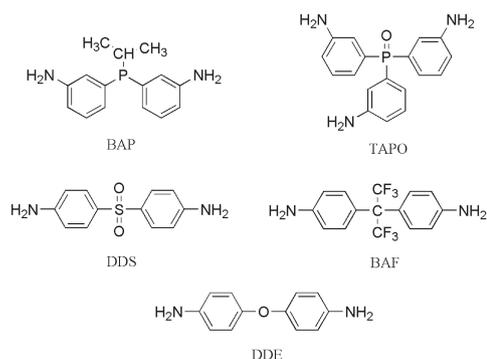
Specifically, the introduction of ether, sulphur, fluorine and phosphorus in the backbone of polymer provides an increase in the polarity of the chain due to the difference of electronegativity among O, P, S, F and C. This fact results in a higher thermal stability of the resulting polymers and is also a successful route to improve the solubility. Since then, fluorine-containing diamines and dianhydrides have been introduced to prepare fluorinated polyimides with properties of low water uptake, low reflective index and low dielectric constant.<sup>29</sup> Fluorine is also known to enhance the solubility of polyimides even in chloroform, toluene and tetrahydrofuran. According to the phosphorylation technique first described by Yamazaki *et al.*,<sup>30</sup> a series of novel organosoluble poly(amide-imide)s with laterally attached ether or S or P or F containing phenyl groups are synthesized from the new phosphorus based dicarboxylic acid and various diamines. On the other hand, presence of P in polymeric chain improves the thermal stability and organo-solubility as well as flame retardancy of polymers.<sup>31,32</sup>

## 2. Experimental

### 2.1 Materials

Diphenyl isopropyl phosphine, triphenyl phosphine oxide, 4,4'-oxydiphthalic anhydride (**ODPA**), 2,2-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane (**BAF**), 4,4'-diaminodiphenyl ether (**DDE**) and 2-(triphenyl phosphoranylidene) succinic anhydride all were purchased from Sigma Aldrich and used as received. L-tryptophan, 4,4'-diaminodiphenyl sulphone (**DDS**) and glacial acetic acid are purchased from Merck and used without any purification. Pyridine (CDH) was purified by distillation under reduced pressure over calcium hydride. Triphenyl phosphite (**TPP**, Merck) was used as received. Anhydrous calcium chloride was dried under reduced pressure at 150°C for 6 h prior to use. N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) was dried over phosphorus pentoxide for at least 15 h and distilled under reduced pressure. Methanol (Fisher Scientific) was received as HPLC grade solvent and used without purification. Ethanol and Palladium on Activated Carbon (Pd/C) were purchased from Sigma Aldrich and used as received. Bis (3-aminophenyl) isopropyl phosphine (**BAP**) and tris (3-aminophenyl) phosphine oxide (**TAPO**) were synthesized by nitration of diphenyl isopropyl phosphine and triphenyl phosphine oxide followed by reduction with Pd/C and hydrazine hydrate

according to the procedure reported in literature.<sup>33</sup> Structures of all diamines are shown below:

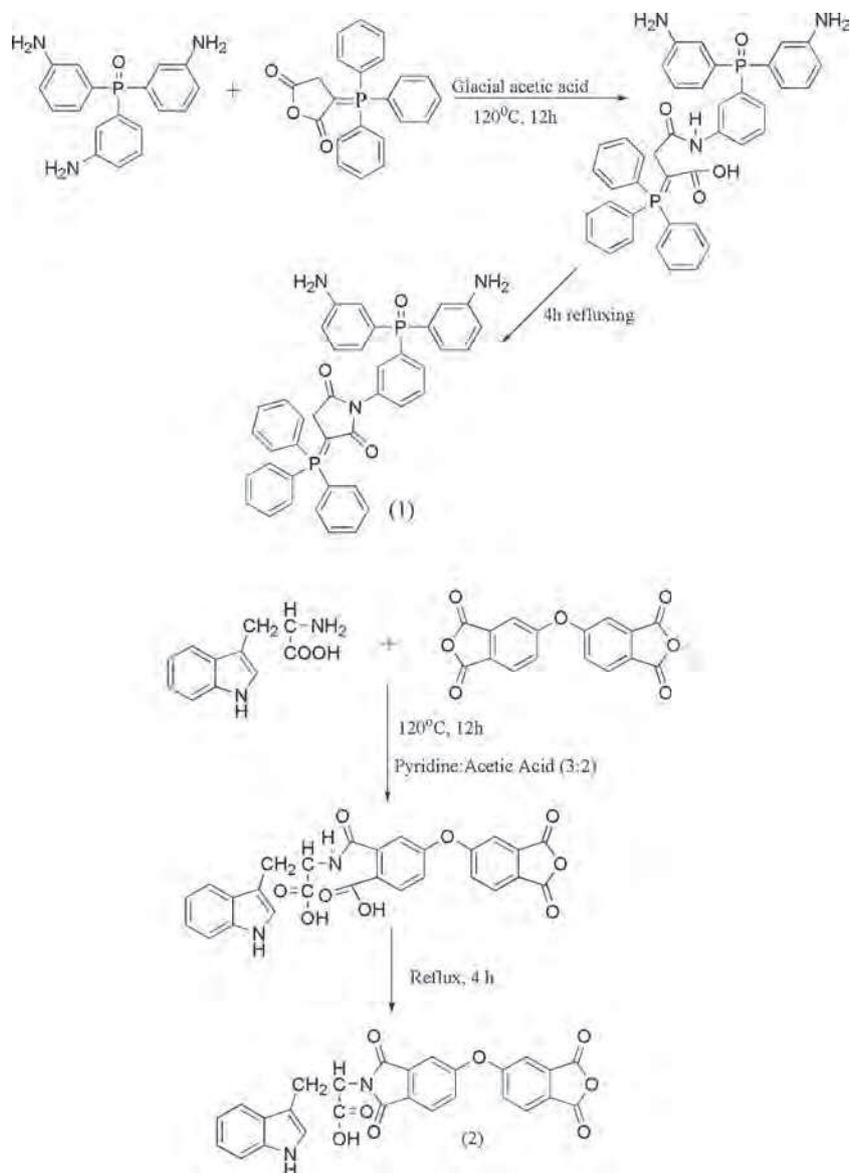


### 2.2 Measurements

FT-IR spectra were recorded on Perkin Elmer RXI spectrophotometer in the range 4000–400 cm<sup>-1</sup>. Elemental analysis was carried out by using GmbH VarioEL CHNS elemental analyser. NMR spectra are recorded on a BRUKER TOP-SPIN 300 MHz spectrophotometer using DMSO-*d*<sub>6</sub> as a solvent and tetramethyl silane as an internal reference at room temperature. The inherent viscosities of the polymers were measured with an Ubbelohde viscometer at 30°C. UV-visible spectra of the polymer films and the dilute N,N-dimethylformamide solution were recorded on Shimadzu UV-1601 UV-visible spectrophotometer. Differential scanning calorimetry (DSC) of the polymers was performed on TA 2100 thermal analyser having DSC 910 module with the heating rate of 10°C/min in nitrogen atmosphere. Thermogravimetric data were obtained on a Perkin Elmer Diamond model at a heating rate of 10°C/min in nitrogen. X-ray diffraction patterns of the polymers are obtained at room temperature on a Bruker Model D-8 Advance diffractometer with a scanning speed of 4°/min, and recorded in the 2θ range of 5°–40°. Weight-average (M<sub>w</sub>), Number-average (M<sub>n</sub>) molecular weights and polydispersity index (M<sub>w</sub>/M<sub>n</sub>) were determined by gel permeation chromatography (GPC). Four Waters Ultrastaygel columns were used for GPC analysis with tetrahydrofuran (THF) (1 mL min<sup>-1</sup>) as the eluent. The eluents were monitored with a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards.

### 2.3 Monomer synthesis

**2.3a Synthesis of phosphorus containing diamine (DA-1):** **DA-1** was prepared according to scheme 1. 2-(Triphenyl phosphoranylidene) succinic anhydride (0.026 mol) was dissolved in glacial acetic acid (25 mL)



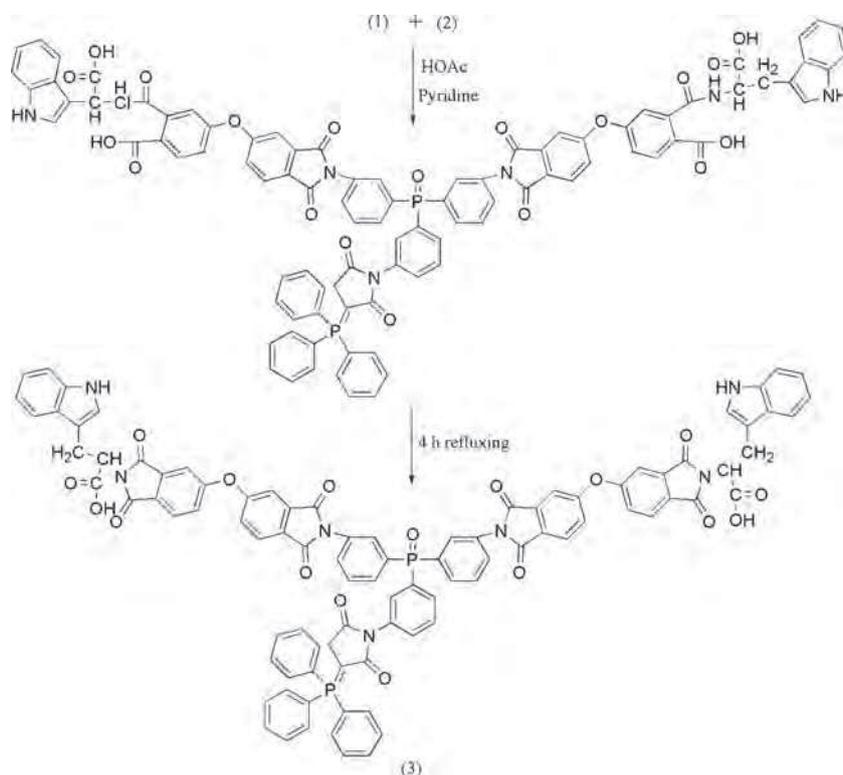
**Scheme 1.** Synthesis of phosphorus containing diamine and monoanhydride.

and **TAPO** (0.026 mol) is added. The solution was stirred for 12 h and then refluxed for 4 h, the resulting mixture precipitated in ice cold water (100 mL), to give brown coloured solid. The precipitate was initially washed with water and then with aqueous sodium bicarbonate solution to remove acid content. The synthesized solid was dried in vacuum at 7°C for 5–6 h and recrystallized with chloroform to give pure compound.

**2.3b Synthesis of monoanhydride (MA-2):** Into a 100 mL round-bottom flask, **ODPA** (0.031 mol), L-tryptophan (0.031 mol), a mixture of acetic acid and pyridine (3:2) (75 mL) and a stirring bar were placed. The mixture was stirred at room temperature for overnight and then refluxed for 4 h. The solvent was

removed under reduced pressure and the residue as dissolved in cold water (100 mL), then the solution is decanted and conc. HCl (7 mL) was added. A cream colour precipitate was formed, filtered off and dried, to give approximately 97% yield. The synthesis of **MA-2** is shown in scheme 1.

**2.3c Synthesis of dicarboxylic acid (DCA-3):** A 250 mL round bottom flask equipped with magnetic stirrer and reflux condenser was charged with phosphorus containing **DA-1** (0.014 mol), synthesized monoanhydride, **MA-2** (0.028 mol) and glacial acetic acid (40 mL) according to scheme 2. The resulting heterogeneous solution was refluxed for 14 h. It was filtered to give approximately 93.2% yield of pale yellow solid. The crude was rinsed with ethanol to remove acetic acid and



**Scheme 2.** Synthesis of dicarboxylic acid (3).

dried in vacuum at 85°C for overnight. The product was recrystallized with DMF/H<sub>2</sub>O (1:1).

#### 2.4 Polymer synthesis

A typical example of TPP-activated polycondensation of polymer synthesis is shown in scheme 3 and described as follows. A mixture of **DCA-3** (1mmol) and aromatic amine (1 mmol), dried CaCl<sub>2</sub> (0.30 g), TPP (2.1 mL) and pyridine (2.1 mL) in NMP (14 mL) was stirred at 110°C for 4 h in a 25 mL flask. The viscosity of the reaction solution is increased after 1 h and an additional volume of NMP is added to carry out the reaction in homogeneous medium. At the end of the reaction, the polymer solution was poured slowly into 250 mL of stirring methanol, to give a fibre-like precipitate which is washed thoroughly with hot water and methanol, filtered and dried in vacuum at 120°C.

All the poly(amide-imide)s were synthesized by a similar procedure.

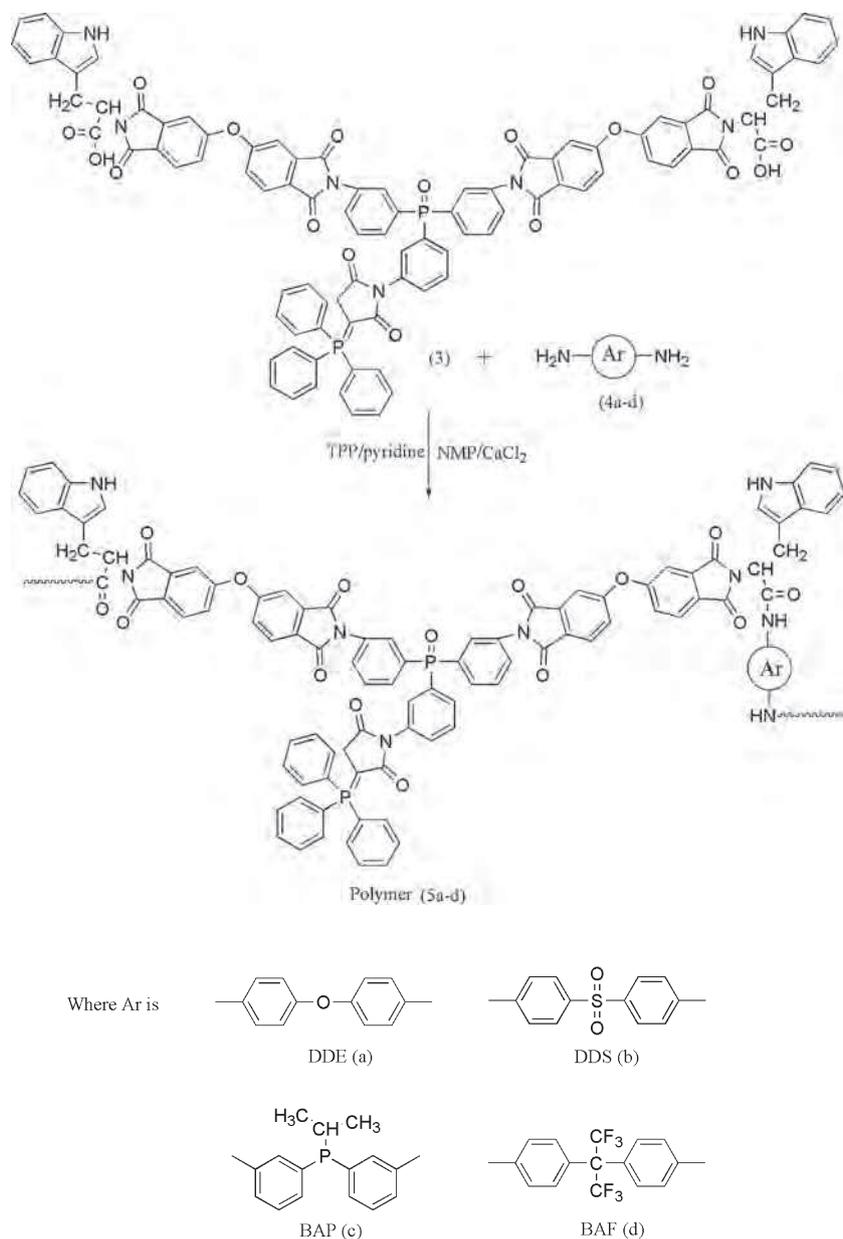
### 3. Results and Discussion

#### 3.1 Monomer synthesis and characterization

As shown in schemes 1 and 2, the phosphorus containing target compound **DCA-3** is synthesized by refluxing

of intermediate compounds i.e., **DA-1** and **MA-2**. All synthesized compounds are characterized by elemental analysis, FT-IR and NMR spectroscopic techniques. Table 1 shows physical characterization and elemental analysis data of all compounds. Figure 1 displays the FT-IR and <sup>1</sup>H-NMR spectra of **DA-1**. Figure 1 (top), shows IR spectrum of **DA-1**. In this spectrum, P=O stretching absorption appears at 1195 cm<sup>-1</sup>, while N-H stretching absorption at 3353 cm<sup>-1</sup>. In addition, an amide C=O stretching absorption peak is observed at 1682 cm<sup>-1</sup> and a peak due to P-Ar at 1418 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectrum of compound **DA-1** is shown in figure 1 (bottom), in which the protons for the amine groups are observed at 3.97 ppm in form of broad and short peak. In this spectrum, all aromatic protons resonate in the region 6.15–7.42 ppm, which are easily attributable and compatible with the proposed structure. In figure 2 (top), the <sup>1</sup>H-NMR spectrum of **MA-2** presents aromatic signals in the range of 6.83–8.27 ppm and a short peak at 11.25 ppm due to proton of carboxylic group. Figure 2 (bottom), shows the <sup>13</sup>C-NMR spectrum of **MA-2**. In this spectrum, carbons of carboxylic acid and anhydride group were observed at 165.1 and 156.8 ppm.

A typical <sup>1</sup>H-NMR spectrum of **DCA-3** is shown in figure 3. This spectrum shows the signal at 10.93 ppm which corresponds to the carboxylic group, in addition to a sharp signal at 10.31 ppm due to N-H



**Scheme 3.** Synthesis of poly(amide-imide)s.

proton of pyrrole ring. Table 2 displays spectral data of all intermediate and target compounds.

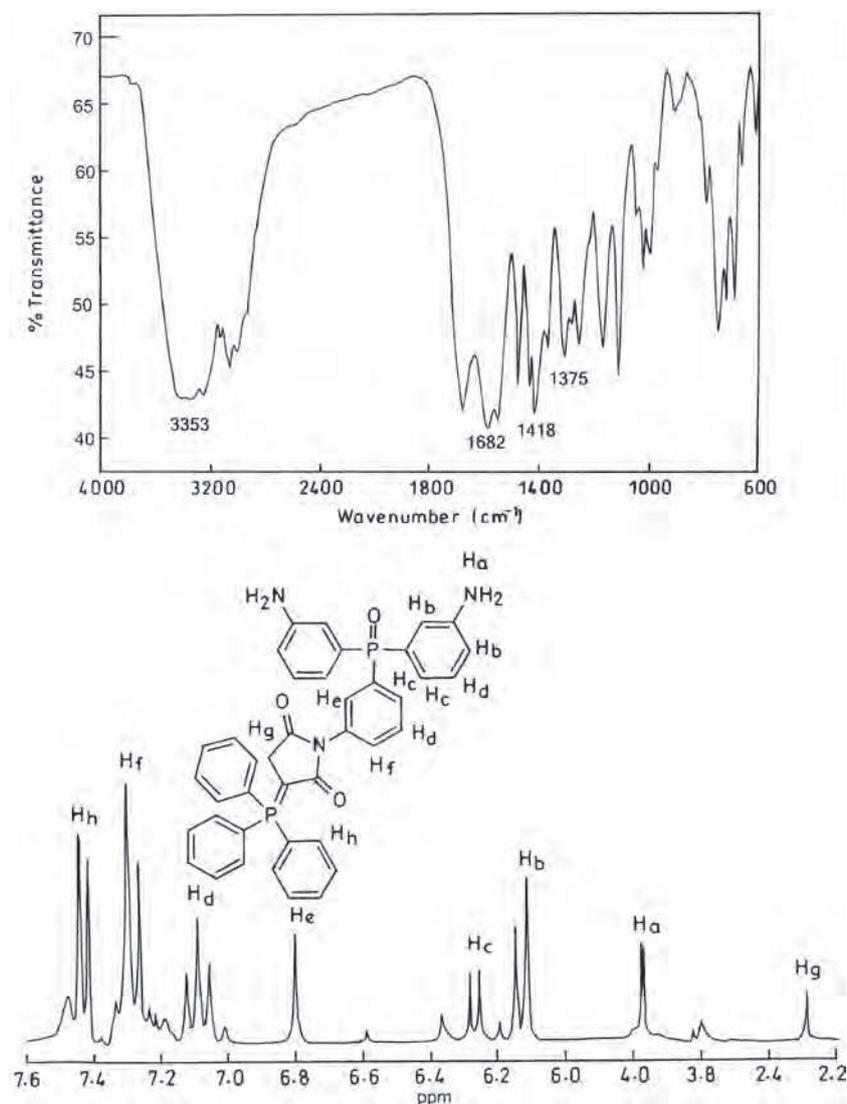
Above characterizations confirm that the target product was synthesized successfully.

### 3.2 Polymer synthesis and characterization

The direct polycondensation of **DCA-3** with different aromatic diamines is carried out using a mixture

**Table 1.** Physical characteristics and elemental analysis data of intermediate compounds and monomer.

Monomer	Yield (%)	Colour	Molecular Formula		% C	% H	% N
DA-1	99.2	Brown	C <sub>40</sub> H <sub>33</sub> N <sub>3</sub> O <sub>3</sub> P <sub>2</sub>	Calcd.	72.17	5.00	6.31
				Found	72.67	4.55	6.67
MA-2	97.1	Pale brown	C <sub>27</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub>	Calcd.	65.32	3.25	5.64
				Found	64.89	3.06	5.51
DCA-3	93.2	Light yellow	C <sub>99</sub> H <sub>61</sub> N <sub>7</sub> O <sub>17</sub> P <sub>2</sub>	Calcd.	69.59	3.79	6.04
				Found	69.14	3.54	6.49



**Figure 1.** IR (top) and  $^1\text{H-NMR}$  (bottom) spectra of diamine, DA-1.

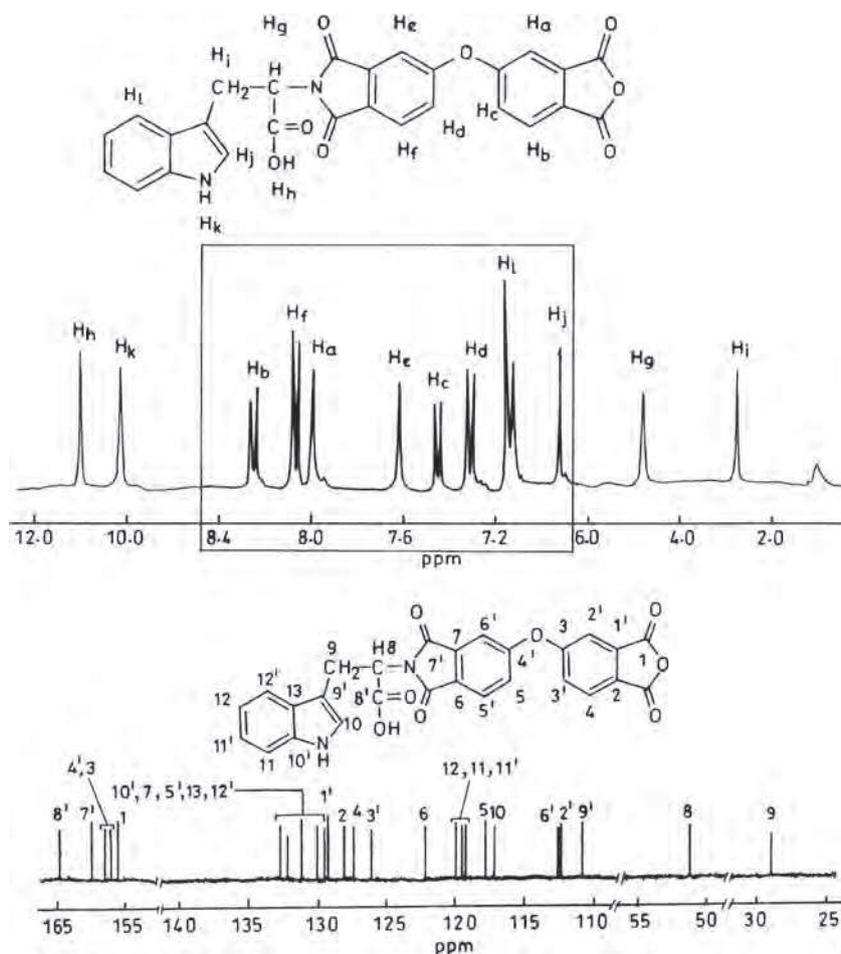
of **TPP** and pyridine as condensing agent outlined in scheme 3. All the poly(amide-imide)s are isolated as tough fibres in quantitative yield. The inherent viscosities values of resulting polymers in NMP at  $25^\circ\text{C}$  at a concentration of 0.5 g/dL and GPC (gel permeation chromatography) analyses as well as elemental analyses are tabulated in table 3. Inherent viscosities of polymers ranged from 0.64–0.78 dL/g. The ratio of average molecular weights ( $M_w/M_n$ ) of **5c** and **5d** found to be 23618/13731 and 18236/9548 respectively. The average molecular weights of polymer **5a** and **5b** were not detectable due to their insolubility in THF.<sup>34</sup> The tested values of elemental analysis of polymers generally agreed well with the theoretical values, as given in table 3.

The structures of polymers are also confirmed by IR and  $^1\text{H-NMR}$  spectroscopy. IR spectrum of polymer, **5b** is shown in figure 4 (top). This spectrum shows

peak at  $1774\text{ cm}^{-1}$  (imide carbonyl  $\text{C}=\text{O}$  asymmetric stretching), at  $1715\text{ cm}^{-1}$  (imide carbonyl  $\text{C}=\text{O}$  asymmetric stretching), imide  $\text{C-N}$  stretching at  $1383\text{ cm}^{-1}$ , and those of amide group around  $3397\text{ cm}^{-1}$  ( $\text{N-H}$  stretching) and  $1665\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching). Figure 4 (bottom), shows characteristic  $^1\text{H-NMR}$  spectrum of polymer, **5b**. The resonance signals of aromatic protons are appeared in the region 7.35–8.32 ppm. A sharp peak is observed due to  $-\text{NH}$  proton of pyrrole ring and a singlet due to secondary amide ( $-\text{CONH}$ ) groups also observed at 8.58 ppm.

### 3.3 Polymer properties

**3.3a Thermal analysis:** All the aromatic poly (amide-imide)s exhibit good thermal stability and it is evaluated by thermogravimetric analysis (TGA) under



**Figure 2.**  $^1\text{H}$ -NMR (top) and  $^{13}\text{C}$ -NMR (bottom) spectra of monoanhydride, MA-2.

nitrogen atmosphere at the heating rate of  $10^\circ\text{C}/\text{min}$  and all data are illustrated in table 4. The initial decomposition temperature (IDT), as well as 5% and 10% weight loss ( $T_{d5\%}$  &  $T_{d10\%}$ ) are determined from TGA curve. The polymer exhibits almost one step decomposition pattern with no significant weight loss below  $526^\circ\text{C}$  and 10% weight loss values ranging  $538^\circ\text{C}$  to  $583^\circ\text{C}$ . Among the polymers, **BAP** based poly(amide-imide), **5c** shows highest char yield i.e., 79% at  $700^\circ\text{C}$ . The char yield of polymer, **5c** can be explained by higher phosphorus content than other polymers (68% char yield of **5a**, 74% of **5b** and 73% of **5d**), results in the formation of phosphorus rich residue from decomposition of isopropyl biphenyl phosphine moiety, which form a protecting layer on the surface of polymer and delay further decomposition.<sup>35,36</sup>

As shown in figure 5 (top), polymer **5d**, containing trifluoromethyl groups has the highest thermal stability. Obviously, the incorporation of trifluoromethyl groups into side chain of the polymer enhances the thermal stability. DDS based polymer, **5b** also exhibits high initial decomposition temperature but slightly lower than the polymer, **5d**. On the other hand, the amount of

carbonized weight residue (char yield) of polymer, **5b** is almost higher than fluorine based polymer.

However polymer, **5a** exhibits much lower initial decomposition temperature, faster degradation behaviour around  $600^\circ\text{C}$  and lower char yield at  $700^\circ\text{C}$  than the other polymers. The low thermal stability can be explained by poor thermal stability of ether linkage in polymeric chain.<sup>37</sup> Obviously, the data from thermal analysis shows that these poly(amide-imide)s have fairly high thermal stability due to presence of very rigid aromatic heterocyclic backbone. The high char yield of the polymers can be ascribed to their high aromatic content in the polymeric chain.<sup>38</sup>

**3.3b DSC measurements:** The glass transition temperature ( $T_g$ ) of polymers is evaluated by differential scanning calorimetry (DSC) under nitrogen atmosphere at the heating rate of  $10^\circ\text{C}/\text{min}$  and characteristic data are summarized in table 4. Hereby,  $T_o$  (the onset temperature, defines the point at which the first deviation from baseline on the low temperature side of a DSC curve is observed) and  $T_g$  (the mid-point temperature of baseline shift) values of the resulting polymers are

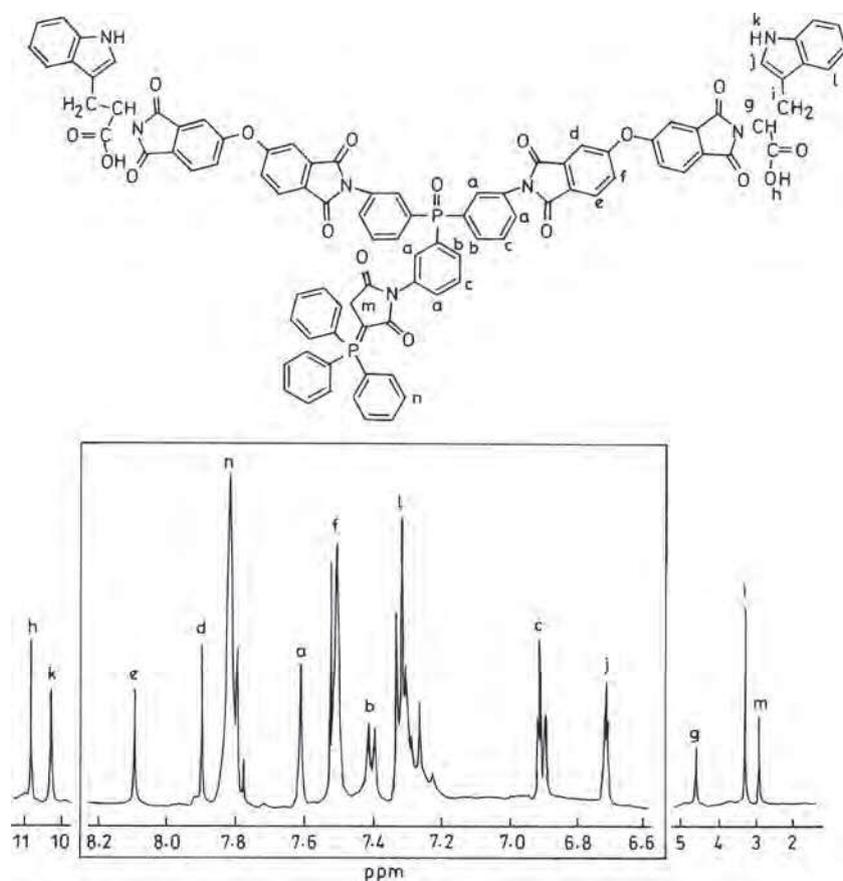


Figure 3.  $^1\text{H-NMR}$  spectrum of dicarboxylic acid, DCA-3.

determined. A typical DSC thermogram of polymer, **5d** is shown in figure 5 (bottom), and the  $T_g$  values of all polymer, **5a–d** are found in the range 271–346°C. As anticipated, the  $T_g$  values depend on the structure of the diamine component.<sup>39</sup>

In general, the chain rigidity increases due to the incorporated groups, which restricts the free rotation of the polymer backbone. Fluorine based polymer shows higher  $T_g$  than other polymers which can be attributed to the increased rotational barrier caused by the  $-\text{CF}_3$  substituents in diamine BAF. Among the polymers, BAP based polymer shows lower  $T_g$  value, due to high phosphorus content. In addition to **DCA-3**, the values of  $T_g$  are normally affected by diamine moieties too, which shows the order **5b** > **5d** > **5a** > **5c** as illustrated in table 4. The  $T_g$  values of polymer, **5a** is less than **5b** and **5d** because of the presence of ether linkage.<sup>40</sup> As the chain rigidity increases due to incorporated groups, it restricts the free rotation of polymer, **5a** and **5b** backbone.

**3.3c Solubility of poly(amide-imide)s in organic solvents:** The solubility of all aromatic polymers is determined qualitatively in various organic solvents and results are tabulated in table 5. Remarkably, all these

polymers exhibit excellent solubility in polar aprotic solvents such as NMP, DMSO, DMF, DMAc and slightly soluble in less polar solvents like m-cresol and pyridine. Polymers **5c** and **5d** are also soluble in common organic solvents such as chloroform and THF.

The excellent solubility of these polymers may be attributed to the presence of twist and non-coplanar aromatic heterocyclic moiety in the polymer backbone, decrease the intermolecular force between polymeric chains and inhibits the dense packing of the polymer chains.<sup>41</sup> The solubility of polymer is greatly enhanced by the incorporation of phosphine oxide moiety and further by bulky  $-\text{CF}_3$  groups, biphenyl phosphorus moiety and more flexible ether group are especially effective for high solubility.<sup>36</sup> The  $-\text{CF}_3$  groups in polymer, **5d** increase its solubility in organic solvents relative to other polymers due to combination of steric and electronic effects. Presence of these bulky  $-\text{CF}_3$  groups in polymer increase free volume, endow a large amount of polarity due to the high electronegativity of F atoms and thereby this polymer shows excellent organo-solubility.<sup>40</sup> Polymer, **5c** caused by entropy advantages resulted from the laterally attached bulky biphenyl phosphine group that inhibits the close packing of the polymeric chain. However, polymer, **5b** is insoluble in

**Table 2.** FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and  $^{31}\text{P-NMR}$  Spectral characterization data of intermediate compounds and monomer.

Monomer	IR (KBr, $\text{cm}^{-1}$ )	$^1\text{H-NMR}$ (DMSO- $d_6$ , $\delta$ ppm)	$^{13}\text{C-NMR}$ (DMSO- $d_6$ , $\delta$ ppm)	$^{31}\text{P-NMR}$ (DMSO- $d_6$ , $\delta$ ppm)
DA-1	3,353 (amine N-H str) 1,682 (amide C=O str) 1,418 (P-Ar str) 1,195 (P=O str) 1,375 (imide C-N str)	2.29 (s, 1H,-CH <sub>2</sub> ), 3.97 (s, 2H,-NH <sub>2</sub> ), 6.15 (d, 1H,Ar-H), 6.28 (d, 1H,Ar-H), 6.81 (s, 1H,Ar-H), 7.12 (t, 1H,Ar-H), 7.33 (d, 1H,Ar-H), 7.42 (m, 1H,Ar-H),	162.6, 155.6, 139.2, 138.9, 132.6, 131.3, 128.8, 127.9, 127.4, 126.6, 124.8, 122.6, 121.1, 119.8, 117.3, 15.9	-25.36
MA-2	3,215 (O-H str) 1,380 (imide C-N str) 1,678 (amide N-H str) 2928 (C-H str of -CH <sub>2</sub> )	2.86 (d, 2H,-CH <sub>2</sub> ), 4.76 (t, 1H,-CH-), 6.83 (s, 1H,-CH-), 7.16 (m, 1H,Ar-H), 7.33 (d, 1H, Ar-H), 7.46 (d, 1H,Ar-H), 7.62 (s, 1H,Ar-H), 7.98 (s, 1H,Ar-H), 8.08 (d, 1H,Ar-H), 8.27 (d, 1H,Ar-H), 10.2 (s, 1H,-NH-), 11.1 (s, 1H,-COOH)	165.1, 161.2, 158.2, 157.6, 156.8, 132.8, 132.6, 131.4, 130.6, 129.7, 129.3, 128.1, 127.3, 126.5, 122.1, 119.8, 119.1, 118.9, 118.6, 117.4, 113.2, 112.3, 111.2, 51.2, 29.6	-
DCA-3	3,265 (O-H str), 1,115 (C-O-C str), 1,194 (P=O str), 1,426 (P-Ar str), 1,779 (imide C=O asymmetric str), 1,719 (imide C=O symmetric str), 1,661 (amide N-H str), 1,370 (imide C-N str)	2.92 (s, 2H,-CH <sub>2</sub> ), 3.18 (d, 2H, -CH <sub>2</sub> ), 4.63 (t, 1H,-CH-), 6.74 (s, 1H,-CH-), 6.92 (t, 1H, Ar-H), 7.34 (m, 1H,Ar-H), 7.42 (d, 1H,Ar-H), 7.61 (s, 1H,Ar-H), 7.82 (m, 1H,Ar-H), 7.91 (s, 1H, Ar-H), 8.09 (s, 1H,Ar-H), 10.31 (s, N-H proton), 10.93 (s, 1H,-COOH)	175.2, 164.8, 163.7, 162.6, 160.8, 158.2, 139.6, 139.1, 136.7, 134.6, 131.8, 130.9, 129.2, 128.2, 127.9, 127.3, 126.1, 125.8, 122.9, 122.8, 121.7, 121.4, 121.2, 120.9, 120.4, 119.9, 118.7, 115.6, 111.6, 110.7, 51.8, 28.7, 16.1	-18.83, -26.82

**Table 3.** Inherent viscosities and elemental analysis of poly(amide-imide)s.

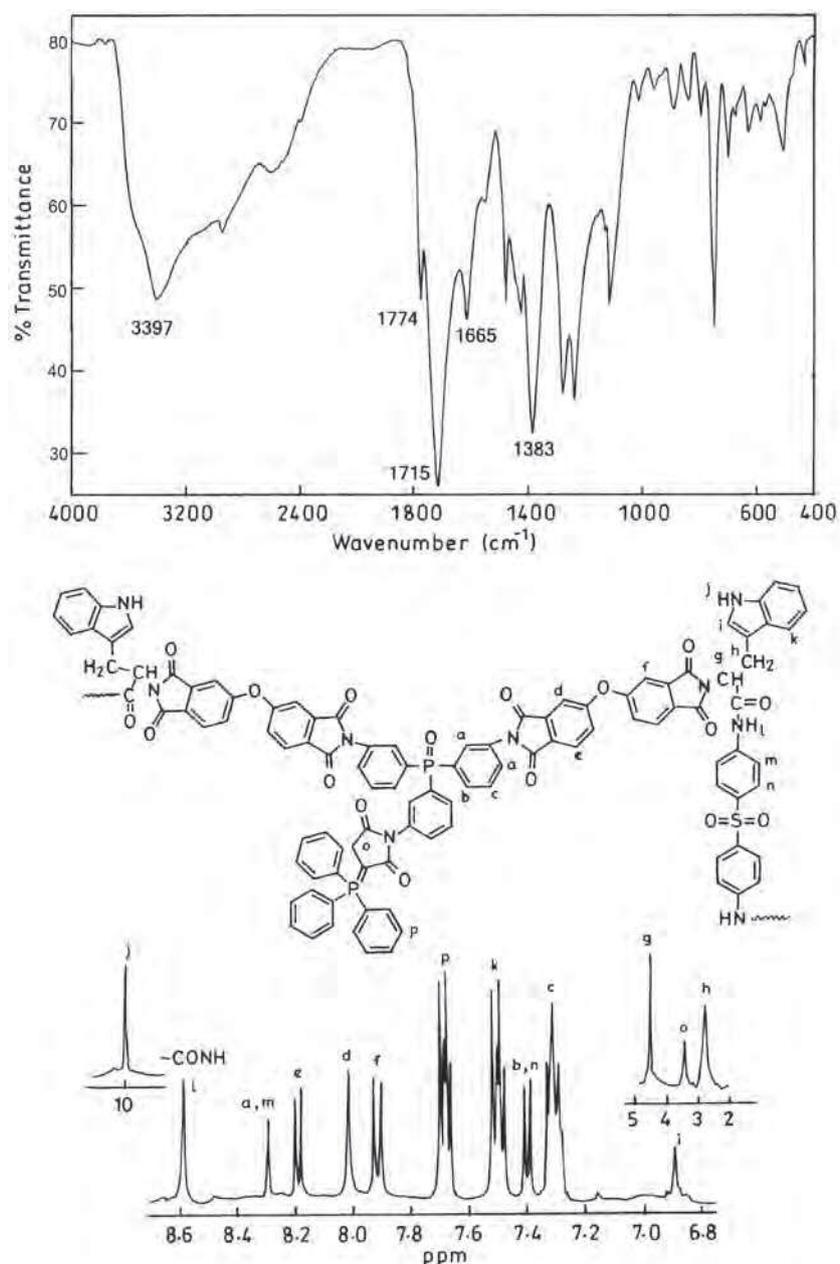
Polymer	$\eta_{inh}$ (dL/g) <sup>a</sup>	Mw/Mn <sup>b</sup>	PDI <sup>c</sup>	Closed Formula	Elemental Analysis	C (%)	H (%)	N (%)
5a	0.76	- <sup>d</sup>	- <sup>d</sup>	(C <sub>111</sub> H <sub>81</sub> N <sub>9</sub> O <sub>16</sub> P <sub>2</sub> ) <sub>n</sub> (1858.83) <sub>n</sub>	Calcd. Found	71.72 71.48	4.39 4.54	6.78 6.90
5b	0.78	- <sup>d</sup>	- <sup>d</sup>	(C <sub>111</sub> H <sub>81</sub> N <sub>9</sub> O <sub>17</sub> P <sub>2</sub> S) <sub>n</sub> (1906.89) <sub>n</sub>	Calcd. Found	69.91 69.47	4.28 4.03	6.61 6.29
5c	0.69	23618/13731	1.72	(C <sub>114</sub> H <sub>88</sub> N <sub>9</sub> O <sub>15</sub> P <sub>3</sub> ) <sub>n</sub> (1916.89) <sub>n</sub>	Calcd. Found	71.43 71.68	4.63 4.29	6.58 6.70
5d	0.64	18236/9548	1.91	(C <sub>114</sub> H <sub>81</sub> F <sub>6</sub> N <sub>9</sub> O <sub>15</sub> P <sub>2</sub> ) <sub>n</sub> (1992.85) <sub>n</sub>	Calcd. Found	68.71 68.48	4.10 3.87	6.33 5.98

<sup>a</sup>Measured in NMP at 25°C at a concentration of 0.5 g/dL

<sup>b</sup>Measured by GPC in THF with polystyrene as a standard

<sup>c</sup>Polydispersity index

<sup>d</sup>Polymer was insoluble in THF at room temperature

**Figure 4.** IR (top) and <sup>1</sup>H-NMR (bottom) spectra of polymer, 5b.

**Table 4.** Thermal properties of poly(amide-imide)s.

Polymer	IDT <sup>a</sup> (°C)	T <sub>d10%</sub> <sup>b</sup> (°C)	Char Yield <sup>c</sup> (%)	T <sub>o</sub> <sup>d</sup> (°C)	T <sub>g</sub> <sup>e</sup> (°C)
5a	526	538	68	284	298
5b	560	579	74	338	346
5c	548	566	79	259	257
5d	562	583	73	317	328

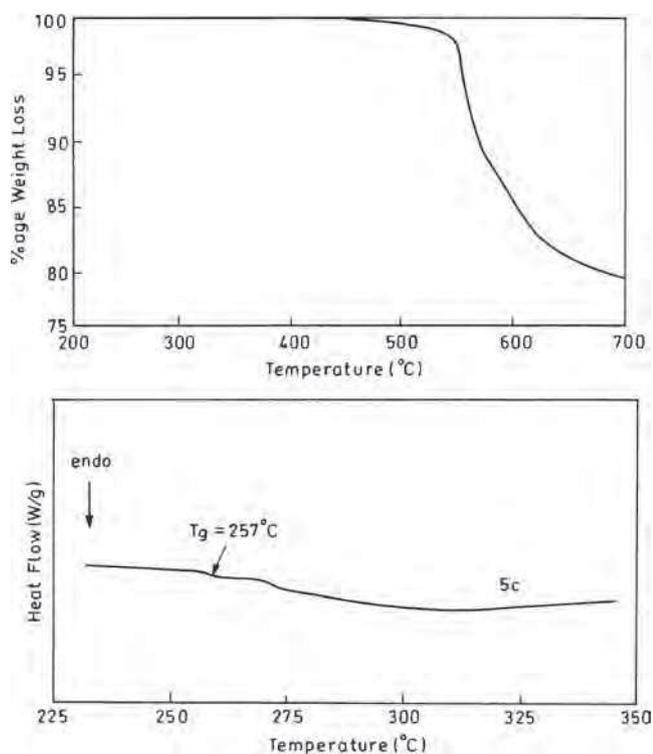
<sup>a</sup>Initial decomposition temperature, determined by TGA in N<sub>2</sub> atmosphere at a heating rate of 10°C/min

<sup>b</sup>Temperature of 10% weight loss, determined by TGA in N<sub>2</sub> atmosphere at a heating rate of 10°C/min

<sup>c</sup>Residual weight % at 700°C in nitrogen

<sup>d</sup>Onset temperature from DSC measurements in N<sub>2</sub>, defines the point at which the first deviation from the baseline on the low temperature side is observed

<sup>e</sup>Glass transition temperatures from the DSC traces in N<sub>2</sub> at heating rate of 10°C/min

**Figure 5.** TGA (top) and DSC (bottom) thermograms of polymer, 5c.

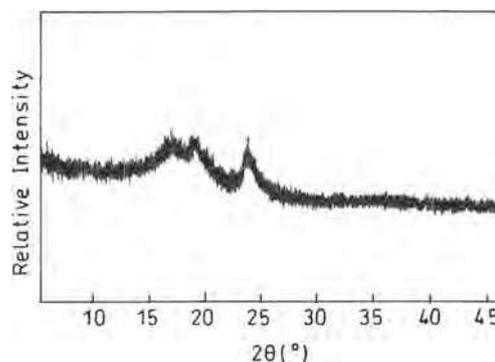
chloroform and THF, owing to the rigid structure of DDS.

**3.3d XRD studies:** The crystallinity of polymers is evaluated by wide angle X-ray diffraction experiment at room temperature. The wide angle X-ray diffractograms shows that the polymer films are essentially amorphous. The amorphous behaviour of the

**Table 5.** Solubility of poly(amide-imide)s in organic solvents.

Solvent	Polymer, 5a	Polymer, 5b	Polymer, 5c	Polymer, 5d
NMP	++	++	++	++
DMF	++	++	++	++
DMSO	++	++	++	++
DMAc	++	++	++	++
THF	+	-	++	++
m-cresol	+	+	++	++
H <sub>2</sub> SO <sub>4</sub>	++	++	++	++
Pyridine	+	+	+	+
Chloroform	+	-	++	++
Acetone	+	-	+	+

++ Highly soluble, + Sparingly soluble, - Insoluble  
DMF :N,N-dimethyl formamide, THF: tetrahydrofuran, DMSO: dimethyl sulphoxide, NMP:N-methyl-2-pyrrolidone, H<sub>2</sub>SO<sub>4</sub>: sulphuric acid, DMAc:N,N-dimethyl acetamide

**Figure 6.** Wide-angle X-ray diffractogram of polymer, 5a.

polymers can be attributed to the structural modification through the incorporation of the non-coplaner triphenyl phosphine moiety. The presence of triphenyl phosphine and non-coplaner amines might decrease the intermolecular forces between the polymeric chains due to loose packing as compared to the unsubstituted polymer. Therefore, crystallization tendency is markedly lowered and the solubilities are significantly enhanced. A wide angle diffractogram of polymer, **5a** is shown in figure 6.

**3.3e Optical properties:** The optical properties of the PAIs films are evaluated by UV-Vis spectroscopy. Cut off wavelength ( $\lambda_o$ , is defined as the mid-point at which the transmittance from the prepared thin films becomes less than 1%) and 80% transmission wavelength ( $\lambda_{80\%}$ , is defined as the mid-point at which the light transmittance from the films becomes less than 80% and this mid-point lies at the left side of plateau region in the UV-Vis absorption spectrum) for PAIs

**Table 6.** Film characteristics and optical properties of resulting poly(amide-imide)s.

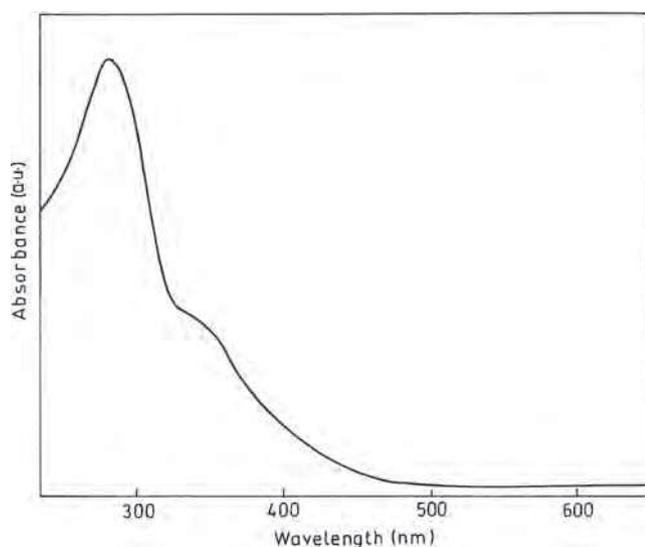
Polymer	$\lambda_{\max}^a$ (nm)	$\lambda_o^b$ (nm)	$\lambda_{80\%}^c$ (nm)	Film quality <sup>d</sup>
5a	278	369	541	Transparent, Flexible
5b	269	373	552	Transparent, Flexible
5c	290	368	544	Opaque, Flexible
5d	265	362	540	Transparent, Flexible

<sup>a</sup>Obtained from the diluted solutions with polymer concentration of  $10^{-5}$  mol/L in DMSO

<sup>b</sup>Cut off wavelength at which the light transmittance from thin film becomes below 1%

<sup>c</sup>Wavelength at which the light transmittance from thin film becomes below 0%

<sup>d</sup>Films were casted by slow evaporation of polymer solution in DMSO

**Figure 7.** UV-Vis absorption spectrum of polymer, 5d.

films are investigated and listed in table 6. These polymers exhibit  $\lambda_{80\%}$  in the range 540–552 nm and their  $\lambda_o$  in between 362–373 nm, which revealed that the polymers are low coloured with high transparency in visible light region. It is observed that the  $\lambda_{80\%}$  and  $\lambda_o$  of polymer, **5d** are lower than that of analogous polymers. Thereby polymer, **5d** shows excellent optical properties compared to other polymers, which is attributed to the trifluoromethyl groups in the polymeric side chain, resulting in the reduction of the intramolecular conjugation and prevents the extensive electronic conjugation.<sup>42</sup>

In addition, the  $\lambda_{80\%}$  and  $\lambda_o$  for **5a**, **5b** and **5c** polymeric films are much longer than those of the corresponding polymer, **5d**. This indicates that ether group in **5a**, DDS in **5b** and biphenyl phosphine group in **5c**, are not efficient in breaking the conjugation length as trifluoromethyl group in **5d**. This is probably because of

the differences in both their electronic states in conjugation with the polymeric chain. The UV-Vis absorption spectrum of polymer, **5d** is shown in figure 7.

#### 4. Conclusions

Four poly(amide-imide)s were synthesized by the reaction of a new aromatic dicarboxylic acid having triphenyl phosphine oxide moiety with different aromatic diamines. The incorporation of triphenyl phosphine oxide and oxyphenyl groups in main chain of polymers modify largely the properties of polymers. All the low-coloured polymer films show high optical transparency in visible region and are highly flexible. The synthesized polymers still maintain excellent thermal stability and reasonable glass transition temperatures ( $T_g$ s) suitable for thermoforming processing. Moreover, the resulting polymers display low crystallinity and good film forming capability.

#### Supplementary Information

Supplementary information contains elementary data of polymer 5a, 5b, 5c and 5d. GPC data of polymer 5c, <sup>1</sup>H-NMR spectra of polymer 5a, 5c and 5d and is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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