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To cite this article: J.N. Mahindrakar, Y.S. Patil, P.H. Salunkhe, S.S. Ankushrao, V.N. Kadam, V.P. Ubale & A.A. Ghanwat (2018): Optically transparent, organosoluble poly(ether-amide)s bearing triptycene unit; synthesis and characterization, Journal of Macromolecular Science, Part A, DOI: [10.1080/10601325.2018.1510291](https://doi.org/10.1080/10601325.2018.1510291)

To link to this article: <https://doi.org/10.1080/10601325.2018.1510291>



Published online: 08 Nov 2018.



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# Optically transparent, organosoluble poly(ether-amide)s bearing triptycene unit; synthesis and characterization

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## ABSTRACT

Aromatic polyamides are famous high performance polymeric materials for their excellent thermal, mechanical, electrical properties, which now a days became a dominant platform for modern polymer chemistry area. Triptycene unit like structures in polymer directly affects the physiochemical properties of polymer, thus polyamides especially with triptycene unit in their backbone with aryl ether linkage imparts combination of properties such as better solubility, melts processing characteristics, and better thermal stability in contrast with those of polymers without an aryl-ether linkage. New triptycene-containing bis(ether amine), 1,4-bis(4-aminophenoxy), 2, 3-benzotriptycene (4a) was synthesized from nucleophilic displacement reactions of P-fluoronitrobenzene with 1,4-dihydroxytriptycene, followed by reduction, and elucidated by FTIR, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy and HRMS. A series of new polyamides containing pendant triptycene group and flexibilizing ether linkages was synthesized by polycondensation of diamine with commercially available aromatic diacid chlorides viz., terephthalylchloride (TPC), isophthalylchloride (IPC) and varying molar mixture of TPC and IPC accordingly. Synthesized Poly(ether-amide)s were found soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, DMF, DMAc, DMSO also could be cast into excellent transparent thin films. Inherent viscosities of polyamides were in the range 0.44–0.57 dL/g. Polyamides exhibited initial decomposition temperature (T<sub>i</sub>), glass transition temperatures (T<sub>g</sub>) and temperature at 10% wt loss (t<sub>10</sub>), which was determined by TGA were noted in the range 212 °C–305 °C, 295 °C–309 °C and 587 °C–631 °C respectively with 24%–54% char yield at 900 °C under nitrogen atmosphere, indicating its better thermal stability and moderate glass transition temperature.

## ARTICLE HISTORY

Received 19 May 2018  
Accepted 2 August 2018

## KEYWORDS

Polyamides; thermal analysis; structure-property relationship; triptycene unit; optical property; inherent viscosity

## 1. Introduction

The aromatic poly(amide)s (PAs), subsequently popular as aramids, those which exhibit high thermal stability, excellent mechanical properties and good chemical resistance, having a widespread range of applications in industry.<sup>[1–4]</sup> Nevertheless, the high-level intermolecular packing along with cohesive energy of these polymeric systems usually hold low solubility in organic common solvents and high transition glass temperatures (T<sub>g</sub>), resulting decrease in their processability and therefore, their technological applications.<sup>[5]</sup> Several efforts reported with regard to improve these parameters not only in PAs but also in other families of aromatic polymers. In general, the incorporation of flexible moieties and cardo units in a rigid polymeric chain, as well as the introduction of heterocycles allows increasing the solubility and decrease the T<sub>g</sub> of the materials.<sup>[2,6–14]</sup> To improve their solution and melting processability, various attempts have been made via structural modifications.<sup>[15–17]</sup> One of the common approaches is the introduction of flexible linkages and/or packing-disruptive bulky groups like in the polyamide backbones.<sup>[18–23]</sup>

Therefore, triptycene is a rigid, bulky, three-dimensional molecular unit having of three benzene blades protruding from a single hinge could be used to achieve desired properties.<sup>[24,25]</sup> One of the structural highlight of triptycene is the intrinsic space between the benzene 'blades', known as the internal free volume. To introduce molecular scale free volume into a polymer backbone the insertion of triptycene moiety as a rigid and shape-persistent unit has been performed. Polymers with triptycene unit might be interesting low-k dielectric materials owing to the high degree of internal free volume.<sup>[26]</sup> It's also been found that incorporation of both ether linkage and triptycene units into the polymers backbone may improves the solubility and processability of aromatic polyamides without much loss in thermal stability.<sup>[27–31]</sup> Because of the unique structural feature of triptycene, synthesizing and charactering new polymers containing triptycene moieties in the skeleton are interesting enough to be investigated further. This present work deals with the synthesis and characterization of two new triptycene bis(ether amine)s, namely 1,4-bis(3-amino-phenoxy)triptycene, and its derived poly(ether-amide) s.

It was expected that participation of three-dimensional triptycene moiety together with the ether linkage into the polymer backbone could improve the solubility, decrease the color intensity and maintain its thermal stability.

## 2. Materials

All the reagents such as terephthalyl chloride (TPC); isophthalyl chloride (IPC), 1,4 naphthanaquinone, anthracene, P-fluoronitrobenzene, hydrazine monohydrate  $\text{NH}_2\text{-NH}_2\text{:H}_2\text{O}$ , 10% Pd/C were purchased from Sigma Aldrich and used as received. N,N-Dimethylformamide (DMF), anhydrous potassium carbonate ( $\text{K}_2\text{CO}_3$ ) were purchased from Fluka. N, N-dimethyl acetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. N-methyl-2-pyrrolidone (NMP; Fluka), dimethyl sulfoxide (DMSO; Acros), tetrahydrofuran (THF; Acros), and pyridine (Py; Wako) were used as received from commercial sources.

### 2.1. Instruments

Viscosity measurements were carried out with a 0.5% (w/v) polymer solution in N, N-dimethyl acetamide (DMAc) at 30 °C with an Ubbelohde suspended level viscometer. Thermo Nicolet iS-10 Mid Fourier transform infrared (FTIR) spectrometer in the 500–4000  $\text{cm}^{-1}$  frequency range,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (400-MHz) were performed using D-6 DMSO as solvent. Spectra of monomer was obtained with a Bruker spectrophotometer. Chemical shifts (delta values) are given as parts per million with tetramethyl silane (TMS) as an internal standard.

$^1\text{H}$  NMR (400-MHz) of Polymers were performed using D-6 DMSO as solvent. X-ray diffraction (XRD) of polymers was recorded on Rigaku X-ray Diffraction System Ultima IV with ULTIMA IV Goniometer. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo Thermal Analysis system under a nitrogen atmosphere with a scan rate of 100 °C  $\text{min}^{-1}$ . Differential scanning calorimetry was performed on a Mettler Toledo DSC at a heating rate of 10 °C  $\text{min}^{-1}$ . UV-Vis Spectroscopy (UV-Vis) spectra were recorded on a Beckman DU-640 spectrometer. The mass spectra were recorded on II MS 30, double bearri mass spectrometer.

## 3. Synthesis

### 3.1. Synthesis of triptycene-1,4-naphthanaquinone (1a) and triptycene-1,4-hydranaphthanaquinone (2a)

Triptycene-1,4-naphthanaquinone (1a) and triptycene-1,4-hydranaphthanaquinone (2a) were prepared according to the published literature with some modifications.<sup>[12]</sup> A typical reaction is as follows: anthracene (10.12 g, 56.67 mmol), 1,4 naphthanaquinone (10.77 g, 68.14 mmol), and (70.8 mL) toluene were added into a round-bottom flask with a stir bar. The mixture was refluxed at 140 °C under stirring in a nitrogen atmosphere for 8 h. The mixture was allowed to cool to

room temperature and then filtered. The obtained solid was then washed three times with hot water (500 mL). The naphthanaquinone product (1a) (18.02 g, 80% yield) was collected and dried at 60 °C under vacuum overnight. To synthesize Triptycene hydranaphthanaquinone (2a), the quinone product (1a) (15.25 g, 45.4 mmol) and glacial acetic acid (165 mL) were added into a round-bottom flask with a stir bar. The mixture was brought to reflux at 118 °C under a nitrogen atmosphere. Hydrobromic acid (48%) (0.7 mL) was added to the flask drop wise and the mixture was allowed to reflux for an additional 30 min. A light tan precipitate was formed. The mixture was allowed to cool to room temperature and then filtered. The resulting hydranaphthanaquinone product (2a) was dried under vacuum at 60 °C for 9 h.

Yield = 13.72g, 90%

M.P. = 346–348 °C.

### 3.2. Synthesis of 1, 4-bis (4-nitrophenoxy)2, 3-benzotriptycene (3a)

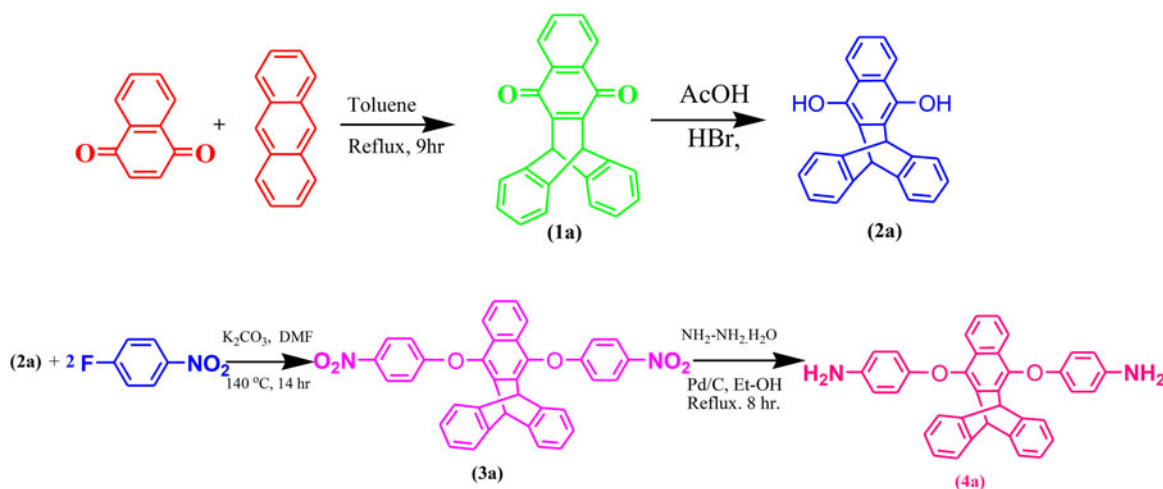
The synthesis of 1, 4-bis (4-nitrophenoxy)2, 3-benzotriptycene (3a) is used as an example to illustrate the detailed synthetic procedure. The hydranaphthanaquinone product (2) (8.23 g, 24.5 mmol), dried potassium carbonate (7.46 g, 53.9 mmol), and DMF (80 mL) were added into a dry round-bottom flask with a stir bar. The mixture was allowed to stir at room temperature for 45 min. To the next, 1-fluoro-4-nitrobenzene (6.92 g, 49.0 mmol) was added into the flask and the mixture was allowed to reflux at 153 °C under a nitrogen atmosphere for 8 h. The mixture was cooled to room temperature and then poured into 400 mL of a methanol–water mixture (1:1 v/v) to precipitate an off white solid. The solid was collected via filtration and washed with methanol. The dinitro-para product (3a) was collected (8.15 g, 63% yield) and dried under vacuum at 80 °C 12 h.

M.P = 160–164 °C.

IR (KBr): 1594, 1339  $\text{cm}^{-1}$  ( $-\text{NO}_2$  stretch), 1262, 1191  $\text{cm}^{-1}$  ( $-\text{C}-\text{O}-\text{C}-$  stretching).

### 3.3. Synthesis of 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene (4a)

The synthesis of 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene (4a) is used as an example to illustrate the detailed synthetic procedure. The dinitro-para product (3a) (5.25 g, 9.93 mmol), 10% Pd/C catalyst (0.27 g), and alcohol (210 mL) were added into a 500 mL round-bottom flask with a stir bar. The mixture was brought to reflux at 80 °C under a nitrogen atmosphere. Hydrazine monohydrate (8.3 mL, 173.1 mmol) was added dropwise and the mixture was allowed to reflux for 8 h. The mixture was cooled to room temperature and the alcohol was removed under reduced pressure. DMF (16 mL) was then added to dissolve the product to facilitate filtration through packed celite to remove the catalyst. The filtered solution was precipitated in



**Scheme 1.** Synthesis of 1,4-bis(4-aminophenoxy)2,3-benzotriptycene(4a).

methanol (400 mL) and a fluffy, white solid was obtained. The diamine para (4a) product was dried under vacuum and stored in a desiccator. The schematic reaction steps are shown as in Scheme 1.

$$\text{Mp} = 220\text{--}224^\circ\text{C}.$$

IR (KBr) : 3411, 3331 $\text{cm}^{-1}$  (N – H stretch)

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ , ppm): 4.64  $\delta$  ppm (s, 4H,  $-\text{NH}_2$ ), 7.8 $\delta$ ppm (d, 2H), 7.34  $\delta$  ppm (d, 2H), 7.21  $\delta$  ppm (d, 2H), 6.51 $\delta$  ppm (d, 2H), 5.72 $\delta$ ppm (s, 2H).

### 3.4. Synthesis of polyamides (PA 01–05)

A representative procedure for synthesis of polyamides is described below.

Into a 100 mL three-necked round-bottom flask equipped with a nitrogen gas inlet, a calcium chloride guard tube and a magnetic stirrer were placed 1,4-bis(4-aminophenoxy)2,3-benzotriptycene (4a) (0.518 g, 1 mmol), in dry N,N-dimethyl acetamide (DMAc) 3 mL under nitrogen atmosphere till solution become clear. The reaction mixture was cooled to  $-15^\circ\text{C}$  with help of ice-salt mixture. IPC (0.201 g, 1 mmol) was added to the solution in two portion and the reaction was stirred for 2 hrs at  $0^\circ\text{C}$  and 12 h at room temperature. Later the reaction mixture was neutralized with 0.075 g (1.04 mm) lithium carbonate and heated at  $80^\circ\text{C}$  for 20 min. The viscous mass was added to a large excess of methanol to precipitate. Fibrous polymers were isolated. The polymer was washed several times with hot water as well as methanol, and was dried under vacuum at  $80^\circ\text{C}$  overnight. A polymer solution was made by the dissolution of about 0.7 g of the polymer sample in 10 mL of hot DMAc. The homogenous solution poured into petri dish which was then placed at  $80^\circ\text{C}$  overnight in oven for the slow release of solvent, and then the film was stripped from petri dish.

## 4. Results and discussions

A new diamine monomer with ether linkage, cardo moiety triptycene group viz, 1,4-bis(4-aminophenoxy)2,

3-benzotriptycene (4a) were utilized. To study the effect of ether linkage, triptycene moiety on solubility behavior a series of polyamides was synthesized by low temperature solution polycondensation of 1,4-bis(4-aminophenoxy)2,3-benzotriptycene (4a) with commercially available aromatic dialdehydes viz., IPC and TPC in various proportions. These poly(ether-amide)s were characterized by IR spectroscopy, inherent viscosity, solubility, thermal analysis and WAXD and UV-Vis Spectroscopy.

### 4.1. Synthesis of 1,4-bis(4-aminophenoxy)2,3-benzotriptycene (4a)

The new 1,4-bis(4-aminophenoxy)2,3-benzotriptycene(4a) was synthesized as outlined in Scheme 1 by reacting 1,4-naphthoquinone with anthracene to yield triptycene hydro-naphthoquinone followed by reduction with Aq. HBr; followed by reaction with p-fluoronitrobenzene in N,N-dimethyl formamide, containing anhydrous potassium carbonate. The ether dinitro which is formed in above step was catalytically reduced by hydrazine monohydrate. The resulting structure of new dietheramine was confirmed by FT-IR and  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and Mass spectroscopy.

The infrared spectrum of 4a (Figure 1) exhibited characteristic absorptions of primary amine  $\text{Ar-NH}_2$  at 3338  $\text{cm}^{-1}$  and 3408  $\text{cm}^{-1}$ . Band at 1262  $\text{cm}^{-1}$  and 1191  $\text{cm}^{-1}$  is due to (C-O-C stretching). The absorption band at 824  $\text{cm}^{-1}$  is due to para catenation of primary amine group. Absorption peak at 3010  $\text{cm}^{-1}$ , 3060  $\text{cm}^{-1}$  for allylic  $\text{Ar(C-H)}$  stretching and aromatic ( $\text{Ar-H}$ ) stretching respectively. 1460  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  for aromatic C=C stretching.

Proton  $^1\text{H}$ -NMR spectrum (Figure 2) of (4a) showed singlet at 3.45  $\delta$  ppm due to primary- $\text{NH}_2$  protons ( $\text{Ar-NH}_2$ ) and multiplet in the range of 7.90–6.83  $\delta$ ppm due to aromatic protons as expected with desired integration and splitting pattern. Peak at 5.71  $\delta$ ppm is due to allylic protons of triptycene moiety.

$^{13}\text{C}$ -NMR spectrum (Figure 3) of (4a) showed fourteen NMR signals corresponding fourteen types of different carbons of which aniline's carbon ( $\text{Ar-NH}_2$ ) appeared at 144  $\delta$ ppm; whereas aromatic carbons showed signals at 152.70,

144.04, 140.60, 125.40, and 134.16  $\delta$ ppm The CH of aromatic rings appeared at 116, 122.43, 124.21, and 127.6  $\delta$ ppm; whereas allylic CH carbons gave NMR signal at 43.60  $\delta$ ppm. Mass spectra showed molecular ion peak  $m/e$  at 519 ( $m+1$ ) of corresponding to molecular weight 518 of (4a)(Figure 4).

#### 4.2. Synthesis of poly(ether-amide)s from 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene (4a)

A series of poly(ether-amide)s were synthesized as outlined in Scheme 2. A series of poly(ether-amide)s were synthesized by low temperature solution polymerization of 1, 4-bis

(4-aminophenoxy), 2, 3-benzotriptycene (4a) with structurally summarized diacidchlorides viz; IPC and TPC in DMAc. The polymerization proceeded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in methanol. The inherent viscosities of all these polymers were measured in DMAc and ranged from 0.44 to 0.57 dL/g. The data representing the behavior of poly (ether-amide)s are displayed in Table 1.

### 5. Polymer characterization

#### 5.1. Infrared spectroscopy

The polymers were characterized by the infrared spectroscopy. The representative IR spectrum of poly(ether-amide) PA-01, (Figure 5) showed the characteristic absorption at  $3336\text{ cm}^{-1}$  (HN-C=O stretching) and  $1509\text{ cm}^{-1}$  corresponds to -N-H bending frequency. The sharp bands occurring at  $1207\text{ cm}^{-1}$  and  $1148\text{ cm}^{-1}$  in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the (C-O-C) ether linkage. The presence of bands at  $3061\text{ cm}^{-1}$  can be assigned to aromatic and aliphatic (C-H stretching) vibrations. The vibration at  $829\text{ cm}^{-1}$  indicates para catenation of aromatic rings.

#### 5.2. $^1\text{H}$ NMR spectroscopy

$^1\text{H}$ -NMR spectrum of poly(ether-amide)s derived from 1, 4-bis (4-aminophenoxy), 2, 3-benzotriptycene (4a) and IPC along with peak assignments is shown in Figure 6. one separate singlet of amide protons was observed at 10  $\delta$ ppm.

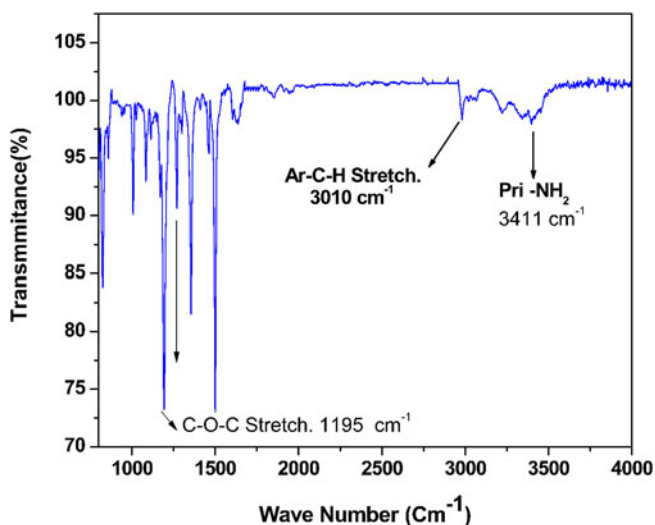


Figure 1. IR spectra of 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene(4a).

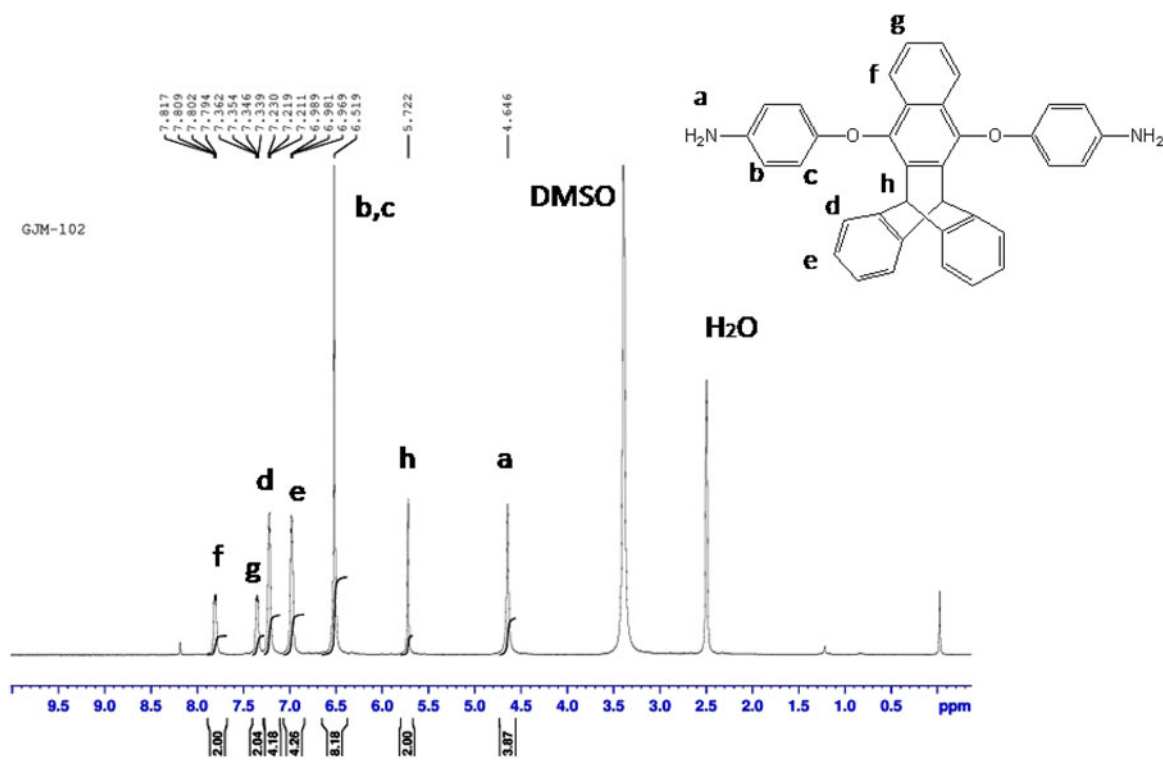


Figure 2.  $^1\text{H}$  NMR spectra of 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene(4a).

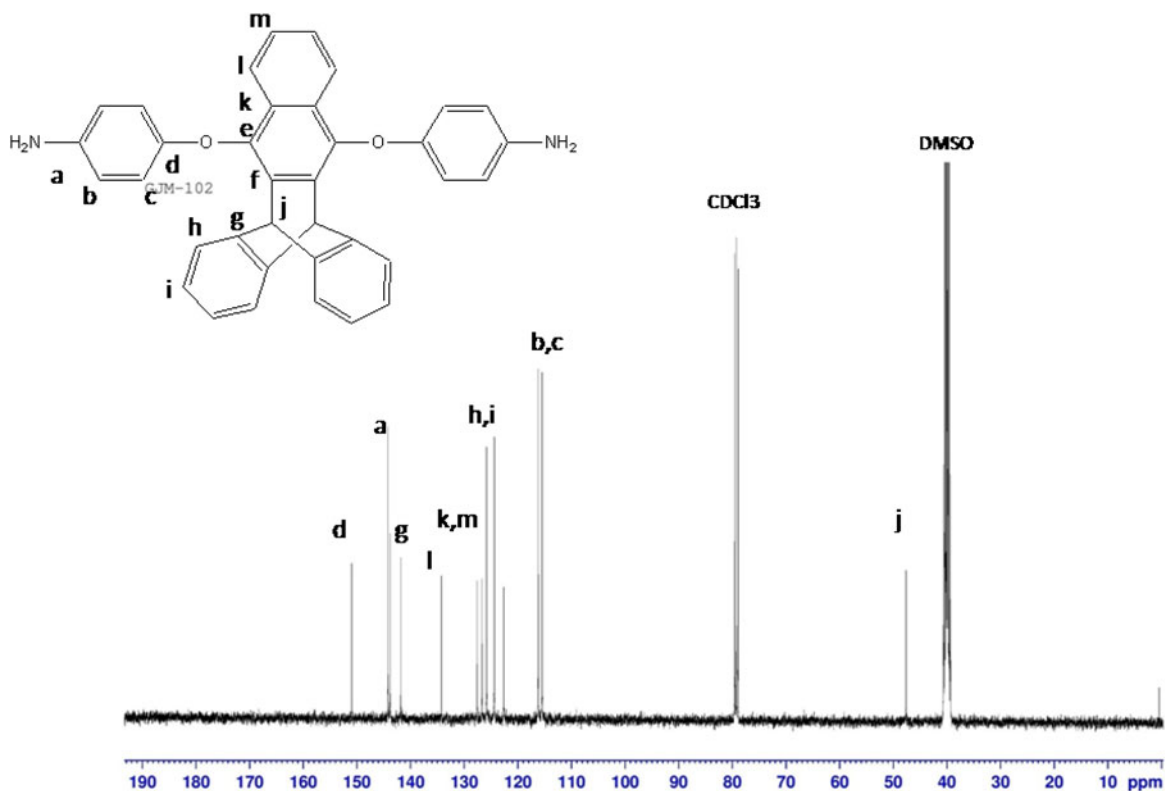


Figure 3.  $^{13}\text{C}$  Spectra of 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene(4a).

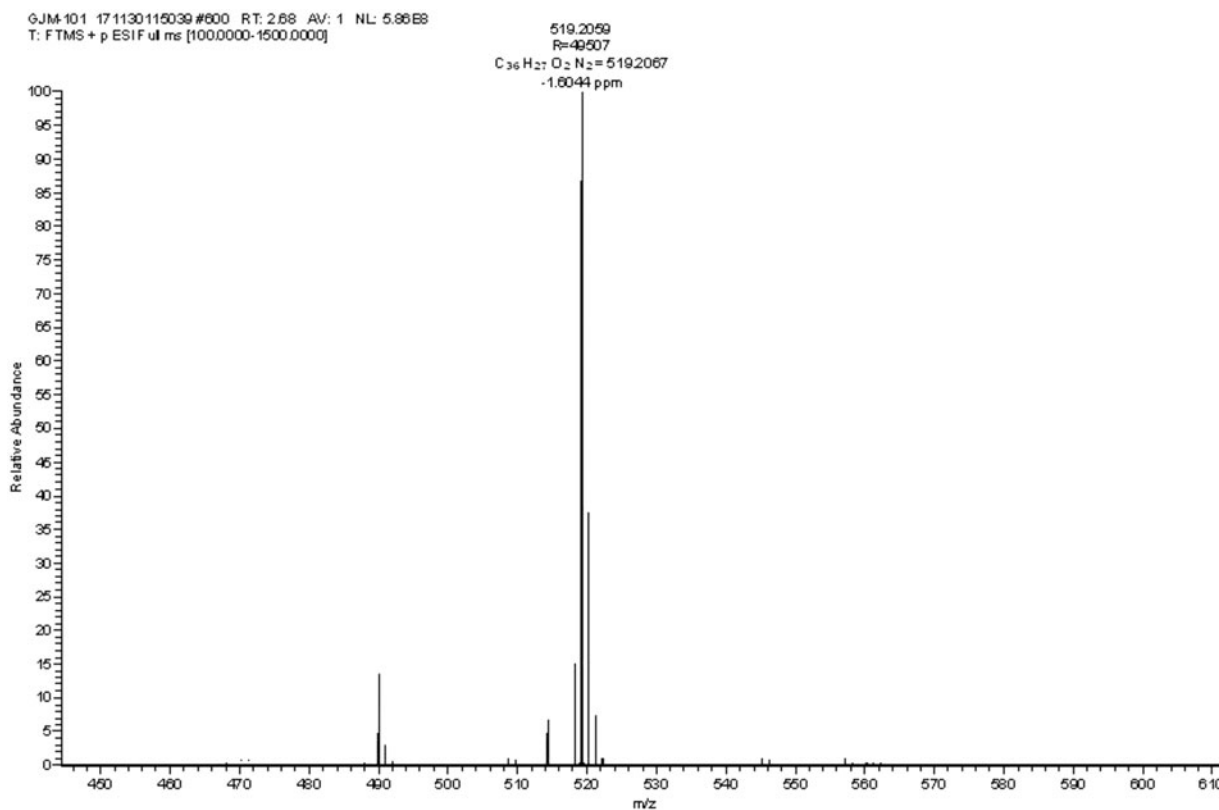
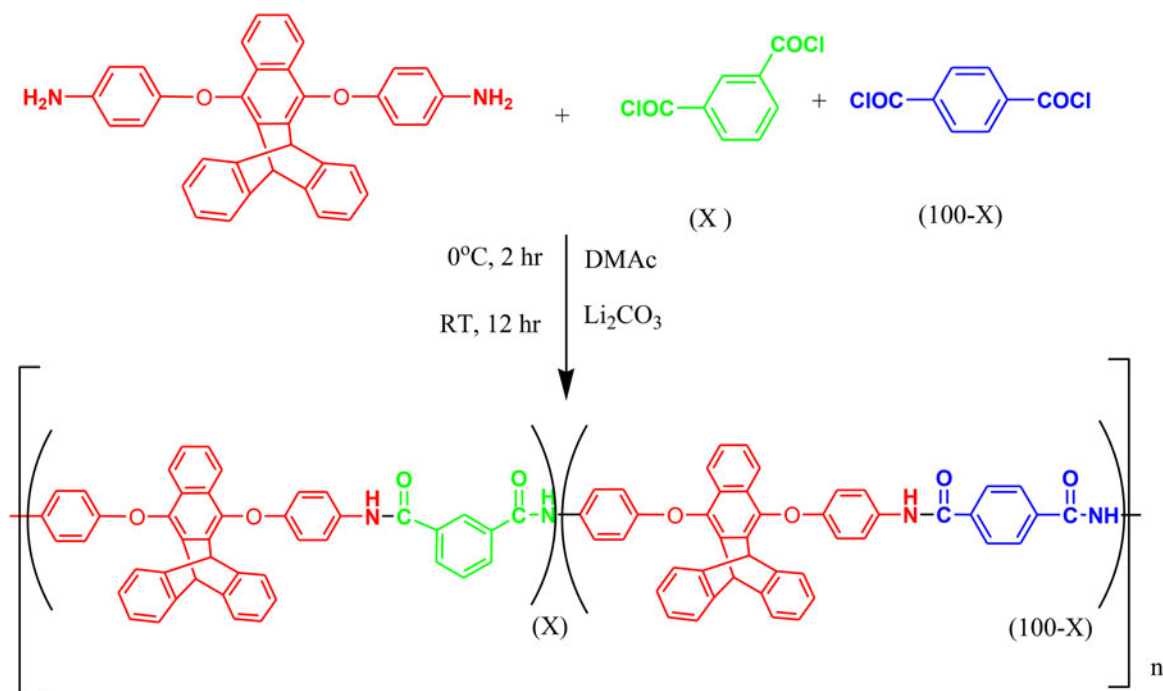


Figure 4. HRMS Spectrum of 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene(4a).

Peak at 5.66  $\delta$ ppm is due to allylic protons of triptycene moiety, and multiplet in the range of 8.57–6.64  $\delta$ ppm due to aromatic protons as expected with desired integration and splitting pattern.

### 5.3. Solubility properties

Solubility characteristics of aromatic poly(ether amide)s are summarized in Table 2. It is observed that PA-01 to PA-05



**Scheme 2.** Synthesis of poly(ether-amide)s from 1, 4-bis (4-aminophenoxy)2, 3-benzotriptycene. PA-01 to PA-05.

synthesized exhibited excellent solubility in common organic solvents and also in various polar aprotic solvents such as N-methylpyrrolidone (NMP), N, N-dimethyl sulphoxide (DMSO), N,N-dimethylacetamide (DMAc), tetrahydrofuran (THF) and need moderate heating to get soluble in polar protic solvents such as chloroform ( $\text{CHCl}_3$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) as well as it found completely soluble in formic acid ( $\text{HCOOH}$ ), Conc. $\text{H}_2\text{SO}_4$ .

Polymer PA-05 which synthesized from 100% TPC, exhibit comparative less solubility due to its stiff structure resulting it intomore close packing of polymer chains therefore why it needs moderate heating to achieve its complete solubility. Overall, good improvement in solubility of these polymers (PA-01 to PA-05), as expected; can be attributed to the introduction of cardo triptycene moiety, and ether linkages inthe polymer backbone. However all polymers were insoluble in acetone only.

#### 5.4. Thermal properties

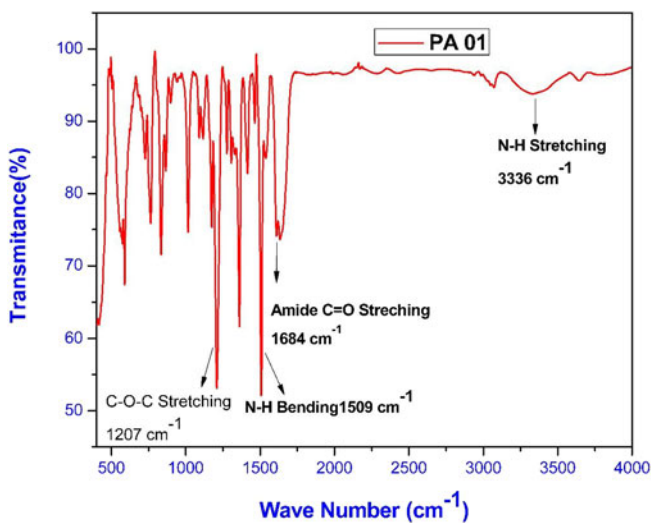
Thermal behavior of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry under nitrogen atmosphere Table 3 incorporates the thermal data such as glass transition temperature ( $T_g$ ), initial decomposition temperature ( $T_i$ ), 10% decomposition temperature ( $T_d$ ) and residual weight at 900 °C. The thermal stability of triptycene containing poly(ether amide)s outlined in Figure 7 was first dried to high temperature and further studied at a heating rate of 10 °C/min in nitrogen atmosphere by thermogravimetric analysis.<sup>[32–38]</sup>

The ( $T_d$ ), temperature at which 10% weight loss was observed, and also char yields at 900 °C were determined from thermograms. ( $T_i$ ) values were in the range of

**Table 1.** Yield and viscosity of poly(ether-amide)s.

Polymer Code	Monomers			Yield (%)	Viscosity (dL/g) <sup>a</sup>
	4a (%)	TPC (%)	IPC (%)		
PA-01	100	00	100	98	0.42
PA-02	100	25	75	99	0.45
PA-03	100	50	50	99	0.47
PA-04	100	75	25	100	0.55
PA-05	100	100	00	99	0.50

<sup>a</sup>alherent viscosity was measured at a concentration of 50 mg/10 ml in DMAc at 30 °C.



**Figure 5.** IR Spectrum of Poly(ether-amide)s PA-01.

295 °C–309 °C. In general, these polymers, like other polyamides, exhibited good thermal stability in nitrogen; 10% weight loss only takes place when they are heated beyond

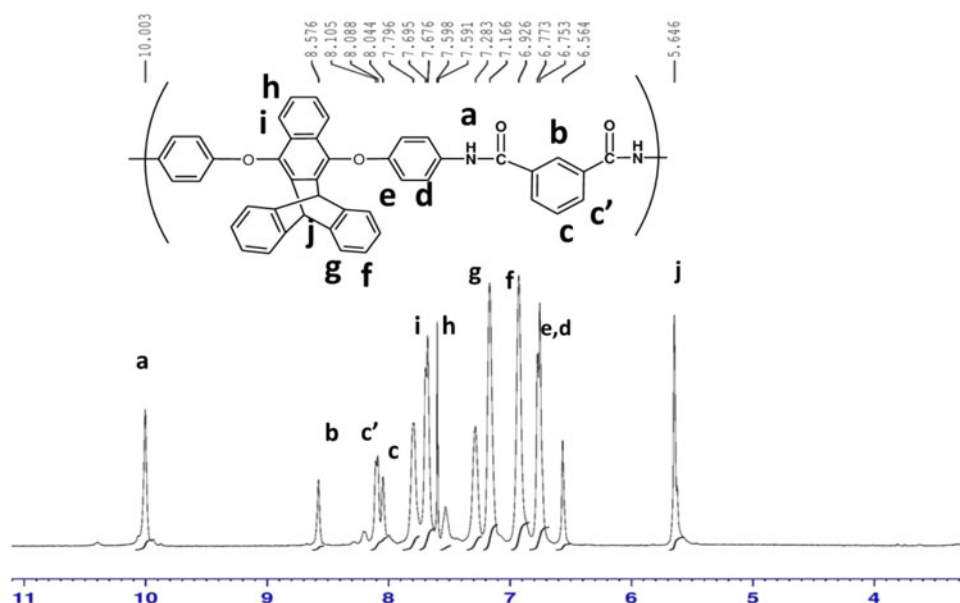


Figure 6.  $^1\text{H}$  NMR of poly(ether amide)s PA-01.

Table 2. Solubility of poly(ether-amide)s.

Polymer Code	Solubility							Conc. $\text{H}_2\text{SO}_4$
	DMF	DMAc	DMSO	NMP	$\text{CHCl}_3$	THF	Acetone	
PA-01	+	++	++	++	+ -	++	--	++
PA-02	+	++	++	++	+ -	++	--	++
PA-03	+	++	++	++	+ -	++	--	++
PA-04	+	++	++	++	+ -	++	--	++
PA-05	+	+	+	+	+ -	+	--	++

++: Soluble; + -: Partly Soluble; +: Soluble on heating; -: Insoluble.

Table 3. Thermal properties of poly(ether-amide)s.

Polymer Code	Thermal behavior <sup>a</sup>			Residual Wt % at 900 °C
	$T_g$ (°C) in $\text{N}_2$	$T_i$ (°C) in $\text{N}_2$	$T_d$ (°C) in $\text{N}_2$	
PA-01	276	212	587	24
PA-02	269	278	568	33
PA-03	284	311	627	29
PA-04	278	301	615	53
PA-05	273	305	631	54

<sup>a</sup>Temperature at which onset of decomposition was recorded by TG at a heating rate of 10 °C/min.

$T_g$  – Glass transition temperature detected at second heating by DSC at 10 °C/min heating rate.

$T_i$  – Initial Decomposition temperature.

$T_d$  – Temperature of 10% decomposition.

$T_i$  – Initial decomposition temperature.

295 °C in nitrogen. The temperature at which balance of TGA can detect first loss in weight of sample was taken as initial decomposition temperature ( $T_i$ ). This ( $T_i$ ) was determined from the same data of TGA analysis. The initial decomposition temperatures ( $T_i$ ) were found in the range 212 °C–305 °C. The char yields were observed in the range 24%–57% at 900 °C.

The glass transition temperature ( $T_g$ ) of poly(ether-amide)s containing triptycene moiety in their backbone, outlined in Figure 8 was studied at a second heating by DSC at a heating rate of 10 °C/min. The synthesized polyamides

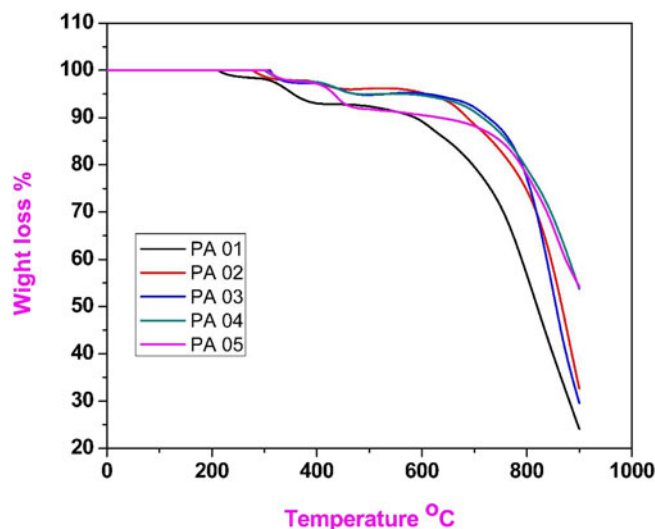


Figure 7. TGA curves of Poly(ether-amide)s.

showed glass transition temperature ( $T_g$ ) in the range 269 °C–284 °C. The glassy morphology of these polyamides is due to the presence of triptycene moiety as cardo group as well as ether linkages in the polymer backbone, which inhibits the crystalline packing.

### 5.5. X-ray diffraction

The triptycene containing poly(ether-amide)s (PA-01 to PA-05) were also characterized by the wide angle X-ray diffractometer. The wide angle X-ray diffraction pattern of all poly(ether-amide)s is shown in Figure 9. Broad halos without sharp peaks were observed in all WAXD patterns, suggesting a generally amorphous structure of the triptycene-based Poly(ether-amide)s. Depending on the monomer structure (i.e., triptycene), quite different diffraction patterns were



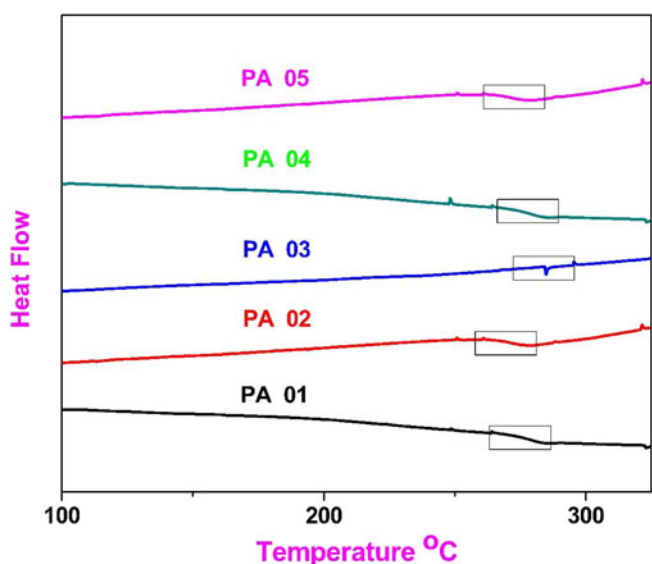


Figure 8. DSC curves of Poly(ether-amide)s.

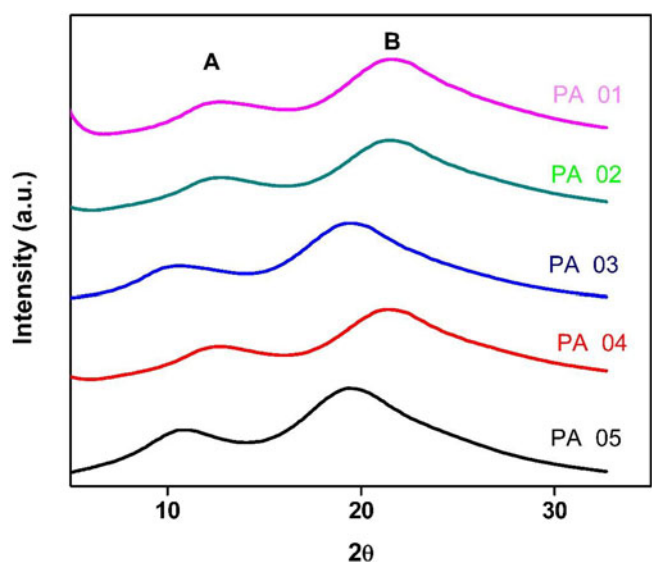


Figure 9. XRD pattern of Poly(ether-amide)s. PA-01 to 05.

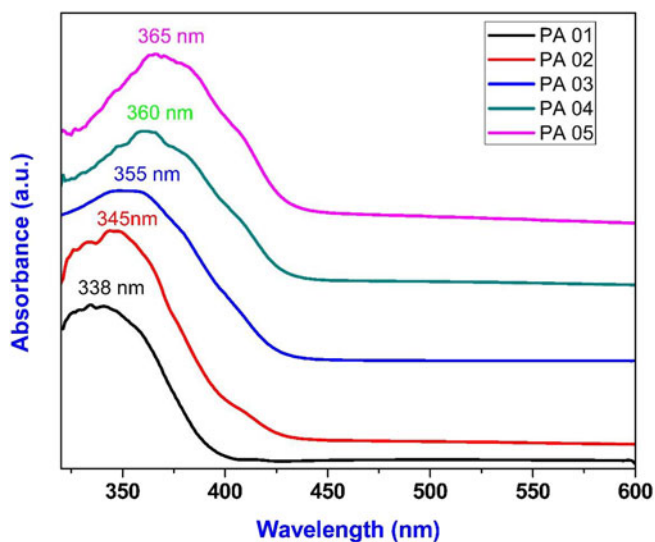


Figure 10. UV Vis Spectra of Poly(ether-amide)s PA-01 to PA-05.

Table 4. Absorption cut off values  $\lambda_{\max}$  (nm) and Energy band gap  $E_g$  (eV).

Sr No.	Polymers	Film thickness ( $\mu\text{m}$ )	$\lambda_{\max}$ (nm)	$E_g$ (eV)
1	PA 01	48	338	3.68
2	PA 02	55	345	3.60
3	PA 03	58	355	3.50
4	PA 04	53	360	3.45
5	PA 05	50	365	3.40

observed for these poly(ether-amide)s signifying different chain packing structures induced by triptycene moieties. All poly(ether-amide)s show two diffraction peaks (i.e., A and B) located at  $2\theta \approx 15^\circ$ , and  $20^\circ$ . These values are likely associated with the main interchain distance disrupted by the rigid triptycene units and  $\pi-\pi$  stacking of benzene blades rings of triptycene moieties. For the entirely triptycene based poly(ether-amide)s two broad peaks were observed, which represent the main interchain distance disrupted by triptycene units and the average interchain distance of amide backbone.

### 5.6. UV-Vis Spectroscopy

UV-Vis Spectroscopy (UV-Vis) spectra were recorded on a Beckman DU-640 spectrometer using DMAc as Solvent. The UV-Vis spectra (Figure 10) of poly(ether-amide)s show blue shifting of the corresponding peaks at 338 nm, 345 nm, 355 nm, 360 nm, and 365 nm  $\pi-\pi^*$  transition for PA-01, PA-02, PA-03, PA-04, and PA-05 respectively.

The optical band gap is determined by assuming the nature of transition ( $m$ ) and plotting  $(\alpha h\nu)^{1/m}$  vs  $h\nu$  where  $m$  represents the nature of transition. The exponent  $1/m$  may have different values, such as  $1/2$ ,  $2$ ,  $3/2$ ,  $3$  for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The optical absorption coefficient " $\alpha$ " near the absorption edge for direct interband transition is given by...

$$\alpha = B (h\nu - E_g)^{1/2} / h\nu \quad (1)$$

Where  $B$  is the absorption constant for direct transition and  $E_g$  is the band gap. For allowed direct transition one can extrapolate the linear portion of to  $\alpha=0$  value to obtain the corresponding band gap. Similarly the Band Gap Energy ( $E_g$ ) was calculated and found in the range of 3.68–3.40 eV (Table 4); Figure 10 describes the UV-visible spectra of poly(ether-amide)s, the cutoff wavelengths (absorption edge;  $\lambda_{\max}$ ) from the UV-vis spectra and are also displayed in Table 4.

The cutoff wavelengths (absorption edge;  $\lambda_{\max}$ ) from the UV-vis spectra are also listed in Table 4. All the poly(ether-amide) films showed cutoff wavelengths shorter than 410 nm and were entirely transparent and near colorless which is shown in Figure 11. All the polymer films in this work exhibited much lighter color. The low color of these poly(ether-amide)s could be explained by the decreased intermolecular electronic interactions. The bulky and three-dimensional triptycene units in polyamide component were responsible in decreasing charge-transfer complexing (CTC) between the polymer chains through a steric hindrance effect.

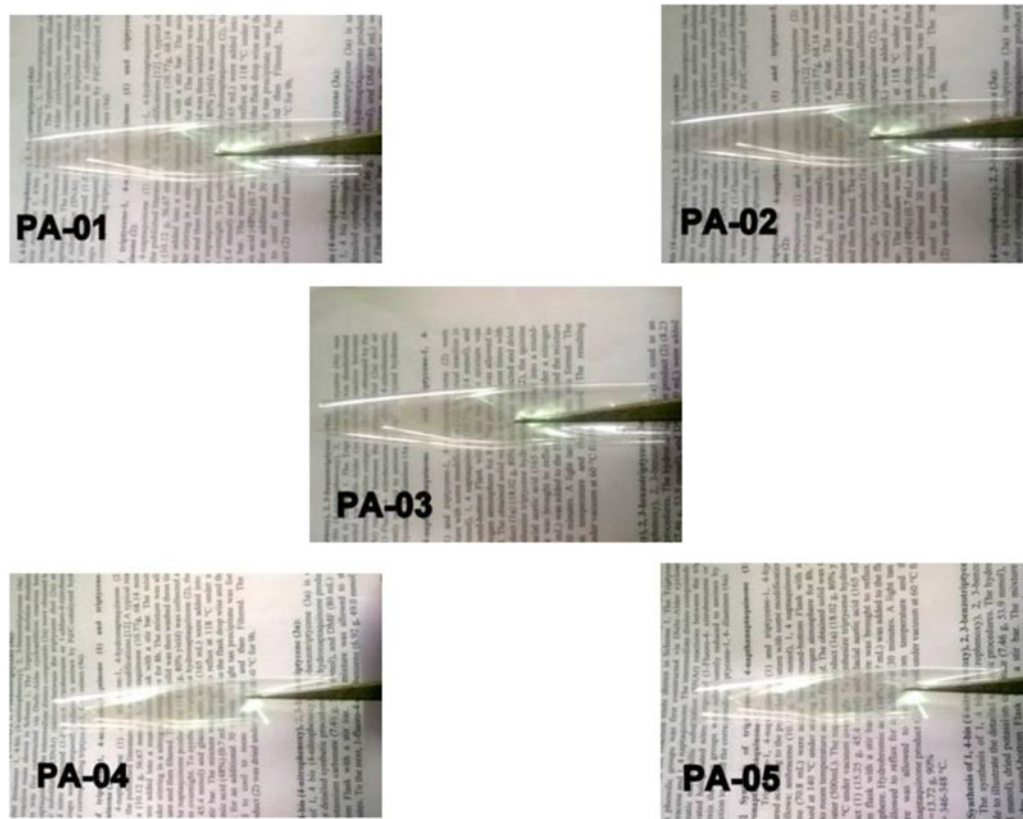


Figure 11. Film images of Poly(ether-amide)s PA-01 to PA-05.

## 6. Conclusions

A series of new poly(ether-amide)s containing pendant triptycene moiety, flexible ether linkage, was synthesized by elevated temperature solution polycondensation of 1,4-bis(4-aminophenoxy), 2,3-benzotriptycene and commercial aromatic diacidchlorides viz., terephthalylchloride (TPC), isophthalylchloride (IPC). Poly(ether-amide)s showed excellent solubility properties. Which attributes to incorporation of cardo triptycene moiety, and ether linkage which leads to significant improvement in solubility of polyamides. Inherent viscosities of polyamides were in the range of 0.44–0.57 dL/g. Inherent viscosities of poly(ether-amide)s indicated the formation of medium to reasonably high molecular weight polymers. Wide angle X-ray diffraction patterns indicated that polyamides were amorphous in nature. ( $T_d$ ) values were in the range 295 °C–309 °C indicating good thermal stability of polyamides and the char yield at 900 °C found in the range of 24%–54%. ( $T_i$ ) values of polyamides were in the range 212 °C–305 °C. The considerable barrier in glass transition temperature and decomposition temperature of polyamides offers a broad processing margin, which could be considered as remarkable advantage. The UV-Vis spectra poly(ether-amide)s shows shifting at 338 nm, 345 nm, 355 nm, 360 nm, and 355 nm  $\pi-\pi^*$  transition for PA-01, to PA-05 respectively. All the poly(ether-amide)s thin films found to be almost transparent, colorless as well as flexible in nature. Thus, above poly(ether-imide)s could be used in relevant fields of applications.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

The authors are thankful to the Solapur University, Solapur for supporting financially through Department Research Fellowship (DRF).

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