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Synthesis and Characterization of New Polyamides Containing Thianthrene Moiety and Based on Dibenzylidene Derivatives

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Author's contribution

This whole work was carried out by author NSAM.

Original Research Article

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ABSTRACT

A new series of polyamides based on diarylidene derivatives were synthesized from 2,5-bis(m-aminobenzylidene)cyclopentanone VIII, 2,6-bis(m-aminobenzylidene)cyclohexanone IX, 2,7-bis(m-aminobenzylidene) cyclheptanone X and bis(m-aminobenzylidene) acetone XI by reaction with diacid chlorides of thianthrene (2,7-Dichloroformylthianthrene -5,5`,10,10`-tetraoxide IV. using solution polycondensation technique. These polymers ranged from yellow to orange color and had inherent viscosity up to 1.08-0.65 dL/g. All the polyamides were insoluble in common organic solvents but dissolved completely in concentrated H2SO4. The thermal stabilities of the prepared polyamides were evaluated by TGA and DSC analyses. The morphological properties of some selected polyamides were detected by SEM.

Keywords: Polyamides; thianthrene; thermal Properties; arylidene polymers.

1. INTRODUCTION

Synthetic polyamides are among the most widely used engineering thermoplastics, owing to many outstanding properties to their semicrystalline morphology and to the intermolecular hydrogen bonding of the amide groups. Polyamides are common multipurpose synthetic polymers used in a wide range of industrial settings and consumer products as fibers,

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amorphous and crystalline plastics, adhesives, etc. They can be produced from aliphatic, both aliphatic and aromatic, and from purely aromatic monomers giving different types of polyamides. These materialshave excellent mechanical, [1] thermal properties, [2−4] and chemical resistance [5]. High performance, thermally stable thermoplastic polymers are currently receiving considerable attention for their potential use as structural resins or resin/fiber composites in commercial aircraft, aerospace vehicles, and engineering materials [6]. High temperature polymers (H-T) are known that have tricyclic aromatic and/or heterocyclic fused rings such as phenoxathine, dibenzo-p-dioxine, thianthrene, phenoxaphosphine, and phenazasiline moieties in their main chain [7-9]. The literature reveals that many polyamides and polyimides containing different heterocyclic moieties have been prepared and studied [10,11]. Recently Prema and Srinivasan reported the preparation and properties of polyamides containing thianthrene units [12]. Up to this date, no report has appeared on the synthesis of linear unsaturated polyamides with thianthrene units in the polymer backbone. The work presented here outlines the synthesis and characterization of new polyamides of diarylidenecycloalkanones that include thianthrene moieties. A major target for this work was to study the effect of cycloalkanone ring size on the thermal stability properties of the polyamides. The crystallinity, solubility, and morphologic properties of this new class of polyamides are also examined.

2. EXPERIMENTAL

2.1 Measurements

Elemental analyses were carried out using an Elemental Analyses system GmbH, VARIOEL, $V_{2.3}$ July 1998 CHNS Mode. IR spectra were recorded on IR-470, Infrared spectrophotometer, Shimadzu by using the KBr pellet technique. The ^{1}H-NMR spectra were recorded on a GNM-LA 400-MHz NMR spectrophotometer at room temperature in DMSO or $CDCl_3$ using TMS as the internal reference. Inherent viscosities of polymer solutions (0.5% w/v) in DMSO were determined at 30 ºC using an Ubbelohde suspended level viscometer. The solubility of polymers was examined using 0.02 g of polymer in 3-5 ml of solvent at room temperature. The electrical conductivities were measured using a Keithly electrometer (610C). The X-ray diffractographs of the polymers were obtained with a Philips X-ray PW1710 diffractometer, and Ni – filtered CuKα radiations. Thermogravimetric analysis (TGA) and differential thermal gravimetric (DTG) were carried out in air with Shimadzu DTG-60 at heating rate of 10ºC/min. in air. The morphology of a selected example of polyamide XVIII was examined by SEM(Jeol JSM-5400 LV instrument). The SEM sample was prepared by evaporating a dilute solution of polymer on a smooth surface of aluminium foil, and subsequently coating it with gold palladium alloy. SEM images were taken on a Pentaz Z-50 P Camera with Ilford film at an accelerating voltage of 15 KV using a low dose technique.

2.2 Reagents and Solvents

Cyclopentanone (Merck, 99%), cyclohexanone (Merck, 99%), cycloheptanone (Merck, 99%), acetone (98%) and anhydrous lithium chloride (Merck) were used without purification. Acetyl chloride and thionyl chloride (Aldrich, 98%) were used without purification. Carbon disulphide, distillation of appreciable quantities of CS_2 should be carried out in a water bath at 55 – 65ºC. The commercial substance may be purified by shaking for 3 hrs with mercury. It is then dried over anhydrous calcium chloride, and fractionated from a water bath at 55 – 65ºC. The pure compound boils at 46.5ºC / 760 mmHg. Anhydrous $AlCl_3$ (Merck) was used as it is. m-nitrobenzaldehyde (Sigma, m.p. 55-58ºC) used as it is. All other reagents were of high purity and were further purified as reported in literature [13].

2.3 Monomer Synthesis

2.3.1 Thianthrene (I)

Thianthrene was prepared as described in the literature [14].

2.3.2 2,7-Diacetylthianthrene (II)

A solution of thianthrene I (8.89g, 0.04 mol) in 50 ml, of dry CS_2 was added dropwise to a stirred mixture of acetyl chloride (25.76 g, 0.326 mol) and anhydrous $AlCl_3$ (22.4g, 0.364 mol) in 150 ml, CS_2 . During the addition, the temperature of the reaction was kept at 10ºC. After the end of the addition, the reaction mixture was stirred at ambient temperature for 20 h and then poured onto crushed ice/HCl. The solid product formed was filtered off, washed with water, dried, and then recrystallized from an ethanol-benzene mixture (4:1) as pale yellow needles, Yield 70%, mp 175ºC, literature (Srinivasan et al. [9]) 175ºC. IR (KBr) 1695 cm^{-1} (C=O); ^{1}H-NMR (δ/$CDCl_3$) showed at 7.35-8.15 (m, 6H of Ar-H) and at 2.65 (s, 6H of 2 $COCH_3$) ppm.

2.3.3 Synthesis of 2,7-Thianthrenedicarboxylic Acid-5,5`,10,10`-tetraoxide (III)

Compound (III) was prepared in 89% yield by oxidation of II by using a procedure similar to that given in ref.(Srinivasan et al. [9]) mp >300 . Analysis Calculated for C_{14} H_8 O_8S_2: C 45.69; H 2.77; S, 17.46. Found: C 45.53; H, 2.09; S, 17.59. IR (KBr) 1715 cm^{-1} (C=O), 3350-3100 cm^{-1} (OH) , 1310,1165 ,1130 cm^{-1} (SO_2). ^{1}H-NMR (δ/DMSO-d_6) showed at 7.5-8.45 (m, 6H of Ar-H) and at 5.8 (s, 2H of COOH$_)$ ppm.

2.3.4 Synthesis of 2,7- Dichloroformylthianthrene -5,5`,10,10`-tetraoxide (IV)

A mixture of diacid (III) (7.2g, 0.02 mol) was boiled in 50 ml, of thionyl chloride in the presence of few drops of pyridene as catalyst. The excess of thionyl chloride was distilled off and the residual matter was recrystallized from benzene- petroleum ether 60-80 (1:1), yield 85%, mp 180 °C. Analysis Calculated for $C_{14}H_6O_6S_2Cl_2$: C, 41.58; H 1.48; S, 15.84, Cl, 17.32. Found: C, 41.50; H, 1.50; S, 15.70; Cl, 17.21.

IR (KBr) 1765 cm^{-1} (C=O), 1320, 1180,1120 cm^{-1} (-SO_2).

2.3.5 2,5-Bis(*m*-nitrobenzylidene)cyclopentanone (V)

A mixture of the *m*-nitrobenzaldehyde (30.21 g, 0.2 mole), cyclopentanone (11.21 g, 0.1 mole), and ethanol (95%, 100 ml) was introduced in a conical flask (250 ml). The mixture was warmed at about 50ºC to obtain a solution, and few drops of catalytic KOH (20%) were added with stirring for 2 hrs. An exothermic reaction was observed, while a highly yellowish solid separated out. It was filtered off, washed thoroughly with water and recrystallized from as yellow needles from ethanol; yield: 97%; m.p.: 205ºC. Anal. Calcd. for $C_{19}H_{14}N_2O_5$: Calcd. %: C, 65.14; H, 4.00; N, 8.00. Found %:C, 65.03; H, 4.10; N, 7.87.

2.3.6 2,6-Bis(*m*-nitrobenzylidene)cyclohexanone (VI)

A mixture of the *m*-nitrobenzaldehyde (30.21g, 0.2 mole), cyclohexanone (11.21 g, 0.1 mole), and ethanol (95%, 100 ml) was introduced in a conical flask (250 ml). The mixture was warmed at about 50ºC to obtain a solution, and few drops of catalytic KOH (20%) were added with stirring for 2 hrs. An exothermic reaction was observed, while a highly yellowish solid separated out. It was filtered off, washed thoroughly with water and recrystallized from as yellow needles from ethanol; yield: 93%; m.p.165ºC. Anal. Calcd. for $C_{20}H_{16}N_2O_5$: Calcd. %:C, 65.93; H, 4.40; N, 7.69. Found %:C, 65.82; H, 4.23; N, 6.57.

2.3.7 2,7-Bis(*m*-nitrobenzylidene)cycloheptanone (VII)

A mixture of the *m*-nitrobenzaldehyde (30.21 g, 0.2 mole), cycloheptanone (11.21g, 0.1 mole), and ethanol (95%, 100 ml) was introduced in a conical flask (250 ml). The mixture was warmed at about 50ºC to obtain a solution, and few drops of catalytic KOH (20%) were added with stirring for 2 hrs. An exothermic reaction was observed, while a highly yellowish solid separated out. It was filtered off, washed thoroughly with water and recrystallized from as yellow needles from ethanol; yield: 95%; m.p. 175ºC. Anal. Calcd. for $C_{21}H_{18}N_2O_5$: Calcd. %: C, 66.67; H, 4.76; N, 7.41. Found %: C, 65.93; H, 4.63; N, 7.27.

2.3.8 2,7-Bis(*m*-nitrobenzylidene)acetone (VIII)

Obtained by the condensation of *m*-nitrobenzaldehyde (30.21 g, 0.2 mole) with acetone (5.81 g, 0.1 mole) for 2 hrs as yellow needles from dioxane; yield: 86%; m.p. 220ºC. Anal. Calcd. for $C_{17}H_{12}N_2O_5$: Calcd. %:C, 63.35; H, 3.73; N, 8.70. Found %:C, 63.13; H, 3.67; N, 8.51.

2.3.9 2,5-Bis(*m*-aminobenzylidene)cyclopentanone (IX)

A flask was charged with a mixture of compound V (2.982g, 8.52 mmol), ethanol (95% 40 ml), and a catalytic quantity of 10% palladium on activated carbon. Hydrazine hydrate (4 ml) diluted with ethanol (10 ml) was added dropwise to the stirred mixture at 60ºC. It was subsequently heated at this temperature for 30 min. The solid gradually dissolved during hydrogenation. The reaction mixture was filtered off and the filtrate was concentrated by rotary evaporation. The residue was dried in a vacuum oven to yield a compact pale yellow solid. An analytical sample was obtained by recrystallization from ether/THF (1:1) in the form of yellowish crystals (1:1 mp 101°C, 90% yield). Anal. Calc. for $C_{19}H_{18}N_2O$: C, 78.62; H, 6.20; N, 9.65. Found: C, 78.17; H, 5.88; N, 9.27. IR (KBr, cm^{-1}): 3460-3190 (NH stretching); 2950-2870 (cyclopentanone C-H stretching); 1660 (C=O of cyclopentanone); 1600 (C=C); 695 (NH deformation). ^{1}H-NMR (DMSO-d_6 ppm): 6.39-7.04 (m, 8H of Ar-H and 2H of 2CH=C); 4.98 (s, 4H of $2NH_2$); 3.10, 3.45 (m, 4H of cyclopentanone).

2.3.10 2,6-Bis(*m*-aminobenzylidene)cyclohexanone (X)

A procedure similar to that used for [XI] was followed. An analytical sample of X (mp. 123ºC 85% yield) was obtained as yellowish crystals recrystallization from ether/THF. Anal. Calc, for $C_{20}H_{20}N_2O$: C, 78.95; H, 6.49; N, 9.21. Found: C, 78.15; H, 6.2 1; N, 9.02. IR (KBr, cm^{-1}): 3350 (NH stretching); 2900 (C-H of acetone); 1695 (C=O of cyclohexanone); 1585 (C=C); 685 (NH deformation). ^{1}H-NMR (DMSO-d_6 ppm): 6.4-7.4 (m, 8H of Ar-H and 4H of 2CH=CH); 4.0-4.5 (4H of $2NH_2$).

2.3.11 2,7-Bis(*m*-aminobenzylidene)cycloheptanone (XI)

A procedure similar to that used for XIwas followed. An analytical sample of XI (mp. 102ºC 90% yield) was obtained as yellowish crystals after recrystallization from ether/THF. Anal. Calc, for $C_{21}H_{22}N_2O$: C, 79.25; H, 6.92; N, 8.81. Found: C, 79.15; H, 6.31; N, 8.23. IR (KBr, cm^{-1}): 3350 (NH stretching); 2900 (C-H of acetone); 1690 (C=O of cycloheptanone); 1590 (C=C); 685 (NH deformation). ^{1}H-NMR (DMSO-d_6 ppm): 6.4-7.4 (m, 8H of Ar-H and 4H of 2CH=CH); 4.0-4.5 (4H of $2NH_2$).

2.3.12 Bis(*m*-aminobenzylidene)acetone (XII)

A procedure similar to that used for XI was followed. An analytical sample of X (mp. 105ºC, 82% yield) was obtained as yellowish crystals after recrystallization from ether/THF. Anal. Calc, for $C_{17}H_{16}N_2O$: C, 77.27; H, 6.06; N, 10.60. Found: C, 77.15; H, 6.01; N, 10.23. IR (KBr, cm^{-1}): 3350 (NH stretching); 2900 (C-H of acetone); 1695 (C=O of acetone); 1590 (C=C); 685 (NH deformation). ^{1}H-NMR (DMSO-d_6 ppm): 6.4-7.4 (m, 8H of Ar-H and 4H of 2CH=CH); 4.0-4.5 (4H of $2NH_2$).

2.3.13 2,5-Bis(*m*-aminobenzylidene)cyclopentanone dibenzamide (XIII)

Triethylamine (8.0 mmol) was added to a solution of 2,5-Bis(m-aminbenzylidene)cyclopentanone IX (4 mmol) in DMF (15 ml). Benzoyl chloride (8.0 mmol) diluted with DMF (8 ml) was added to the stirred solution under N_2 at 0°. The mixture was subsequently stirred at room temperature in a stream of N_2 for 2 hr. The solid product was filtered off, washed with dilute aq. $NaHCO_3$, then with water and dried to afford XIII. An analytical sample was obtained by recrystallization from Ethanol/Ether (mp 180°C, 84% yield). Anal. Calc, for $C_{33}H_{26}N_2O_3$: C, 79.51; H, 5.22; N, 5.62. Found: C, 79.10; H, 5.44; N, 5.06. IR (KBr, cm^{-1}): 3300-3200 (NH stretching); 3020 (cyclopentanone C-H stretching); 1690-1620 (amid C=O, cyclopentanone C=O and C=C); 680 (NH deformation); 1435 (cylopentanone C-H deformation); 1310 (C-H stretching of the olefinic bond). ^{1}H-NMR (DMSO-d_6 ppm): 10.5 (2H of 2NHCO); 8.1 (8H, aromatic ortho to C=O); 7.1-7.7 (m, 10H other aromatic and 2H olefinic); 3.2-3.5 (m, 4H of cyclopentanone).

2.3.14Bis(*m*-aminobenzylidene)acetone dibenzamide (XIV)

Using a procedure similar to that described for compounds XII, XIII, analytical sample of XIV (mp 240°C, 89% yield) was obtained in the form of pale yellow crystalls after recrystallziation from ethanol/ether (2:1). Anal. Calc. for $C_{31}H_{24}N_2O_3$: C, 78.81; H, 5.08; N, 5.93. Found C, 78.10; H, 4.85; N, 5.56. IR (KBr, cm^{-1}) 3300-3200 (NH stretching); 3020 (acetone C-H stretching); 1690-1620 (amide C=O, acetone C=O and C=C); 670 (NH deformation); 1420 (acetone C-H deformation);1305 (C-H stretching of the olefinic bond). ^{1}H-NMR (DMSO-d_6 ppm): 10.5 (2H of 2NHCO); 8.0 (m, 4H, aromatic ortho to C=O and 2CH=C olefinic); 7.1-7.7 (m, 14H other aromatic and 2H olefinic).

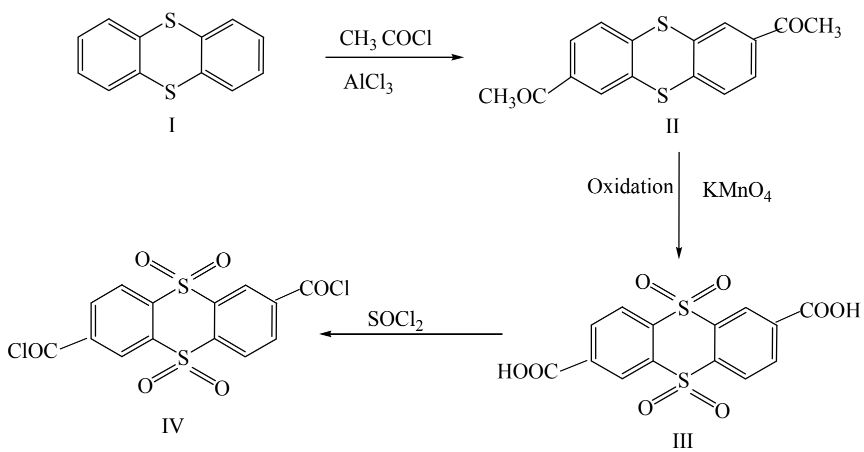
2.4 Synthesis of POLYAMIDES (XVI-XIX)

These polymers were prepared according to the following general procedure, as described here for the polyamide XVI.To a flask charged with a mixture IX(1.740 g, 6.0 mmol),DMF or NMP (15 ml), triethylamine (1.214 g, 12mmol) and a solution of 2,7-Dichloroformylthianthrene -5,5`,10,10`-tetraoxide(IV) (1.215 g, 6.0 mmol) in DMF (15ml) was added dropwise and mainting the stirred solution at 0ºC under N_2. The mixture was subsequently stirred at ambient temperature in a stream of N_2 for 3 hr, then it was poured into ice-water to give a yellowish to deep yellow colored solid. This was filtered off, washed with dilute aqu. $NaHCO_3$, then with water, ethanol, acetone and finally dried under reduced pressure (1 mmHg) at 70ºC for 2 days, The synthesized polyamides XVI-XIX their physical properties are listed in Table 1.

3. RESULTS AND DISCUSSION

3.1 Synthesis of 2,7- Dichloroformylthianthrene--5,5`,10,10`-Tetraoxide (IV)

A thianthrene precursor was prepared as described in the literature Dougherty et al. [14] by reaction of sulfur and benzene with $AlCl_3$ in the presence of carbon disulfide as a reaction medium to afford thianthrene in good yield. Acetylation of thianthrene with acetyl chloride by a Friedel-Crafts reaction catalyst was used to obtain II. By oxidation of II with $KMnO_4$ in week basic medium at pH 8.5, III was established in good yield, mp> 300ºC. The corresponding acid chloride IV was acquired in 87% yield by the interaction of the diacid III with excess thionyl chloride and a few drops of pyridene as catalyst. All steps followed for the preparation of IV are depicted in Scheme 1.



Scheme I : Synthesis of 2,7-Dichloroformylthianthrene-5 ,5`,10,10`- tetraoxide IV.

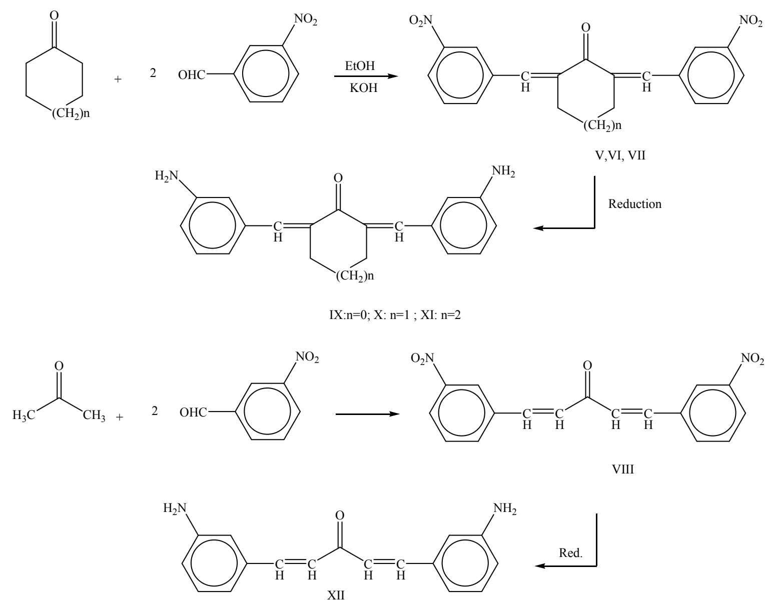
3.2 Synthesis of Diarylidene Monomers

Scheme 2 formulates the methods utilized for the preparation of the diarylidenecycloalkanone and diarylideneacetone monomers VIII, IX, X and XI. As shown, these monomers were prepared by the base-catalyzed condensation of two moles of m-nitrobenzaldehyde with one mole of cyclopentanone, cyclohexanone, cycloheptanone, or acetone respectively followed by hydrogenation using palladium on activated carbon in ethanol at 50ºC. Note that the hydrogenation step in Scheme 2 should not be excessively prolonged in order to the presence of carbonyl and olefinic function. The IR and ^{1}H-NMR spectra of these three monomers did not show detectable hydrogenation of these segments under the particular experimental conditions employed. Moreover, literature survey revealed that hydrogenation of the cyclohexanone carbonyl group requires acidic medium, a platinum catalyst, and a pressure of 30-45 psi to preferentially give the axial alcohol [15].

Table 1. Elemental Analyses, Inherent Viscosity and Yield of Polyamides XVI-XIX

Polymer code	Repeating unit	C%		H%		N%		S%		η_{Inh} (dl/g)	Yield %
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
XVI	$C_{33}H_{22}O_7N_2S_2$ (622)	63.67	62.98	3.53	3.07	4.50	4.12	10.29	9.91	0.73	68
XVII	$C_{34}H_{24}O_7N_2S_2$ (636)	64.15	63.16	.77	3.09	4.40	4.10	10.06	9.43	1.08	73
XVIII	$C_{35}H_{26}O_7N_2S_2$ (650)	64.62	63.71	4.00	3.47	4.31	4.01	9.85	9.16	0.92	65
XIX	$C_{31}H_{18}O_7N_2S_2$ (594)	62.63	62.51	3.03	2.24	4.71	4.51	10.77	10.22	0.65	72

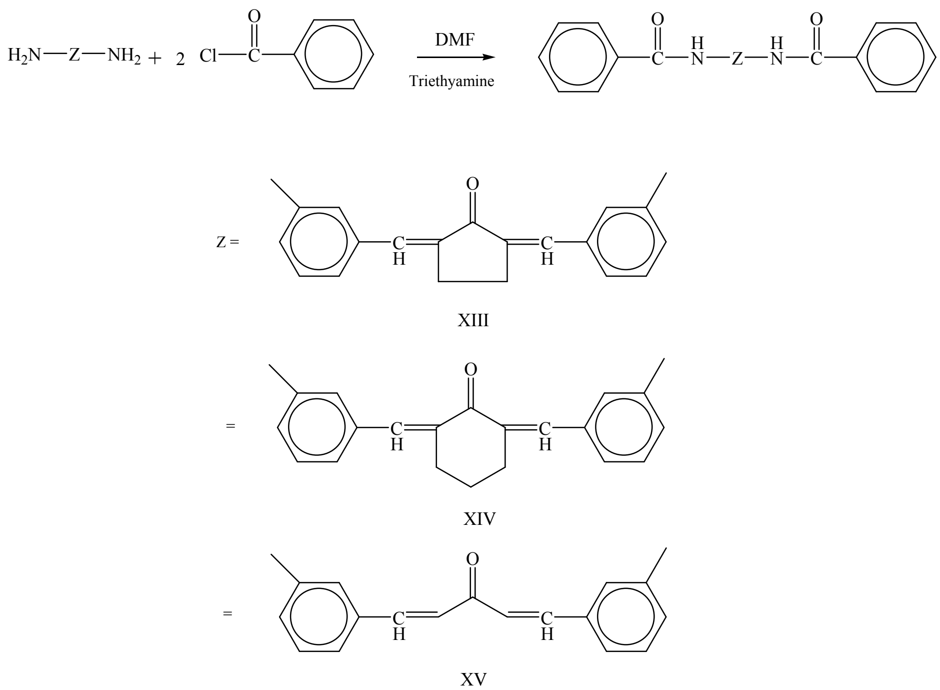
**η Inherent viscosity measured in H2SO4 at 25ºC*



Scheme 2. Synthesis of diarylidene monomers IX-XII

3.3 Synthesis of Model Compounds

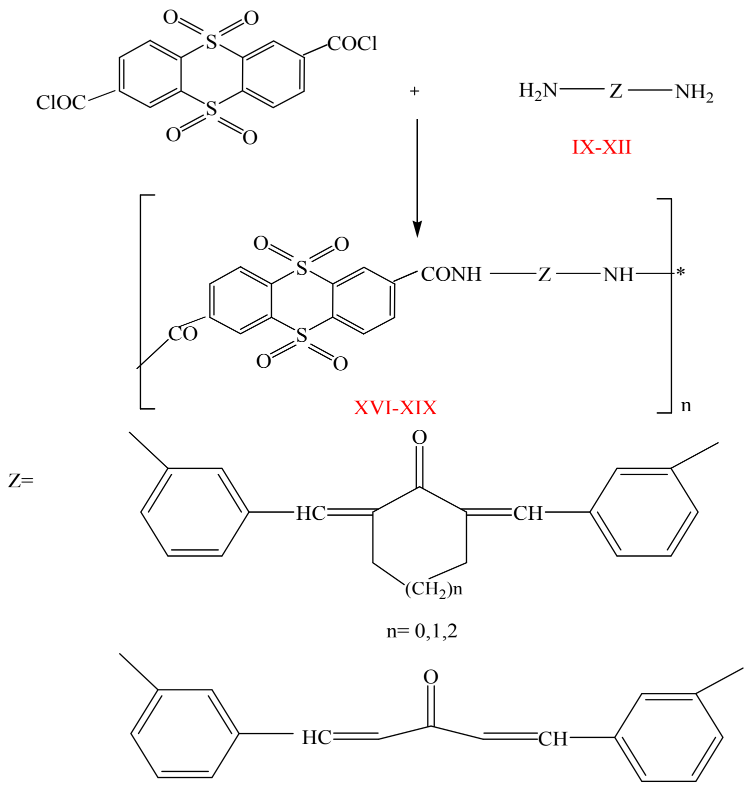
Before attempting the polymerization, model compounds were prepared by the reaction of diamines (IX-XII) with two equivalent of benzoylchloride. A typical example is the reaction of 2 mols of benzoylchloride with 1 mol of IXTheidentity of these model compounds were confirmed by both elemental and spectral IR and ^{1}H NMR data (Scheme 3).



Scheme 3. Synthesis of Model Compounds XIII-XV

3.4 Synthesis of Polyamides

A new class of polyamides containing dibenzylidenecycloalkanone and dibenzylidene acetone in the main chain were prepared from the polymerization of IX-XII with diacid chloride as shown in Scheme 4.



Scheme 4. Synthesis of polyamides XVI-XIX

Polyamides were synthesized by a low temperature solution polycondensation technique [16,17] in a solvent like NMP which dissolves the diamines and acts as a good acid acceptor for the HCl liberated during the polymerization reaction and also in the presence of LiCl, as catalyst. LiCl-NMP solution is powerful enough to keep the growing polymer chain in solution as its molecular weight builds up. Reaction times varied from 5-6 hrs. Polyamides were immediately isolated (see experimental part) when the reaction solution was poured into an ice/water mixture, with yields in the range of 68-73%. The resulting polyamides were characterized by elemental analysis, IR, solubility, viscocity measurements,thermal analysis, and morphological properties. The elemental analyses of all the different polymers coincided with the characteristic repeating units of each polymer. It should be noted that the elemental analyses for the polymers deviated up to 1.31% from the theoretical values. However, it is not uncommon for polymers to trap solvents within the matrix, especially for polyamides of high molecular mass and those containing polar groups, which are capable of hydrogen bonding with solvent molecules [18].

Spectral data supported the structural assignments for the polymers and are in good agreement with spectral data obtained for the model compounds. The IR data obtained in KBr discs for all the polyamides showed the absorption band for N-H stretching at 3350-3200 cm^{-1} characteristic for secondary amino group. The appearance of carbonyl absorptions at 1630-1650 cm^{-1}, known as the amide I band, is due to carbonyl stretching vibration. A strong amide II band, due to the coupling of N-H bending and C-N stretching of the C-N-H group was noted at 1535-1515 cm^{-1}. In addition, 1630-1645 cm^{-1} for (C=O, cycloalkanone), and at 1590-1600 cm^{-1} for (C=C). The lowering of the usual carbonyl frequency from 1715 to 1690 -1680 cm^{-1} is due to the resonance effect [19]. Because the polyamides were examined in the solid state, hydrogen bonding could be the major contributing factor in their lower carbonyl absorption frequency [20].

3.5 Polymer Characterization

The various characteristics of the resulting polyamides including solubility, viscometry, X-ray diffraction analysis, thermal analysis, and morphological properties were also determined and the data were discussed below.

The solubilities of the polyamides XVI-XIX were tested in various solvents including a DMF-DMA mixture, NMP, DMSO, rn-cresol, a $CHCl_3$,-acetone mixture (1: 1 ratio), trifloroacetic acid, concentrated H_2SO_4, and methanesulfonic acid. It was found that polyamideXVI ,is insoluble in a DMF-DMA mixture, NMP, m-cresol, and an acetone - $CHCl_3$, mixture, while polyamide XVI , is slightly insoluble in those solvents. All the polymers are completely soluble in DMSO. In strong protic solvent such as concentrated $H_2SO_4$and methanesulfonic acid, all the polymers were readily soluble, giving a violet color. The greater solubility of polymer XVIII may be attributed to the greater flexibility of the cycloheptyl ring in the polymer main chain [21] (see Table 2).

The X- ray diffractograms of selected examples of polyamidesXVI and XVII (Figs. 1,2) were measured in the region 2θ = 5-60°. The selected examples were crystalline or semicrystallimne, this may be due to the presence of cyclohexyl moiety in the backbone as well as the presence of different structure, which may be due to the increase in the polymer chain flexibility and that might be responsible for the approach and mutual attractions of adjacent chains [22].

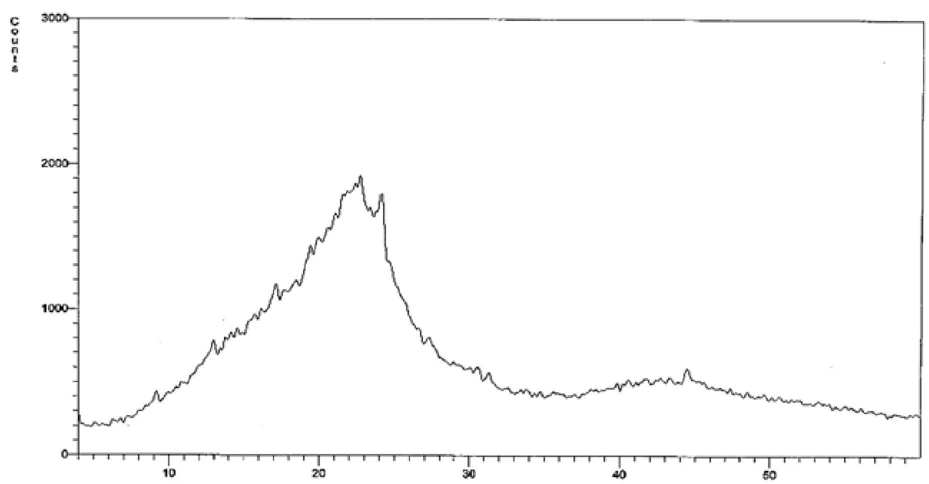


Fig. 1. X-ray Diffraction pattern of polyamide XVI

While the degree of crystallinity varied polymer to another depending on the rest of structures. The higher degree of crystallinity in the two series may be attributed to a large class of structures that are intermediate in the ordered states between crystals in the arrangement of their atoms and molecules. Moreover, the presence of C=O polar group, in addition to high C=C band levels induces some order between two adjacent chains of the polymers, leading to some extended of crystallinity. Moreover, polyamide based on diarylidenecyclohexanoneXVII had more slightly higher degree of crystalinity than polyamide based on diarylidenecyclpentanone XVI this may be due to the flexibility of cyclohexanone moiety when compared with those of cyclopentanone [23].

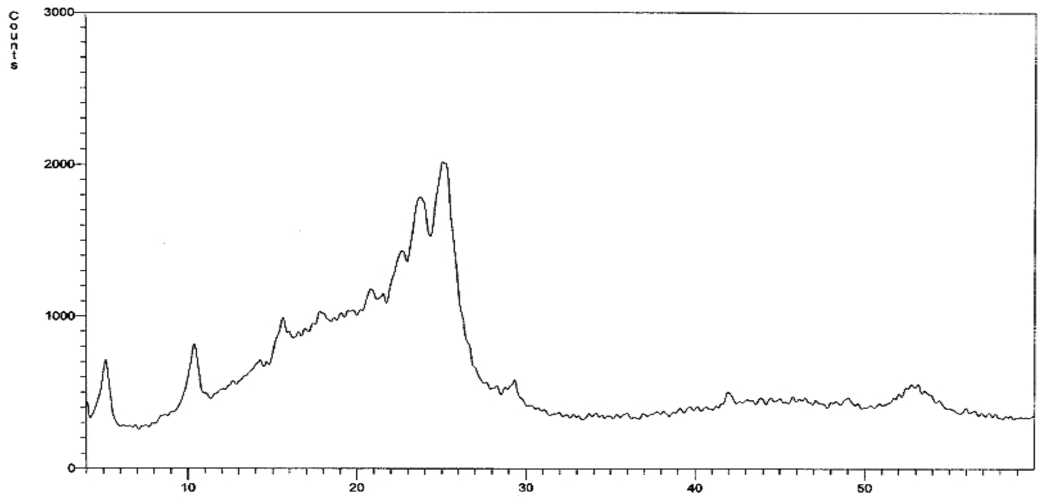
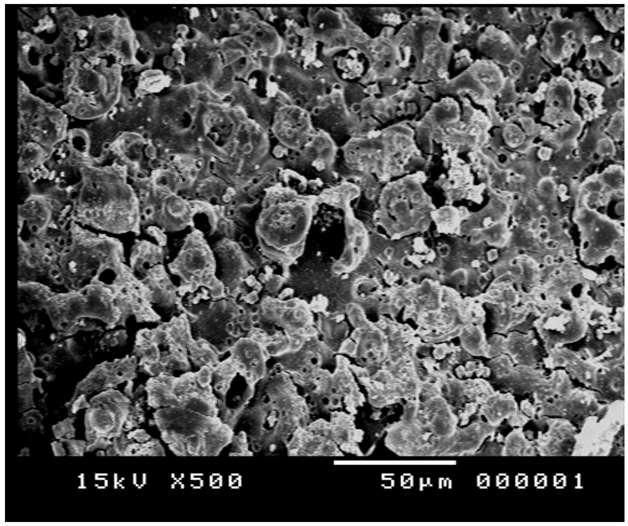


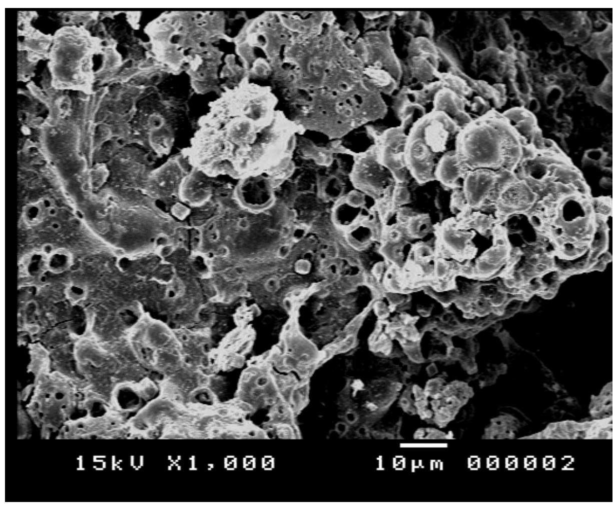
Fig. 2. X-ray Diffraction pattern of polyamide XVII

The SEM study of polyamide XIX Fig. 3 (a) shows that the polymer has a polymorph globular structure with some coalescence present. The higher magnifications in Fig. 3(b) show that the globular and subglobular structures appeared in a continuous chain with some coalescence present.

The thermal behavior of polyamides XVI-XIX, was evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in nitrogen at a heating rate of 10ºC/min. The TG curves of these polymers are given in Figs. 4-6, and Table 3 gives the temperatures for various percentage weight losses. All the polyamides showed similar decomposition patterns. The temperature for a 10% weight loss is considered to be the polymer decomposition point, and it ranged between 390 and 410ºC. The effect of ring size on the thermal stability of polyamides can be seen from Table 3; polyamide XVI which contain the cyclopentanone ring, is more thermally stable than other polymers. Introduction of the cyclohexanone ring in a polymer decreases stability: polyamide XVI loses 10% at 400ºC and polyamide XVII loses 10% at 395ºC. This decrease of stability may be attributed to the flexibility of the cyclohexyl ring. The introduction of the cycloheptyl ring in a polymer chain also decreases thermal stability (10% weight loss for polymer XVII at 395ºC). The prepared polymer XVI was cast into a self-supporting film from a dichloromethane solution (5% w/v). The cast film was compact and transparent, with a faint yellow color. The electrical conductivity of the prepared polyamides was measured by the Arrhenius technique and gave values in the range 10^{-11}-10^{-12} Ohm cm^{-1}. This indicates that all the polyamides are insulators.



(A)



(B)

Fig. 3. SEM images of polyamide XIX surface at different magnifications, a: x =500; and b: x = 1000

Table 2. Solubility characteristics of polyamides XVI-XIX

Polymer code	DMSO	DMF	NMP	Chloroform acetone	THF	Methylene chloride	H_2SO_4
XVI	±	±	±	±	±	±	+
XVII	±	±	±	±	±	–	+
XVIII	±	±	±	±	±	–	+
XIX	+	+	±	+	±	±	+

(+) Soluble at room temperature RT.(±) Partially soluble at RT.; (–) Insoluble

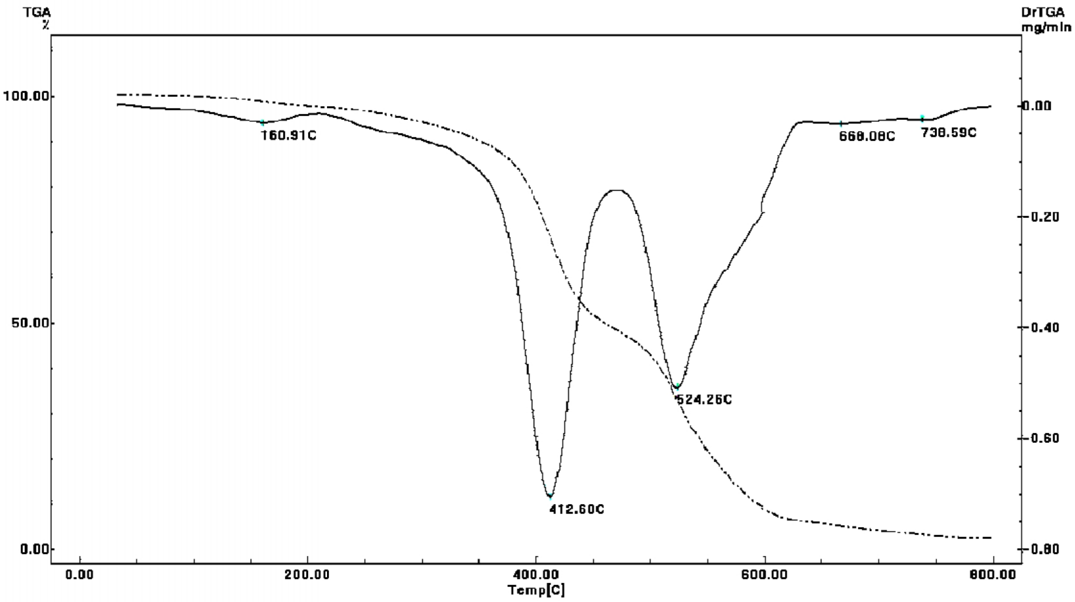


Fig. 4. The TGA and Dr TGA traces of polyamide XVI in nitrogen at a heating rate of 10ºC/min

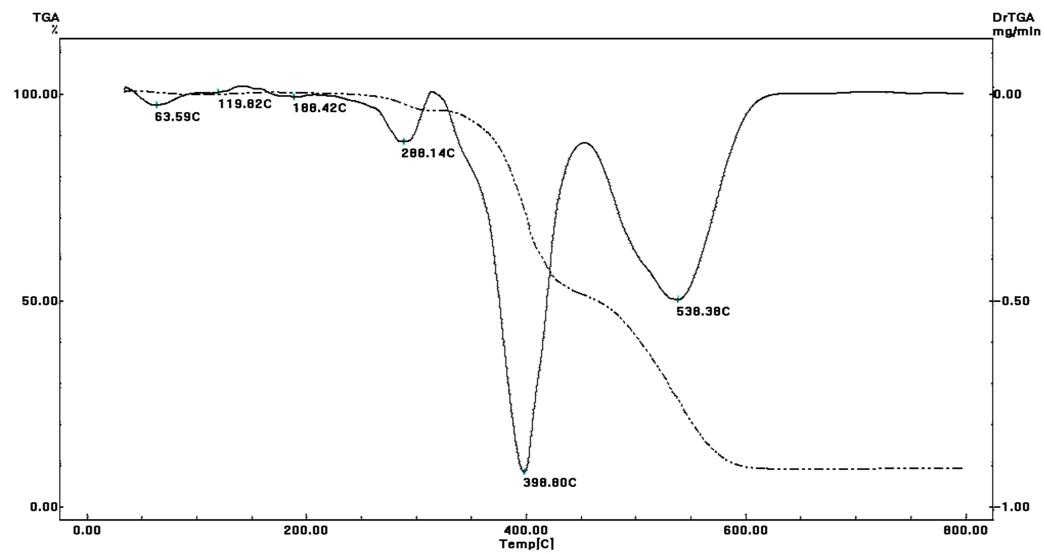


Fig. 5. The TGA and Dr TGA traces of polyamide XVII in nitrogen at a heating rate of 10ºC/min

Table 3. Thermal Properties of Polyamides XVI-XIX

Polymer	Temperature (ºC) for various decomposition levels				
Code	10%	20%	30%	40%	50%
XVI	410	450	455	485	510
XVII	400	425	460	470	480
XVIII	395	410	430	450	485
XIX	390	405	450	470	490

** Heating rate: 10°C min-1*

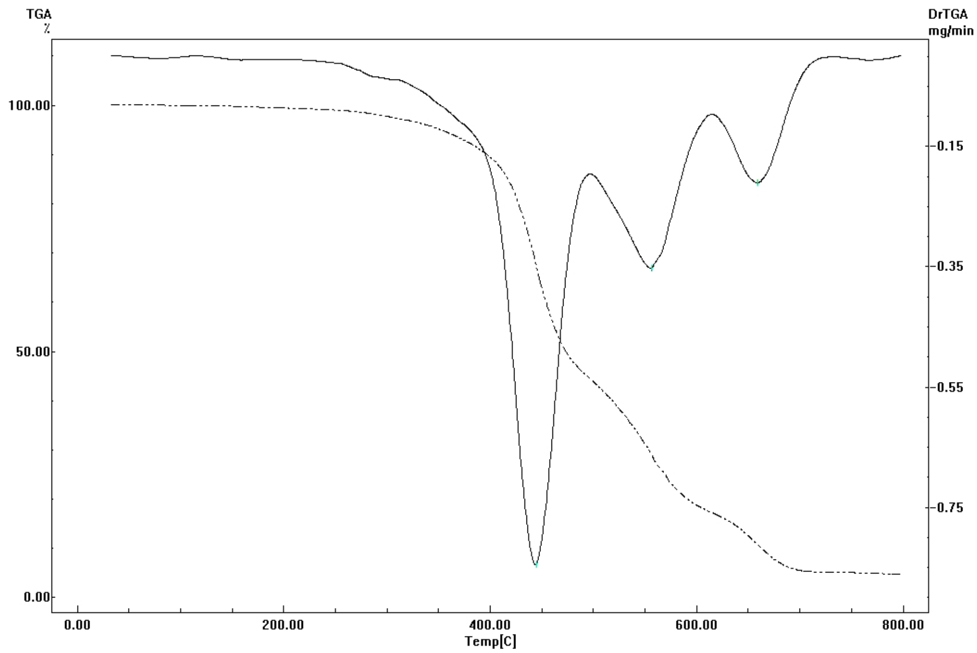


Fig. 6. The TGA and Dr TGA traces of polyamide XIX in nitrogen at a heating rate of 10ºC/min

4. CONCLUSIONS

Linear unsaturated polyamides based on diarylidenecycloalkanones and diarylideneacetone and containing thianthrene moiety in the main chain have been synthesized. A solution polymerization technique at low temperature was used. All the polyamides were soluble in DMSO and strong acid solvents. Thermogravimetric analyses showed that the polyamide based on cyclopentanone was somewhat more thermally stable than cyclohexanone based polyamide. Polymers containing diarylidenecyclohexanonehad more slightly higher degree of crystalinity than those containing diarylidenecyclpentanone. The electrical conductivity of the prepared polyamides was measured by the Arrhenius technique and gave values in the range 10^{-11}-10^{-12} Ohm cm^{-1}. This indicates that all the polyamides are insulators.

COMPETING INTERESTS

Author has declared that there are no competing interests.

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