Thermal Stability of New Polyamide Containing 1-Phenethyl-4-Piperidone Moiety in the Main Chain

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Abstract: A new polyamide based on pyridine moiety was synthesized from 3,5-bis(4-aminobenzylidene)-1-Phenethyl-4-Piperidone (II) by reaction with 2,6-Pyridinedicarbonyl chloride using solution polycondensation technique. The polymer was obtained has yellow color and had inherent viscosity 0.86 dL/g. The solubility of polyamide was insoluble in common organic solvents but dissolved completely in concentrated H2SO4. The thermal properties of the polyamide was evaluated and correlated to their structural units by TGA and DSC measurements. Electrical conductivity in the range of 2.4 X 10-11 Ω-1 cm-1.at room temperature.

Keywords: Polyamide; 1-Phenethyl-4-Piperidone ; Thermal stability.

Introduction:

Heterocyclic polyamides have high thermal stability and excellent oxidative stability, and generally exhibit outstanding mechanical properties. Because of these properties, they are important in commercial and industrial applications[1-4]. Thermal properties have been further improved by incorporation of thermally stable moieties, such as oxadiazole,carbazole, amidazole and thiazole rings, in the polymer back bone [5-8]. Expanding the utilization of these high-performance materials, one of the main goals in the field of polyamides is the prepare of diamine monomers, which give soluble polymers. The improved solubility and lower glass transition temperature of polyamides can be achieved by designing polymers with bulky pendent groups that prevent chain alignment [9-11]. It has been shown that the introduction of pyridine rings in the aromatic polyamide usually enhances their thermal stability, solubility electrical,conducting and optical properties [12]. So, recently polyamides containing pyridine rings have been synthesized [12-15].

In continuation of our interest in the study of the behavior of arylidene monomers[16-18], we report here a route for the synthesis of new polyamide based on 1-phenethyl-4-piperidone by solution polycondensation with 2,6-pyridine-dicarbonyl chloride under mild condition.The major aim of this work is to investigate the effect of inclusion of 1-phenethyl-4-piperidone moiety in the polymer back bone, on the polymer properties. In addition other characteristic of these new polymer such as: thermal stability, solubility, viscosity and conductivity were also examined and discussed.

2. Experimental Procedure

2.1.Instrumentation:

Melting points of the synthesized samples were determined on an Electro thermal IA9100 melting point apparatus and are reported as such. The elemental composition was determined by Elementary Vario EL III instrument. The infrared spectra in the range 4000-650 cm-1 of solid samples of the synthesized monomers and polymers were obtained using a Cary 630 FTIR spectrophotometer. The 1H-NMR spectra were recorded on Varian a Gemini 200 MHz NMR spectrophotometer at room temperature in DMSO solvent using TMS as the internal reference. Mass spectra were recorded on a Shimadzu Qp-2010 mass spectrometer. The inherent viscosities were measured using an Ubbelohde viscometer using a suspension in DMF at 25°C (0.5dIg-1). The thermal properties of the samples were investigated using Differential Scanning Calorimetry (DSC). The DSC recordings were carried out in inert nitrogen using a Shimadzu DSC-50 thermal analyzer. Pellets for electrical conductivity measurements have been pressed at constant pressure 1000 Psi using IR die-silver paste was used to make contacts between the polymer pellets and two graphite electrodes. Conductivity was measured at room temperature under air using a 610 Keithley Electrometer.

2.2.Reagents and Solvents

2,6-Pyridinedicarbonyl chloride, 4-nitrobenzaldehyde, 1-phenethyl-4-piperidone and palladium on activated carbon 5 % (Aldrich) were used as purchased. All other solvents and reagents were of high purity and were further purified by standard method[20,21].

2.3.Monomer Synthesis:

2.3.1. 3,5-Bis(p-nitrobenzylidene)-1-phenethyl-4-piperidone)

In a 150 ml around-bottomed flask was disolved a mixture of 4-nitrobenzaldehyde 6.04g (40mmol) and of 1-phenethyl-4-piperidone 4.06g (20mmol) in 25 ml ethanol while stirring at 50 oC. A few drops of alcoholic potassium hydroxide were then added to the reaction mixture with a continuous stirring for a period of two hours where the yellow precipitate was formed. The desired product V was collected by filtration and recrystallized from ethanol, yield 80%, mp 163 oC . Anal Calcd for C27H23N3O5: C, 69.01; H, 4.93; N,8,95%. Found: C, 69.35; H, 4.61; N,8,34%. IR (cm-1); 2990 (C-H aliphatic stretching); 1660 (C=O); 1600 (C=C); 1340, 1530 (NO2) and 1435 (piperidone C-H deformation). The mass spectrum showed molecular ion peak at m/z = 469 (13.4%) in agreement with its molecular formula (C27H23N3O5), and other peaks appeared at , m/z = 423 (M+-NO2, 7.3%) and m/z = 364 (M+-CH2CH2C6H5, 9.8%).1H-NMR (DMSO-d6 ppm): 8.2 (s, 2H of 2CH=C), 7.9-7.7 (m, 8H of benzylidene), 7.1-7.0 (m, 5H of Ar-H), 3.9 (s, 4H of methylene group of piperidone), 2.8(t 2H of CH2 attached with phenyl group) and 2.6(t 2H of CH2 attached with –N= of piperidone).

2.3.2. 3,5-Bis(p-aminobenzylidene)-1-phenethyl-4-piperidone (II).

A 3,5-Bis(p-nitrobenzylidene)-1-phenethyl-4-piperidone 3.99 g (8.52 mmol) was placed in a 100ml flask with 30ml of absolute ethanol and then the solid mixture was dissolved by warming it while stirring. A catalytic amount of 10% palladium on activated carbon was added to the mixture and hydrazine hydrate (3 ml) diluted with absolute alcohol (9 ml) was then in a drop wise to the mixture. The reaction mixture was kept at 50°C for two hours. The desired product VI was collected by filtration and recrystallized from ethanol, yield 80%, mp 110°C. Anal Calcd for C27H27N3O: C, 79.10; H, 6; 65; N, 10.26%. Found: C, 79.50; H, 6.80; N, 10.19%. IR (cm-1): 3390-3195 (NH stretching); 2850-2940 (C-H of piperidone); 1685 (C=O of piperidone); 1600 (C=C) and 680 (NH deformation). The mass spectrum showed molecular ion peak at m/z = 409(10%) in agreement with its molecular formula (C27H27N3O), and other peaks appeared at m/z = 304 (M+-ph-CH2-CH2, 54%) and at m/z = 303 (M+-NH2-ph-CH2, 52%). 1H-NMR (DMSO-d6, ppm): (s, 2H of 2CH=C), 7.9-7.7 (m, 8H of benzylidene),5.2(b, 2H of -NH2), 7.1-7.0 (m, 5H of Ar-H), 3.9 (s, 4H of methylene group of piperidone), 2.8(t 2H of CH2 attached with phenyl group) and 2.8(t 2H of CH2 attached with N of piperidone).

2.4. Synthesis of Polymer :

The polymer was prepared To a flask charged with a mixture II (6.0 mmol),DMF (15 ml), triethylamine (12mmol), a solution of 2,6-pyridinedicarbonyl chloride (6.0 mmol) in DMF (15ml) was added dropwise and mainting the stirred solution at 0C under N2. The mixture was subsequently stirred at ambient temperature in a stream of N2 for 3 hr, then it was poured into ice-water to give a yellowish to browen colored solid. This was filtered off, washed with dilute aqu. NaHCO3, then with water, ethanol, acetone and finally dried under reduced pressure (1 mmHg) at 70C for 2 days.

3. RESULTS AND DISCUSSION

3.1. Monomer Synthesis

3.1.2. Synthesis of Aromatic Monomer (Diamine).

The preparation of the 3,5-bis(p-aminobenzylidene)-1-phenethyl-4-piperidone monomer II was carriedout by the base-catalyzed condensation of two moles of 4-nitrobenzaldehyde with one mole of 1-phenethyl-4-piperidone followed by reduction with palladium on activated carbon as catalyst in ethanol at 50C.

The IR and 1H-NMR spectra of the monomer did not shows detectable hydrogenation of the carbonyl and olefinic functions under the employed experimental conditions . Moreover, literature survey revealed that hydrogenation the carbonyl and olefinic functions of the cyclohexanone carbonyl group requires acidic medium, a platinum catalyst, and a pressure of 30-45 psi to preferentially give the axial alcohol[21,22].

3.3. Synthesis of Polyamide

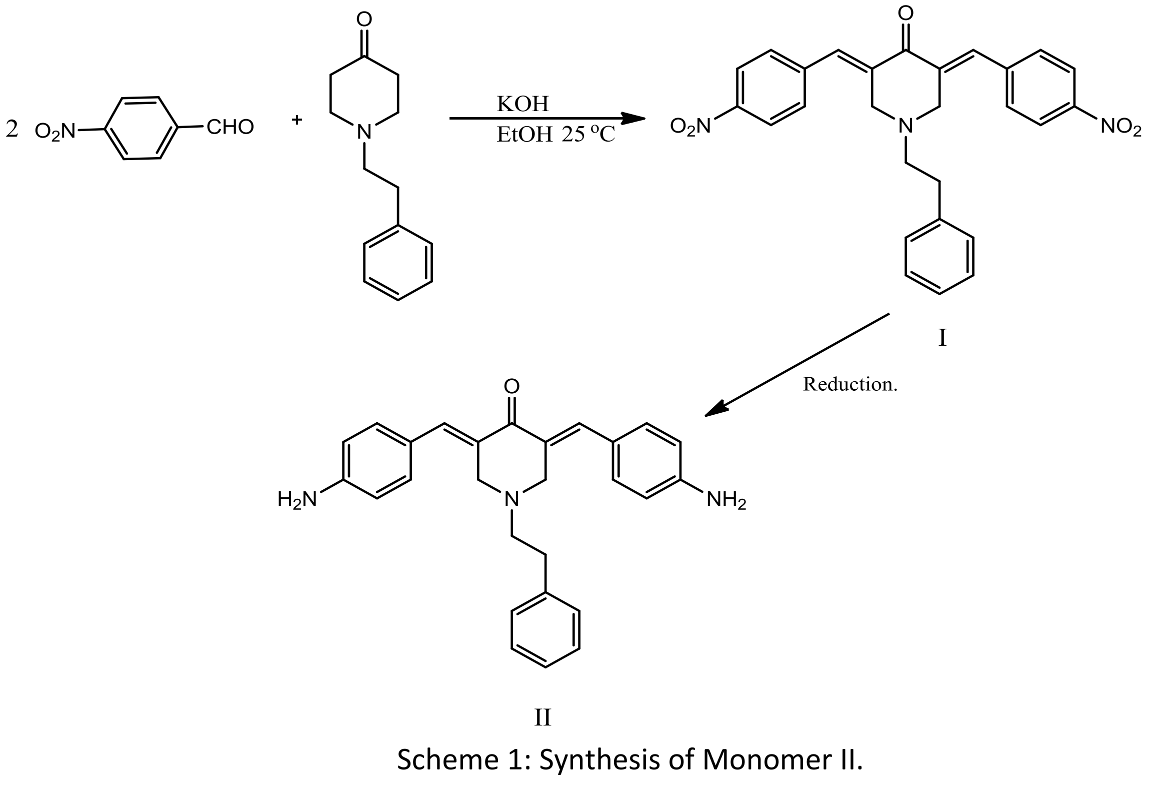
A new class of polyamide containing 1-phenethyl-4-piperidone in the main chain was prepared from the polymerization of monomer II with 2,6-pyridinedicarbonyl chloride as shown in Scheme 2.

The polyamide was synthesized by a low-temperature solution polycondensation technique [23-26] using triethylamine as a catalyst in DMF which dissolves the diamines and acts as a good acid acceptor for the HCl liberated during the polymerization reaction triethylamine as catalysts. It should be noted that the addition of triethylamine as an acid acceptor gave high molecular weight polyamide with inherent viscosities 0.86 dI/g.

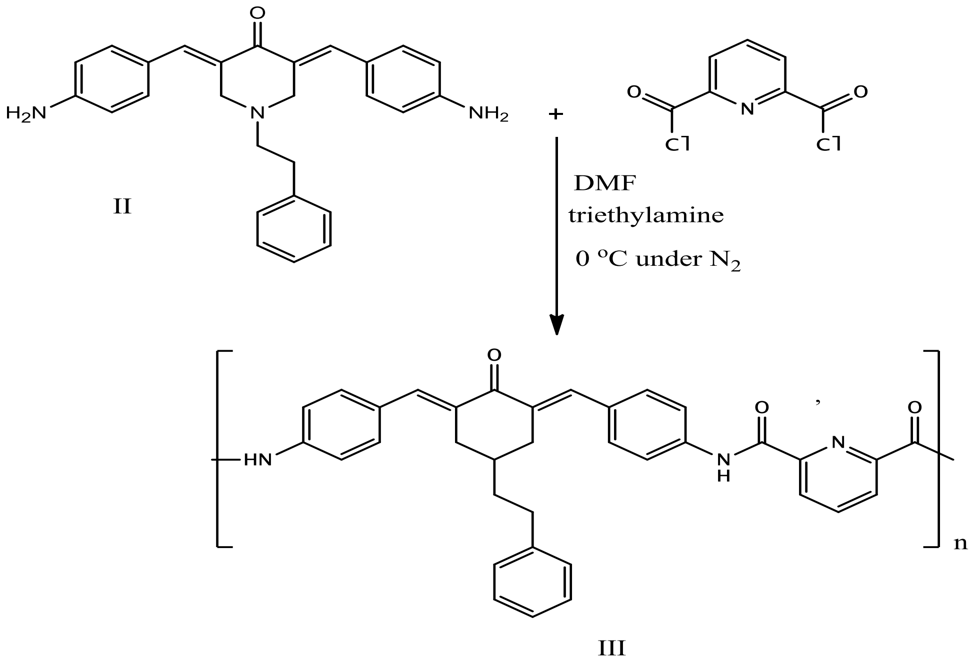
Reaction times varied from 2-4 hrs. and the polymer was immediately isolated, when the reaction solution was poured into methanol/water mixture, with yield 85%.

The resulting polyamide was characterized by elemental analysis, IR spectroscopy, solubility, viscometery and thermal analysis. The elemental analysis of the polymer coincided with the characteristic repeating units of the polymer . Spectral data support the structural assignments for the polymer. The IR data of the polyamide showed the absorption band for N-H stretching at 3300 cm-1 characteristic of secondary amide (1-1 bonded) linkages. The appearance of carbonyl absorptions at 1700 cm-1, known as the amide II 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, is identified at 1535cm-1.

The solubility of polyamide synthesized in this study was determined for the powdery sample in various organic solvents including dimethylsulfoxide (DMSO), N-N dimethylformamide (DMF), tetrahydrofuran(THF), Dichloromethane(DCM), Tetrachloromethane(TCE), chloroform-acetone (1:1) and concentrated sulphuric acid at 3.0% (w/v). It was found that all the polymers dissolved readily in concentrated H2SO4 forming dark brown solutions was due to the formation of strong hydrogen bonding [28]. Concentrated H2SO4 is a generally used as a solvent for most of the polyamide[27] from which the polymer can be precipitated with water or methanol. It is believed that concentrated H2SO4 protonates the nitrogen of the amide bond to overcome the hydrogen bonding forces, thus solubilizing the polyamide [28].



Scheme 1: Synthesis of Monomer II.



Scheme 2: Synthesis of Polyamide III.

The polymer was soluble in various aprotic polar solvents such as DMSO, DMF and THF. The good solubility of these polymers may be elucidated by the loose packing of the macromolecules because of pendent phenyl rings and low crystallinity[28]. In common organic solvents and halogenated hydrocarbons the polymer were partially soluble, which may be attributed to the presence of the rigid pyridine position of the main chain causes increase in solubility. Therefore, the bulkiness of the pendent groups may play a more important role than rigidity in the improvement of the polyamides solubility[25].

The inherent viscositie (hinh) of polyamide was determined in DMF at 25°C with an Ubbelohde suspended level viscometer. The inherent viscosity value is defined as: hinh = (2.3 log t/to)/C . Where to and t represent the viscometer flow periods for DMF and the polymer solution respectively; while solution concentration C is 0.5 g /100 ml. The inherent viscosity of the resulting polyamide was equal 0.86 dl g-1.

The thermal behaviour of polyamide was evaluated by thermo gravimetric analysis (TGA) in air at a heating rate of 10°C /min. The thermograph of polyamide is given in (Fig1). which shows the temperature of various percentages of weight loss. TGA curve shows a small weight loss in the range 2-4% starting at 50°C until 150°C, which may be attributed to loss of observed moisture and entrapped solvents. The thermograph also indicate, the polyamide decompose in two stages. The first stage between 150°C and 300°C depends upon the nature of the polyamide. This result is in good agreement with decomposition of amide-linkage observed by Andrews and Grulke [29]. The second stage of degradation of polyamide occurred between 350°C and 550°C.

The rate of degradation in the first stage is somewhat faster than in the second one. In DSC studies with heating rate of $10^{o}C/$ min (Fig2).The heating trace of the polyamide display a glass-transition (Tg) at120 ^{o}C and revealed multiple endotherms peaks such as melting temperature (Tm) at 370 ^{o}C and broad peak at $485^{o}C$ which is the decomposition temperature (Td) of the polymer . Moreover the DSC thermogram revealed that one exotherm peak at 290 ^{o}C which is attributed to the presence of the degree of recrystallization of polyamide(Tc).The electrical conductivity of polyamide was measured according to the Arrhenius relation at room temperature, 300 K. The results indicated that the solid sample of polyamide possesses an electrical conductivity value of 2.4 X 10-11 Ω-1 cm-1.

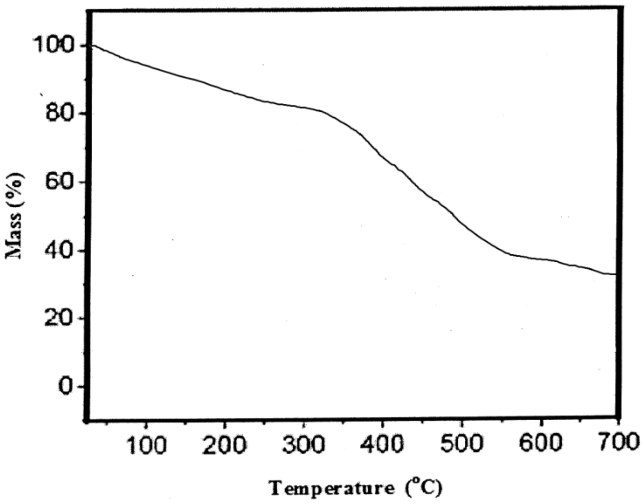


Fig 1. Thermogravimetric Curves of Polyamide.

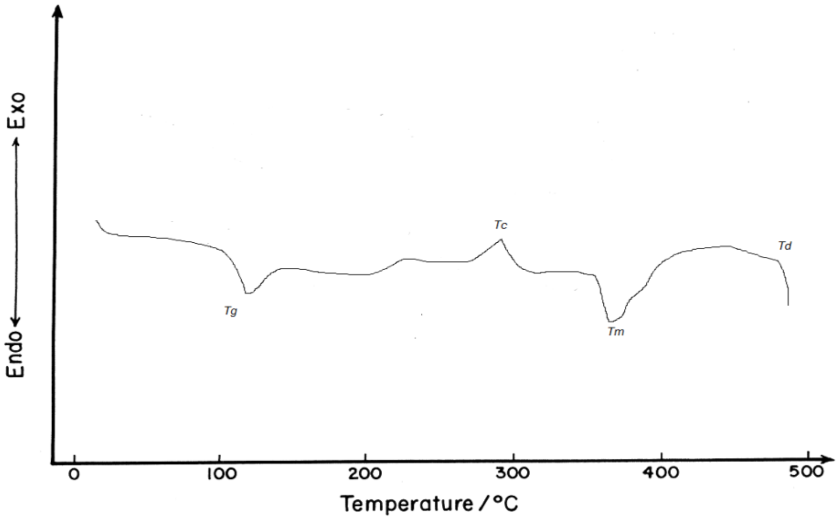


Fig 2. DSC Traces of Polyamide.

4. Conclusion

Linear unsaturated polyamide containing 1-phenethyl-4-piperidone has been prepared. A solution polymerization technique at low temperature was used. The polymer was soluble in various aprotic polar solvents such as DMSO, DMF and H2SO4. Thermogravimetric analyses showed that the pyridine containing polyamide is thermally more stable compared with the other polyamides. The degree of glass transition of this polymer in the range 120 ^{o}C.

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