

Synthesis And Characterization of New Hetero Aromatic Polyamide From benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diamine

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Abstract:

A novel hetero aromatic polyamide has been synthesized using benzo[1,2-d:4,5-d'] bis(thiazole)-2,6-diamine, a diamine monomer, copolymerized with terephthaloyl chloride (TPC) by condensation polymerization. The yield of purified polymer was found to be more than 60% and was confirmed by FTIR and NMR analysis. It shows inherent viscosity of 0.4 dLg⁻¹. The thermal behavior of the polymer was studied by using Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA). The glass transition temperature (T_g) of the polymer was found to be 201 °C by DSC analysis. The polymer was found to be stable up to 403 °C which confirm its high temperature performance. It also shows good solubility in aprotic polar organic solvents. The high thermal performance and good solubility, make it easily processable for desired application.

Keywords: Benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diamine, Condensation polymerization, Hetero aromatic polyamide, High performance material, High glass transition temperature, Soluble poly amide, Thermal stability.

1 INTRODUCTION

With the introduction of high performance thermoplastic materials like "Kevlar" (poly (p-phenyl terephthalamide)) having good chemical resistance, high thermal stability and ultrahigh mechanical strength, aromatic polyamides got commercial acceptance in industry [1]. U.S. federal trade commission has given separate generic name to aromatic polyamides containing more than 85% of the amide groups bounded directly to two aromatic rings as aramid [2]. These high performance aromatic polyamides are important as they can replace metals and ceramics in several fields, on virtue of their excellent mechanical, electrical and chemical properties. This drives attention of many researcher to study these polyamides as high performance material for special applications [3]. This unusual property of aramides is due to an efficient micro crystalline region resulted from strong hydrogen bonding which leading to a compact rod like rigid structure [4]. Due to strong cohesive forces these polymers exhibit higher transition temperature, generally above its degradation temperature. However, the lack of solubility of these polymers in common organic solvents make their industrial processing difficult [5]. While structural rigidity is important criteria in

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field of membranes. This high rigidity is usually associated with high T_g values [6]. To fulfill the increasing need of new processible engineering plastics, various studies have been carried out to introduce substituent's having various chemical structures on the benzene rings of monomers. Also monomers containing several phenyl rings separated by flexible bridges, or heterocyclic monomers have been used [7]. Now, much attention has been given to the preparation of solution processible poly imides by designing new di-amine or di-anhydride monomers [8]. Introduction of heterocyclic ring such as pyridine enhances the electron affinity, to improve electron transportation properties and thus provide various reaction sites for modification of polymer chain [9]. Hence such a polymers have higher thermal property, low flammability and excellent solubility in organic solvents [10].

In the present work, we have synthesized benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diamine (BbTDA) which was used as hetero aromatic di amine monomer for copolymerization with terephthaloyl chloride (TPC) by condensation polymerization. The new hetero aromatic polyamide, poly benzo[1,2-d:4,5-d'] bis thiazol amide (PBbTA) copolymer thus synthesized was characterized for its structural elucidation, thermal properties, inherent viscosity, solubility and crystallographic properties.

2 EXPERIMENTAL

2.1 Materials

Ammonium thiocyanate, benzoyl chloride, 1,4-

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phenylenediamine, terephthaloyl chloride, liquid bromine, sulfuric acid (98%) were of analytical reagent grade and obtained from Hi-Media, India. Anhydrous *N,N*-dimethyl acetamide (DMAc), acetone, dimethyl formamide (DMF), dichloromethane (DCM), ethanol and pyridine were purchased from SD fine chemical, India as analytical grade and used without further purification.

2.2 Characterization Methods

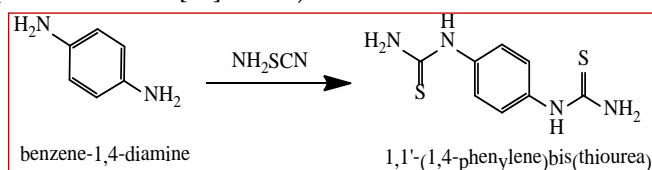
Fourier transform infrared (FTIR) spectroscopy analysis was performed using a Bruker Alpha instrument, with universal sampling module (KBr pellets), over the range of 4000 - 400 cm^{-1} . $^1\text{H-NMR}$ spectra were carried out on a 400 MHz instrument (Bruker Ascend-400) using DMSO- d_6 as a solvent and TMS as an internal standard. Viscometric measurements were made with U-tube viscometer of type BS/U (size A) at 30 $^\circ\text{C}$ (0.5 g dL^{-1}). Melting point were determined by capillary melting point apparatus and values were reported uncorrected. Glass transition temperature (T_g) value was obtained with a TA-Q-100 (USA) Differential Scanning Calorimeters (DSC) (10 $^\circ\text{C min}^{-1}$ under N_2 flow). Thermo gravimetric analyses (TGA) were carried out in a Perkin Elmer, STA 6000 simultaneous thermal analyzer system equipped with a TC-10A processor and a TG-50 thermo balance with a Mettler MT5 microbalance (temperature range between 30 $^\circ\text{C}$ and 650 $^\circ\text{C}$ at 20 $^\circ\text{C min}^{-1}$ under N_2 flow). X-ray diffraction (XRD) spectrometer from Rigaku, model - mini flex (broad angle), was used for studying the crystallography of polymer sample (using monochromatic Cu-K α radiation source, $\lambda = 0.15418 \text{ nm}$).

2.3 Polymer Synthesis

2.3.1 Step - I.

Preparation of *p*-Phenylene Bis Thiourea

The preparation was done according to the procedure reported by Roy G. Nevelle and John J. McGee [11] (scheme 1). Benzoyl chloride (2.8 g, 0.02 mol) in 10 ml of acetone was added drop wise to the reflux solution of ammonium thiocyanate (1.52 g, 0.02 mol) in 10 ml of acetone. The mixture was refluxed for additional 5 minutes, and then 1, 4- phenylene diamine (1.1 g, 0.01 mol) in 10 ml acetone was added drop wise. After addition, the reaction mixture was refluxed for 15 minute. The white thiourea derivative was filtered and washed with acetone, copiously with water and then with acetone. Crude yield obtained was 75%. The product had a melting point 217 $^\circ\text{C}$ (literature value [11] 218 $^\circ\text{C}$).

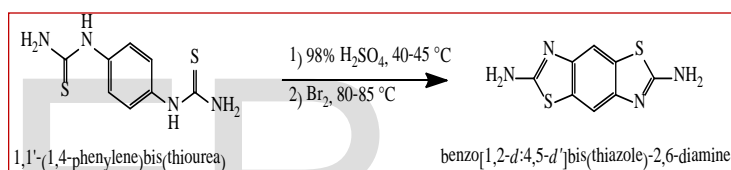


Scheme 1: Synthesis of 1,1'-(1,4-phenylene)bis(thiourea)

2.3.2. Step - II

Preparation of benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diamine (BbTDA)

Preparation of BbTDA was done according to the procedure reported by Desai et. al. [12] (scheme 2). *p*-phenylene bis thiourea (2.26 g, 0.01 mol) was added to 10 ml of 98% H_2SO_4 in a flat-bottomed flask at 40-50 $^\circ\text{C}$. To this liquid bromine (0.65 ml, 0.012 mol) was added drop wise at 80-85 $^\circ\text{C}$ over 2 hours, with constant stirring. After the addition, the mixture was stirred under reflux for 8 h. The pH of the mixture was adjusted to 10 with 28% NaOH to get 98% crude product which was recrystallized from water/ethanol to give 70% recrystallized product. The melting point of recrystallized product obtained was 318 $^\circ\text{C}$ (literature [12] value M.P. 320 $^\circ\text{C}$).

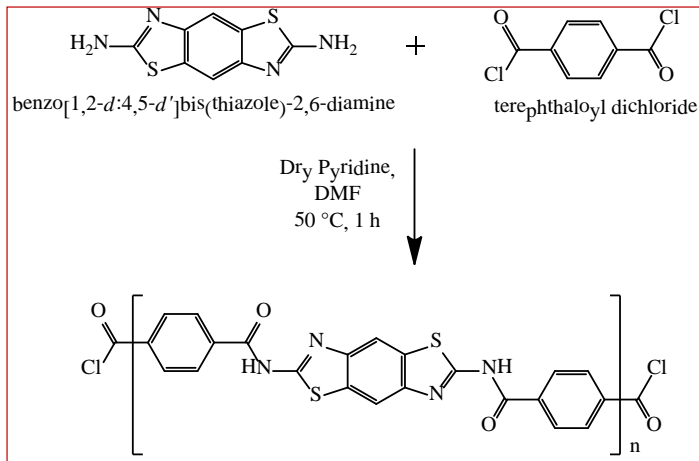


Scheme 2. Synthesis of benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diamine

2.3.2 Step - II Synthesis of Poly (benzo[1.2-d:4.5-d'] bis (thiazole) amide (PBbTA)

The synthesis of polyamide was carried out by following typical condensation polymerization procedure (Scheme 3). In three neck round bottom flask, 2.2 g of BbTDA (0.01 mmol) was added in 3.2 mL of dry pyridine (0.04 mmol) under stirring. To this 10 mL of dimethyl formamide (DMF) was added to dissolve the BbTDA. To this, solution of 4.06 g of terephthaloyl chloride (0.02 mmol) dissolved in 10 mL dichloromethane (DCM) was added slowly. After addition, the resultant reaction mixture was stirred for 1 h at 50 $^\circ\text{C}$ and then cooled to room temperature. The resulting mixture was poured into cold water with constant stirring. Crude product was filtered, washed thoroughly with water and dried at 100 $^\circ\text{C}$ for 12 hours. Re-precipitation of crude product with DCM/heptane gives 60% purified compound, having melting point 364 $^\circ\text{C}$.

IR (KBr pallet), 3104 cm^{-1} (broad N-H); 1649 cm^{-1} (C=O); 1510 cm^{-1} and 1410 cm^{-1} (C=C); 1221 cm^{-1} (C-O) 831 cm^{-1} and 729 cm^{-1} (substituted aromatic ring C-H bending). $^1\text{H-NMR}$ (DMSO- d_6) 8.05 ppm (d) 8-H, 8.02 (s) 2-H, 9.69 (s) 2-H.



Scheme 3. Synthesis of polymer

3 RESULTS AND DISCUSSION

3.1 Polymer Characterization

3.1.1 Structural Characterization of PBbTA

Structure of the synthesized polymer, PBbTA was elucidated using FTIR, ¹H NMR and XRD studies.

Fig. 1 shows FTIR spectra of synthesized polymer. The broad peak at 3104 cm⁻¹ correspond to the amine group (-NH) stretching whereas the peak at 1646 cm⁻¹ corresponds to the carbonyl (C=O) stretching of amide.

N-H and C-N bending bands appears at around 1604 cm⁻¹ and 1510 cm⁻¹ respectively.

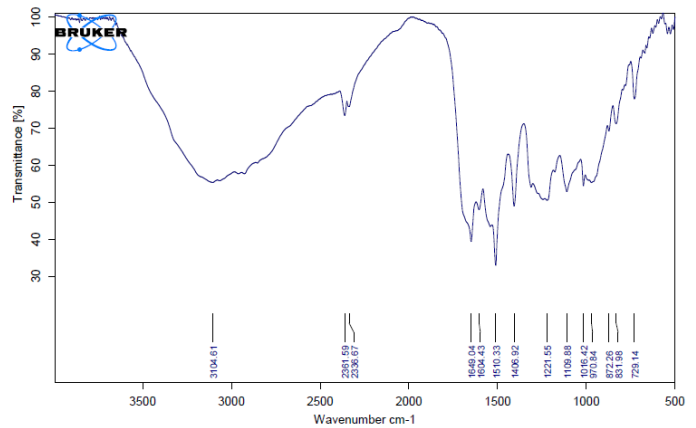


Fig. 1 FTIR spectra of PBbTA

Fig. 2 shows proton NMR spectra of the polymer. The doublet peak at 8.05 ppm (8 H) is characteristic for the benzoyl ring and the singlet at 8.02 ppm (2H) is corresponds to the benzothiazole ring. The amide peak identified at 9.69 ppm (2 H for -NH₂).

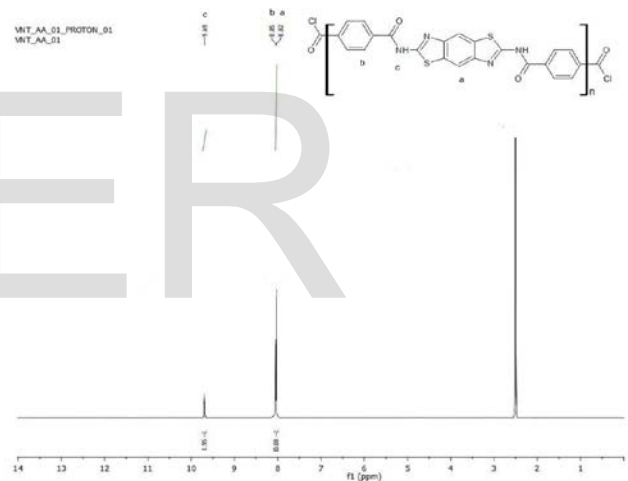


Fig.2 ¹H-NMR spectra of PBbTA

Fig. 3 shows X-ray diffraction pattern of the PBbTA powdered sample. The characteristic crystalline peaks for aromatic poly-amides were missing in the spectra. The spectra shows broad peak which indicates the amorphous nature of the polymer. The polymer show 15% Crystallinity which may be due to the less packed structure of PBbTA caused due to bulky and rigid structure of the hetero aromatic components.

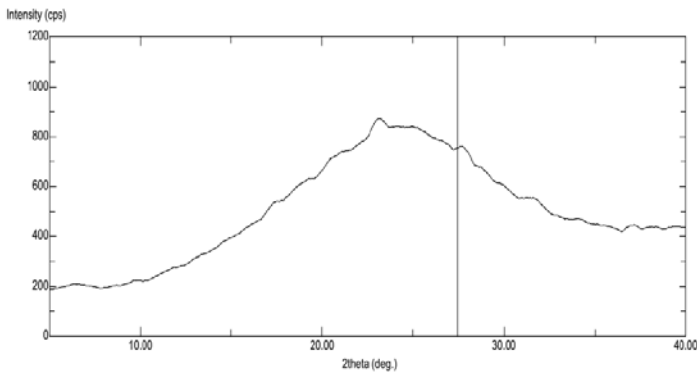


Fig.3 X-ray diffraction pattern of PBbTA

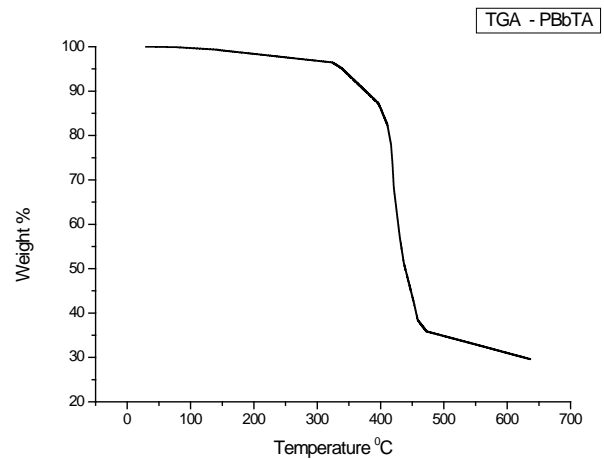


Fig.5 Thermo gravimetric analysis graph of PBbTA

3.1.2 Thermal Analysis

Thermal analysis of the PBbTA was done using DSC and TGA. Fig. 4 show DSC thermo gram of the polymer with glass transition temperature (T_g) of around 201 °C. While TGA graph in figure 5 shows the degradation temperature (T_d) at 403 °C. The polymer PBbTA get degraded at this temperature to give more than 30% char formation. The thermal property of hetero aromatic polyamides is a major criteria which decide its application as a high performance material for special applications [3]. The use of any polymer for high temperature application required to satisfy some conditions such as it must have higher glass transition temperature, degradation temperature and should have good flame retardant behavior. Thus the synthesized PBbTA shows similar properties which are required for high performance polyamides.

3.1.3 Physical Properties of the Polymer

Physical properties of polymer such as viscosity and solubility in different solvent, are important criteria for its application study.

Inherent viscosity of PBbTA was measured at a single point in di methyl acetamide (DMAc) solution at 30 ± 0.1 °C (0.5 g dL^{-1}). Inherent viscosity values obtained were in the range of 0.41 dL g^{-1} . It gives indication about build up of moderately higher molecular weight of the polymer chain.

The solubility of the polyamide was qualitatively tested in several polar organic solvents. As the solubility of the aromatic polyamide is major criteria for their easy processability, it will be beneficial if the polymer shows solubility in different organic solvents. The solubility was tested by adding 0.01 gm of polymer sample into 2 ml of organic solvent at 30 °C the solubility of polymer at higher temperature was also studied. The results obtained were summarized in the table 1.

Table .1 Solubility of PBbTA in different Solvents.

Solvent	Solubility (25 °C)	Solubility (100 °C)
NMP	+	+
DMAc	+	+
DMMSO	+	+
Formic Acid	+	+
Acetic Acid	±	+ *
THF	-	- *
Acetone	-	-
Pyridine	+	+
DMF	±	±

Soluble +, partially soluble ±, Insoluble -, *For the solvent THF and acetone solubility was studied in boiling solvent.

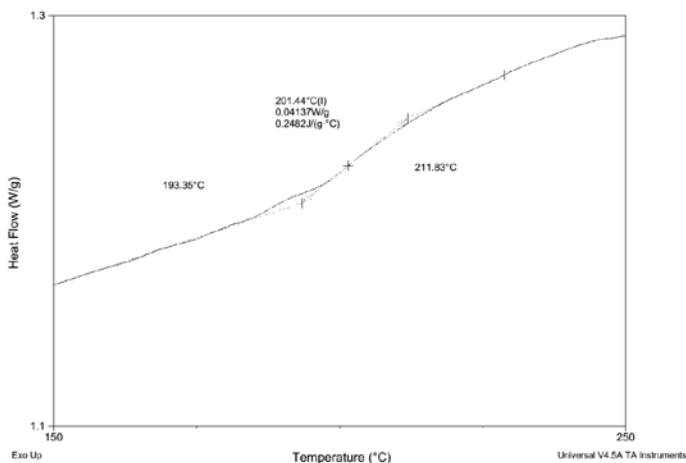


Fig.4 Differential scanning calorimetric plot for glass transition temperature of PBbTA

The polymer showed good solubility in polar aprotic solvents like DMAc, DMSO, NMP and formic acid while it showed poor solubility in acetone, DMF and THF. The solubility of the polymer in different solvents is attributed to the decreased packing density which has been confirmed by XRD pattern showing lower crystallinity. The less packed structure gives better interaction with the solvent and thus good solubility of material. Also the presence of the hetero atom on the ring like nitrogen and sulfur enhances the electron density on ring which enhances the interaction with solvent molecules [10].

4. CONCLUSIONS

In conclusion, we have successfully synthesized a novel hetero aromatic polymer using benzo [1,2-d:4,5-d'] bis(thiazole)-2,6-diamine as a monomer. The structure of synthesized polymer was confirmed by using FTIR, ¹H-NMR analysis while crystallinity was determined by XRD. The characteristic properties such as high thermal stability and good solubility in polar aprotic solvents has broaden the scope for the synthesized polymer for various applications.

5. REFERENCES

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