RASĀYAN *J. Chem.*
Vol. 16 | No. 2 |964-971| April - June | 2023
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

# SYNTHESIS AND CHARACTERIZATION OF PSEUDO LADDER MONO HYDROXY PENDANT POLYBENZOBISTHIAZOLE AROMATIC HETERO-CYCLIC THERMOPLASTIC POLYMER

**Roli Verma[1,✉], Kirti Srivastava[1], R. S. Jagadish[1]and Rama Dubey[2]**
[1]Department of Chemistry, JSS Academy of Technical Education, Noida, U.P India
[2] SPD Division, Defence Research Laboratory, DRDO Tezpur, Assam, India
✉Corresponding Author: roliverma@jssaten.ac.in

**ABSTRACT**

Anisotropic polymerization of 5-hydroxy isophthalic acid and isophthalic acid with 2,5-diamino 1,4-benzene dithiol dihydrochloride (DABDT.2 HCl) affords the polymer poly {[benzo (1,2-d: 4,5-d') bisthiazole-2, 6 diyl]-1,3 phenylene} and poly {[benzo (1,2-d: 4,5-d') bisthiazole-2, 6 diyl]-1,3(5-hydroxy phenylene)}. Both the polymers were soluble in methanesulphonic acid and chlorosulphonic acid. The polybenzobisthiazoles do not show any glass transition temperature (Tg) by DSC analysis. The polybenzobisthiazoles were stable up to 400°C in a nitrogen environment, according to thermo gravimetric measurements. Elemental analysis and spectroscopic comparison of the polymers with the appropriate model compounds were used to confirm the polymer structures. The polymers' inherent viscosity reached 4.2 dL/g (methanesulphonic acid, 30°C).

**Keywords:** Pseudo Ladder; Polybenzobisthiazole; Rigid-Rod Polymers; Copolymers.
RASĀYAN *J. Chem.*, Vol. 16, No. 2, 2023

## INTRODUCTION

The exceptional tensile qualities and endurance to high temperatures in hostile environments of rigid-rod polymers, such as polybenzazoles (PBX), polybenzimidazoles (PBIs), polybenzothiazoles (PBZTs), and polybenzoxazoles (PBOs), set them apart from the new generation of structural polymeric materials. However, for some aerospace applications, their compressive properties are subpar. As a result, recent efforts have been focused on increasing the PBX polymer's compressive strength. The compressive failure was considered to be caused by the PBX micro fibrils' inability to provide lateral support. The required support might be offered if a device were added to increase the lateral contacts between the microfibrils. A theoretical investigation showed that high compressive strength might be achieved by using lateral chain supports, such as an interdigitations network created by suitable side chains separated at regular intervals along the rigid polymer backbone.[1] There have been several attempts to increase the compressive strength of these highly orientated materials, most of which focus on enhancing intra- or intermolecular interactions. The obvious way to achieve this lateral support at the molecular level is to crosslink the rigid-rod polymer chains. This strategy involves introducing highly linked groups[4,5], branding molecular entanglements with bulky side groups.[2] There have been various initiatives in this area, with cross-linking being thought to be the most promising strategy.[6-21] In an effort to increase compressive strength, hydrogen bonding has been introduced. Only a few studies have described the synthesis of pseudo ladder stiff rod structures up to this point. These articles report strong intermolecular hydrogen bonds between the hydroxy moieties and the nearby nitrogen atoms of the benzothiazole unit. The capacity of the hydroxyl (-OH) functional group to generate coordination and hydrogen bonding as well as to undertake various nucleophilic substitution reactions led to its selection. The polymerization conditions needed to create high molecular weight PBZT polymer later revealed it to be comparatively innocuous. The creation of intramolecular rather than intermolecular hydrogen bonds has been attributed to the lack of improvement in compressive strength.[8] Kumar *et al.* have reported that strong intermolecular associations result in fibers with high compressive and torsional moduli. The aforementioned characteristics are influenced by improved intermolecular interactions, which also increase fiber density. As a result, a dihydroxy PBZT was synthesized, however, it had a lower fiber


http://doi.org/10.31788/RJC.2023.1628360

compressive strength than PBZT.[9] During the present investigation, we have synthesized and characterized 1,3 phenylene PBZT and mono hydroxy PBZT and their model compounds with catenation angles less than $180^0$C. The spectral data of monomers and polymers are also shown along with the results.

## EXPERIMENTAL

### Materials and Method

Solid monomers were recrystallized and solvents were distilled and dried before use. Micro Estimation of C, H, N, S was performed on Elementar Vario EL. A Nicolet MX-1, FT-IR spectrometer was used to record the infrared spectra of model compounds and polymers found in KBr pellets. $^{13}$C-Solid state NMR spectra were provided by SIF, IISc Bangalore, and were recorded using Brucker- DSX 300 Solid-State NMR. ( Carbon frequency 75.45 MHz). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the powder polymer samples were carried out with a Du Pont 1090 thermal analyzer with a 951 TG module to assess the relative thermal stability of polymers. The heating rate was maintained at 20ºC/min in a nitrogen atmosphere and a Du Pont 9900 thermal analyzer with a 910 DSC module was used to study the thermal transitions. The inherent viscosity was measured using an Ostwald viscometer in methanesulphonic acid (1%solution) at 30ºC.

### Synthesis of Model Compound

### 1,3-Bis- (2-Benzothiazolyl)- Phenylene (3)

2-Aminothiophenol (1) (1.170 gm, 9.3459 mmol) and 40 gm of freshly prepared polyphosphoric acid (PPA) were taken into a three-neck 250-mL reaction flask fitted with a mechanical stirrer, nitrogen inlet, and guard tube. The reaction vessel was initially purged with nitrogen. The mixture was heated at 100ºC and maintained at that temperature for 1 hr. Isophthalic acid (2) (0.7057, 4.2481 mmol) was added to the flask and the temperature was raised and maintained at 150ºC for 24 hr. After completion of heating the mixture was cooled up to 50ºC. The mixture was then added to the water. The precipitate of an off-white tint was collected, carefully rinsed with water, and then vacuum-dried. Yield 2.34 gm (quantitative yield). M.p-165ºC. IR (KBr) – 3065, 1698, 1519, 1472,1429, 1313, 1261, 1243, 958, 893, 857,750,729, 674 cm$^{-1}$. (Figure- 5(a) Anal. Calcd. For:( $C_{20}H_{12}N_2S_2$): C, 69.76 %; H, 3.48 %; N, 8.13 %. Found: C, 67.96 %; H, 3.50 %; N, 7.99 %.

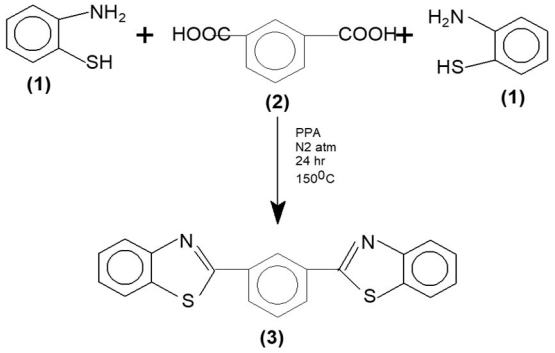



Fig.-1: Scheme of Synthesis of 1,3-Bis- (2-benzothiazolyl)- phenylene (3)

### 1,3-Bis- (2-benzothiazoly)- 5-hydroxy phenylene (5)

2-Aminothiophenol (1) (1.170 gm, 9.3459 mmol) and 40 gm of freshly prepared polyphosphoric acid (PPA) were taken into a three-neck 250-mL reaction flask fitted with a mechanical stirrer, nitrogen inlet, and guard tube. The reaction vessel was initially purged with nitrogen. The mixture was heated at $100^0$C and maintained at that temperature for 1 hr. 5-hydroxyisophthalic acid (4) (0.7732, 4.2481 mmol) was added to the flask and the temperature was increased and maintained at $150^0$C for 24 hr. After completion of heating the mixture was cooled up to $50^0$C. The mixture was then added to the water. The precipitate was dirty white in color, and it was extensively washed with water and vacuum-dried. Yield – 3.16 gm (quantitative yield). M.p- $170^0$C. IR (KBr) – 3180, 3058, 1653, 1591,1496, 1425, 1318, 1273, 1239, 1186,

1093, 978, 893, 857,753,722, 674 $Cm^{-1}$Fig.(6(a). Anal. Calcd. For:( $C_{20}H_{12}N_2S_2$): C, 69.76 %; H, 3.48 %; N, 8.13 %. Found: C, 68.96 %; H, 3.10 %; N, 6.69 %.

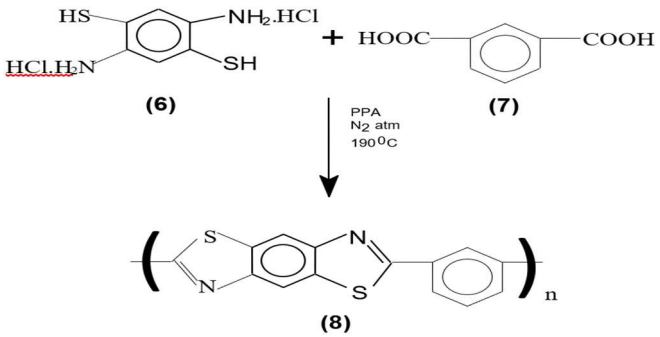



Fig.-2: Scheme of Synthesis of 1,3-Bis- (2-benzothiazoly)- 5-hydroxy phenylene (5)

**Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3 – phenylene} (8)**

Into a three-neck 250ml reaction flask were placed 2,5 – diamino – 1,4 – benzenedithiol dihydrochloride (6) (9.803 gm, 40 mmol) and 67.3 gm of freshly prepared polyphosphoric acid (PPA). The mechanical stirrer, nitrogen inlet, and guard tube were all fitted in the reaction vessel. Initially, nitrogen was flushed into the reaction mixture. The reaction mixture was agitated for 24 hours at room temperature with a stream of nitrogen, then for another 24 hours at 60 to $70^0$ C to dehydrate the amine monomer. Low nitrogen pressure was used for this stage. After dehydrochlorination, the temperature was decreased to $50^0$C, and the resultant solution became transparent with no signs of bubbles then isophthalic acid (7) (6.6gm, 40 mmol) and additional $P_2O_5$ (23.92) gm was added in a nitrogen atmosphere to give 82-84 % PPA and compensate for water generation during condensation polymerization. The reaction mixture was then heated to $90^0$C and maintained at this temperature for 12 hr. The reaction mixture took on a coppery hue. The reaction mixture was then heated at 120°C for 5 hours, $165^0$C for 5 hours, 180°C for 5 hours, and 190°C for 5 hours. The thick mixture was then added to the water. Filtration was used to collect the polymer (8) precipitate, which was then extensively cleaned with hot water and an aqueous ammonium hydroxide solution. Finally, the precipitated polymer was dried in a vacuum at $100^0$C for 16hr. Yield – 2.15gm. The inherent viscosity of 3.74 dL/g was obtained in methanesulphonic acid at room temperature. The FTIR spectrum (KBr) exhibited absorptions at 3178, 3072, 1677, 1602, 1550, 1513, 1377, 1307, 1227, 1083, 859, 760, 679, and 528 $cm^{-1}$. Anal. Calcd. For. ($C_{14}H_6N_2S_2$) n: C, 63.15%; H, 2.25%; N, 10.52%. Found: C, 2.86%; H, 2.14%; N, 9.01%.

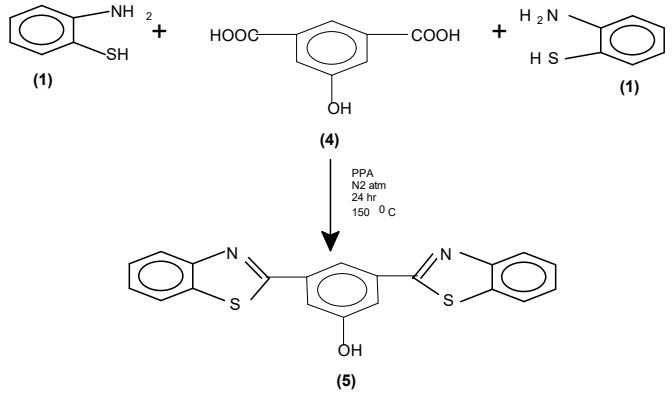



Fig.-3: Scheme of Synthesis of Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3 – phenylene}(8)

**Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3(5 –hydroxy phenylene)} (9)**

2,5-diamino-1,4-benzenedithiol dihydrochloride (6) (9.02gm, 36.81 mmol) and 24.06 gm of freshly made polyphosphoric acid were added to a three-neck 250 ml reaction flask (PPA). The mechanical stirrer, nitrogen inlet, and guard tube were all installed in the reaction vessel. At first, nitrogen was used to flush into the reaction mixture. The reaction mixture was agitated for 24 hours at room temperature with a

stream of nitrogen, then for another 24 hours at 60 to $70^0$ C to dehydrate the amine monomer. Low nitrogen pressure was used for this stage. After dehydrochlorination, the temperature was lowered to 50°C, and 5-hydroxy isophthalic acid (4) (7.06gm, 36.8 mmol) and additional $P_2O_5$ (23.92) gm were added in a nitrogen atmosphere to give 82–84% PPA and account for water generation during condensation polymerization. The resulting solution was clear and showed no signs of bubbles. Low nitrogen pressure was used for this stage. After dehydrochlorination, the temperature was lowered to 50°C, and 5-hydroxy isophthalic acid (4) (7.06gm, 36.8 mmol) and additional P2O5 (23.92) gm were added in a nitrogen atmosphere to produce 82–84% PPA and account for water generation during condensation polymerization. The resulting solution was clear and showed no signs of bubbles. The reaction mixture was then heated to 90ºC and maintained at this temperature for 12 hr. The reaction mixture became copper colored. Further, the reaction mixture was heated as follows: 120ºC for 5hr, 165ºC for 5hr, 180ºC for 5hr, and 190ºC for 5hr. The thick mixture was then added to the water. Filtration was used to collect the polymer (9) precipitate, which was then extensively cleaned with hot water and an aqueous ammonium hydroxide solution. The precipitated polymer was then dried in a vacuum for 16 hours at 100°C. Yield –3.15 gm. The inherent viscosity of 4.05 dL/g was obtained in methanesulphonic acid at room temperature. The FTIR spectrum (KBr) exhibited absorptions at 3433, 1653, 1561, 1514, 1457, 1393, 1289, 1211, 985, 877, 749, and 676 $cm^{-1}$. Anal. Calcd. For. ($C_{14}H_6N_2S_2$) n: C, 63.15%; H, 2.25%; N, 10.52%. Found: C, 62.16%; H, 2.22; N, 9.11%.

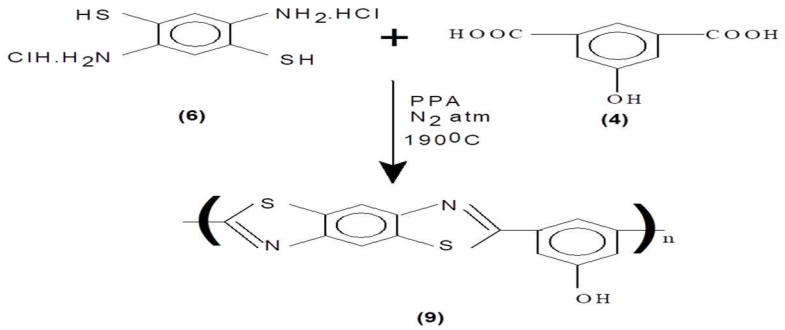



Fig.-4: Scheme of Synthesis of Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3(5 –hydroxy phenylene)}(9)

## RESULTS AND DISCUSSION

### Characterization of Model Compounds

The FT-IR spectra of the model compounds 1,4-bis- (2-benzothiazolyl)-1,3 phenylene (3) and 1,4-bis- (2-benzothiazolyl)-1,3 (5-hydroxy) phenylene are shown in Fig.-5(a) and 6(a) (5). The spectrum of PBTs reveals the total disappearance of $NH_2$ at 3320 $Cm^{-1}$, SH for 2-aminothiophenol at 2460 $Cm^{-1}$, and C=O for dicarboxylic acid at 1700 $Cm^{-1}$. Intense bands that develop in the range of 1300–1500 $cm^{-1}$ indicate the production of the benzothiazole ring and are attributed to hetero ring stretching vibrations of varying intensity that are attributed to the stretching vibrations of carbon–carbon bonds in aromatic rings. Figure 6(a) assigns the bands that emerge at 3180.4 and 3058 $Cm^{-1}$ for (OH) stretching, but Fig.-5(a) does not. Hence, the spectrum verifies the emergence of model compounds. The model compounds (3) and (5) were insoluble in common deuterated solvents to permit their NMR characterization.

### Polymer Characterization

### Infrared Analysis

Figure-5(b) shows the Fourier transform infrared spectra of PBT with a 1,3-phenylene ring and PBT with a 5-hydroxy phenylene ring. Figure-6(b) shows the typical benzothiazole absorption at 1093 $cm^{-1}$ and 1616 $cm^{-1}$ (C=N) stretching, which points to the development of the bendithiazole ring. It also shows the typical adsorption bands in the range of 1300-1500 cm-1. The absence of a hydrogen bridge in the monohydroxy PBT molecule is confirmed by the strong and broad band of normal molecularly bound -OH groups visible in spectrum Fig.-6(b) at 3400 $cm^{-1}$. As a result, the spectra and the suggested structure of the polymers are in good agreement.

**$^{13}$C Solid NMR**

The 13C NMR spectra of polymers (8) and (9) are shown in Fig.-7(a) and 7(b), respectively. The polymeric samples were treated to solid-state NMR because the polymers were insoluble in typical deuterated solvents. The spectrum displays the characteristic benzothiazole chemical shifts of benzo-fused five-membered heterocycles with two heteroatoms bonded to a side chain. The carbon ratios in the corresponding repeat units of the polymer chain are essentially what the integrals of bands in the spectra reflect. The benzothiazole carbons [15] in the polymer (8) show the expected 13C chemical shifts: C(a) 117.55 ppm; C(b) 134.6 ppm; C(c) 153.23 ppm; and C(d) 170 ppm. Similar to polymer (9), which displays the usual benzothiazole carbon 15 13C chemical shifts of C(a) 118.16 ppm, C(b) 137.46 ppm, C(c) 154.72 ppm, C(d) 169.10 ppm, C(f) 129.29, and C(g) 198.99 ppm. The polymer's proposed structure is well-aligned with the signals for carbon.

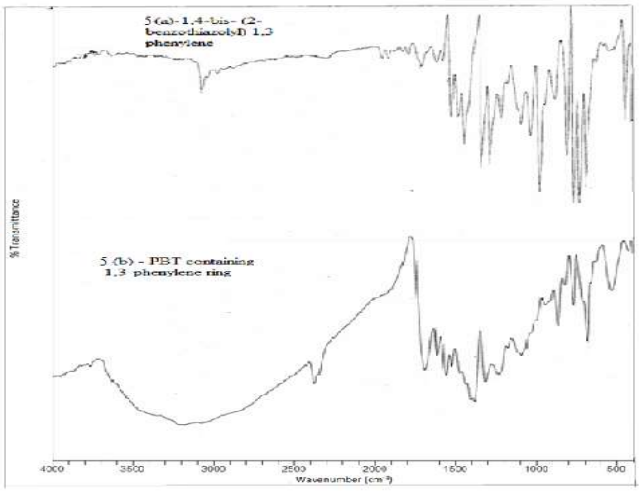



Fig.-5: (a) - IR Spectra of 1,4-bis- (2-benzothiazolyl) 1,3 phenylene and Fig.5(b)- Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3 – phenylene}

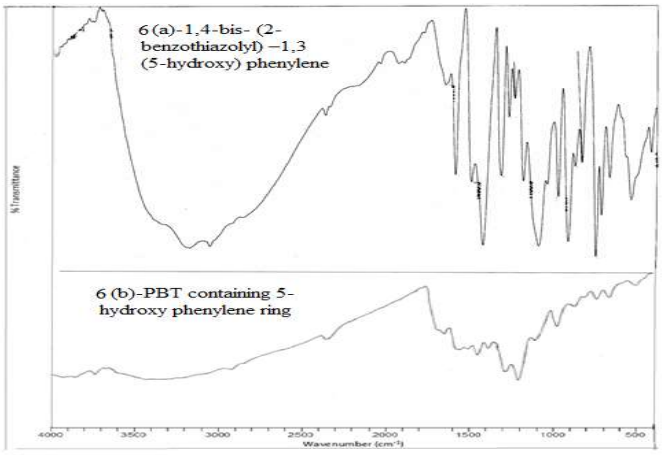



Fig.-6: (a) - IR Spectra of 1,4-bis- (2-benzothiazolyl) –1,3 (5-hydroxy) phenylene and Fig.6(b)- Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3(5 –hydroxy phenylene)}

**Thermal Characterization**

As predicted, differential scanning calorimetry revealed that none of the polymers exhibited any softening or melting behavior before the breakdown temperature (DSC). This is anticipated as an overwhelming result of the fused ring structure maintaining the softening of the polymers based on benzobisthiazole. Figure-8(a) and Fig.-9(a). Thermogravimetric examination of both polymers revealed a single-step thermal breakdown characteristic in nitrogen (TGA). Figures-8(b) and 9(b) illustrate how residual water

and solvent cause early weight loss from room temperature to roughly 15°C. About 400 °C is needed for polymer (8) to degrade, while 347 °C is needed for polymer (9).

These observations are in agreement with previous studies on the thermal properties of PBZT polymers modified with a variety of simple pendant groups. The DSC results do not show any glass transition temperature (Tg). As also suggested in the literature that these polymers have Tg above their decomposition temperature, it is due to the presence of a rigid backbone. This is further confirmed by solubility results. Since these polymers were not soluble in common solvents such as DMF, DMSO, dmac, and NMP. The solubility behavior indicates that these polymers can be solution-processed. The TGA behavior of PBTs with I, 3 phenylene, and 1,3-(5-hydroxy phenylene) polymers have onset of thermal degradation values in the range of 347-400 °C. These values indicate that polymers are thermally stable up to high temperatures.

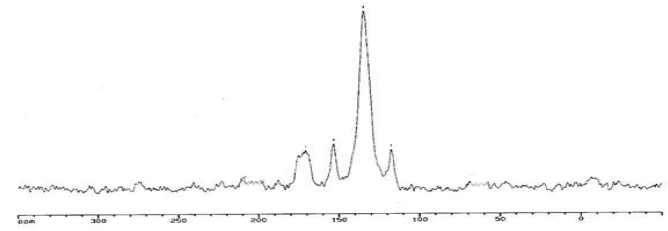


Fig. 7(a) $^{13}C$ NMR spectrum of Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3 – phenylene}

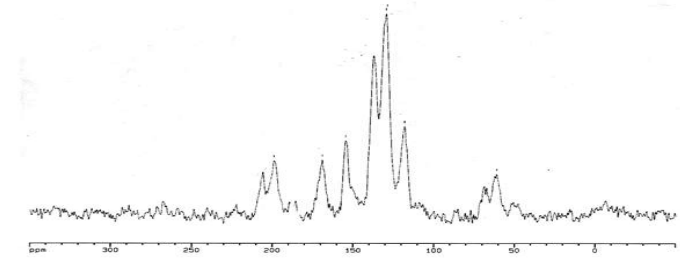


Fig. 7(b) $^{13}C$ NMR spectrum of polymer Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3(5 –hydroxy phenylene)}

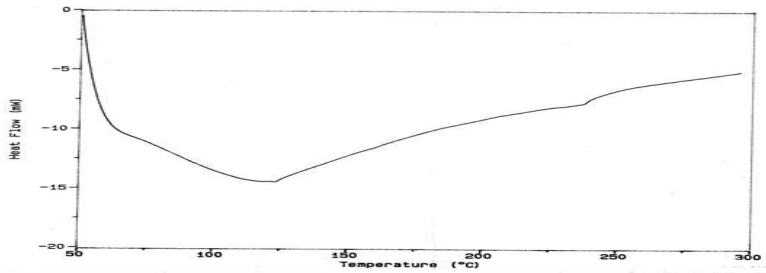



Fig 8(a) DSC of Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3 – phenylene}

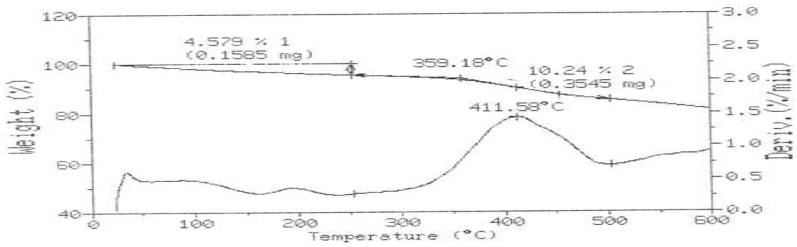



Fig 8(b) TGA of Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3 – phenylene}

Table-1: Summary of Homopolymerization Parameters and Viscosity

| Run | Polymer concentration (wt%) | Polymerization temperature ($^0$C) | Anisotropic Polymer | Intrinsic Viscosity in MSA 30$^0$C (dl g- 1) |
|---|---|---|---|---|
| 1 | 5 | 190 | No | 4.1 |
| 2 | 10 | 190 | No | 6.2 |
| 3 | 10 | 150 | Yes | 5.9 |

| | | | | |
|---|---|---|---|---|
| 4 | 5 | 150 | Yes | 4.9 |
| 5 | 5 | 150 | Yes | 6.5 |

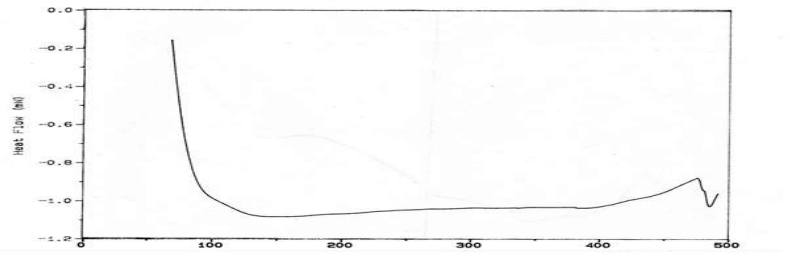
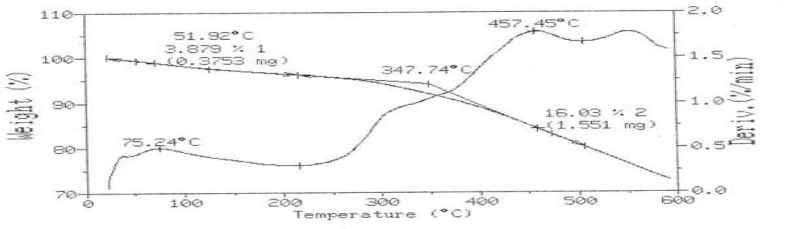



Fig 9(a) DSC of Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3(5 –hydroxy phenylene)}




9(b) DSC of Poly {(benzo [1,2-d: 4,5-d']- bisthiazole 2,6-diyl) 1,3(5 –hydroxy phenylene)}

## CONCLUSION

The polymerization of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT. 2HCl) with isophthalic acid and 5-hydroxyisophthalic acid in polyphosphoric acid (PPA) in an inert environment has been documented. Due to strong intramolecular hydrogen interactions between hydroxyl moieties and nitrogen atoms of neighboring benzothiazole units, spectroscopic studies have revealed a planar structure. Elemental analyses and spectroscopic methods verified the production of polymers. The produced polymers were soluble in chlorosulphonic and methane sulphonic acids. The polymers' inherent viscosities ranged up to 4.2 dL/g.

## ACKNOWLEDGMENTS

The authors are grateful to the JSS Academy of Technical Education Noida and DMSRDE, DRDO Kanpur for the support, material characterization, and successful completion of the research work.

## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

## AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

Roli Verma https://orcid.org/0000-0002-4847-9917
Kirti Srivastava https://orcid.org/0000-00224935471
R.S.Jagadish https://orcid.org/0000-0003-0003-107X
Rama Dubey https://orcid.org/0000-0002-1423-0611



## REFERENCES

1. W. W. Adams, R. K. Eby, D. E. Mclemore, eds. The Materials Science and Engineering of Rigid-Rod Polymers, *Materials Research Society Symposium Proceedings*, **134**(1989)

2. V.V. Kozey, H. Jiang, V.R. Mehta, S. Kumar, *Journal of Material Research*, **10,** 1044(1995), https://doi.org/10.1557/JMR.1995.1044
3. Xiao-Dong Hu, S. E. Jenkins, B.G.Min, M.B.Polk, S. Kumar *Macromolecular Materials and Engineering* ,**288(11)**, 823 (2003),https://doi.org/10.1002/mame.200300013
4. D. R. Dean, D. M. Husband, M. Dotrong, C. S. Wang, M. H. Dotrong, W. E. Click, R. C. Evers *Journal of Polymer Science Part A: Polymer Chemistry,* **35(16)**,3547(1997), https://doi.org/10.1002/(SICI)1099-0518(19971130)35:16<3457::AID-POLA13>3.0.CO;2-E
5. D.J. Sikkema, *Polymer*, **39**, 5981(1998), https://doi.org/10.1016/S0032-3861(97)10289-0
6. T.D. Dang, C.S. Wang, W.E. Click, H.H. Chuah, T.T. Tsai, D.M. Husband, F.E. Arnold. *Polymer*, **38**, 621(1997), https://doi.org/10.1016/S0032-3861(96)00537-X
7. S. Bhattacharya, H.H. Chuah, M. Dotrong C.S. Wang, K.H. Wei, D. Vezie, A. Day, W.W. Adams. Proceedings (ACS Division) *Polymeric Materials Science and Engineering,* **60**, 512(1989).
8. U. Santosh, M.H. Dotrong , H. H. Song, C.Y.C. Lee. Polymeric Materials Science and Engineering, Proceedings (ACS Division) *Polymeric Materials Science and Engineering*, **40**, 65(1991).
9. W.J. Sweeny. *Journal of Polymer Science Part A: Polymer Chemistry,* **30**, 1111(1992), https://doi.org/10.1002/pola.1992.080300618
10. C. Ricket, P. Neuenschwander, U.M. Sutter, *Macromolecular Chemistry and* Physics, **195(2),** 511(1994), https://doi.org/10.1002/macp.1994.021950210
11. T. Jiang, J. Rigney, M.G. Jones, L.J. Makoski, G.E. Spilman, D.F. Mielewski, D.C. Martin, *Macromolecules*, **28**, 3301(1995), https://doi.org/10.1021/ma00113a035
12. Y.H. So, B. Bell, J.P.Heeschem, R.A. Nyquist, C.L. Murlick. *Journal of Polymer Science Part A: Polymer Chemistry,* **33**, 159(1995), https://doi.org/10.1002/pola.1995.080330118
13. X. Hu, S. Kumar, M.B. Polk, D.L. Vander hart. *Journal of Polymer Science Part A: PolymerChemistry,***36**,1407(1998),https://doi.org/10.1002/(SICI)10990518(19980715)36:9<1407::AID-POLA8>3.0.CO;2-P
14. L.R. Denny, I.J. Goldfarb and E.J. Soloski. *Material Research Society* Symposium, Proceeding **395**, 134 (1989).
15. R. Saxena and L. D. Kandpal, Polybenozobisthiazole- Critical Issues in its Performance and Properties, in: *Polymides and Other High Temperature Polymers* (Proceedings of IInd International Symposium Editor K. L. Mittal), VSP Publishers Boston USA, 225(2003)
16. R. Saxena, L.D.Kandpal and G.N.Mathur, *Journal of Polymer Science Part A: Polymer Chemistry*,**40, (22)**,3959(2002), https://doi.org/10.1002/pola.10481
17. J. Olvera-Mancilla, J. Palacios-Alquisira, Vladimir Alonso Escobar-Barrios and Larissa Alexandrova, *Journal of Macromolecular Science, Part A*, **56(6)**, 609(2019), https://doi.org/10.1080/10601325.2019.1593046
18. Olvera-Mancilla J, Palacios-Alquisira J, Alexandrova L. *High Performance Polymers*, **30(6)**,699(2018), https://doi.org/10.1177/0954008317716977
19. A. Kausar *Polymer-Plastics Technology and Materials*, **58(18)**, 1965(2019), https://doi.org/10.1080/25740881.2019.1599945
20. M Toba, Y Takeoka, M Rikukawa, K Sanui , *Synthetic Metals,* **152(1–3)**, 197(2005), https://doi.org/10.1016/j.synthmet.2005.07.295
21. J. Zhu,a Suying Wei,b Max Alexander Jr.C. David Cocke,a Thomas C. Hoa and Zhanhu Guoa . *Journal of Materials Chemistry*, **20(3)**, 568, (2010), https://doi.org/10.1039/b917684e

[RJC-8360/2023]