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### **Synthesis and Characterization of Flexible Linkage Containing Diol**

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#### **ABSTRACT**

Aromatic diols are very efficient precursor for the synthesis of high performance polymer such as polyether, polyesters, polyurethanes etc. The diol synthesized from various diamines which are structurally modified having different functional group. These diamines react with p-hydroxy benzoic acid by Yamazaki polycondensation method. Synthesized diols were characterized by spectroscopic ally i.e IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and mass spectra. All diols having amide linkage show solubility in polar aprotic solvent.

**KEYWORDS:** Aromatic diols, Synthesis, high performance polymer, amide linkage

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## INTRODUCTION

Various high performance polymers include polyamides, polyimides, poly(amide-imide)s, polyesters, poly(phenylene-ether)s, polysulfones, poly(aryl ether-ketone)s, poly(oxadiazole)s, poly(ether- amide), poly(ether- amide- imide), poly(naphthalene)s, liquid crystalline polymers<sup>1-4</sup> etc. There are many synonyms for the term high performance plastics, such as high temperature plastics, high-performance polymers, high performance thermoplastics or high-tech plastics etc.

High performance polymers are characterized by their excellent balance of thermal and mechanical properties which makes them useful materials for their wide applications.<sup>5-8</sup> During the last years, several new families of high performance polymers and engineering plastics have been reported which find enhanced application potential in the more challenging areas like aerospace, defense, energy, electronics, automotives etc. as compared to the conventional polymers.<sup>9-14</sup> Such polymers provide improved properties like higher service temperatures, good mechanical strength, dimensional stability, thermal degradation resistance, environmental stability, solvent resistance, electrical properties etc. even at elevated temperatures.

The solubility or processability or tractability of the polymers (i.e polymers solubility and heat softening) is very important. To achieve enhanced structural modification such as reduction of crystallinity, introduction of flexibilising units such as ether, sulphone, alkylene etc., phenylation of the backbone, copolymerization and introducing kinked structure in the polymer backbone. These changes increase solubility with disturbing rigidity of the chain.<sup>15-19</sup>

The problem of thermal stability and processability are the main problems for polymer chemist. Organic molecules are not heat resistant and are oxidized below 250-350°C in air. On the other hand an approach to improve thermal stability is detrimental to tractability.<sup>20-23</sup> Hence past twenty years research has been directed not towards thermal stability of polymers but towards retention of as much stability while introducing solubility and processability.<sup>24-25</sup>

In present investigation to introduce a new diol having different functional group which increase the solubility of polymer because it disturbs the structure regularity.

## EXPERIMENTAL

### *1. Materials*

All chemicals were purchased from Merck and Aldrich chem. Benzyl chloride, sulphur, 4-hydroxybenzoic acid, 4,4'-aminophenyldiphenyl ether (ODA) 4,4'-diamino diphenyl sulphone (SDA) and p-phenylenediamine, m-aminoacetophenone from (S.d.fine chemicals) thionyl chloride, pyridine, chloroform, sulphuric acid, hydrochloric acid, etc. were good quality laboratory reagents and used after appropriate purification and distillation method. N, N- Dimethyl formamide (DMF),

N,N Dimethyl acetamide (DMAc), toluene were used after distillation and these solvents were dried over 4A molecular sieves.

## 2. Characterization

1. IR spectra were recorded at a resolution of  $4\text{ cm}^{-1}$  with co-addition of 32 scans using a Thermo-scientific Nicolet iS10 smart IR.  $^1\text{H}$ NMR spectra were recorded with a Bruker 400 MHz and 100 MHz for  $^{13}\text{C}$  measurements using  $\text{CDCl}_3$  or DMSO solvent. Mass spectra were recorded on Shimadzu LC-MS-2020 spectrometer.

## 3. Monomer synthesis

**3.1.** Synthesis of 2,5-bis(4-amino phenyl)-3,4-diphenyl thiophene (APDPT) (III) used as a starting material for synthesis was prepared as per reported procedure .

**3.2.** Synthesis of N, N'-bis(4-hydroxyphenyl) 4-(3-phenyl-thiophene-2-yl)benzamide (HPPTBA) (IV)

In 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer calcium guard tube and nitrogen gas inlet were placed 0.418 g (1 mmol) 2,5 bis(4-amino phenyl)-3,4-diphenyl thiophene (APDPT) (III) , 0.276 g (2 mmol) p-hydroxybenzoic acid, 0.200 g lithium chloride (8 wt%) based on solvent N -methyl pyrrolidine (NMP) and pyridine mixture and 0.744g (0.63 mL triphenyl phosphite (TPP), 0.5 mL pyridine and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to  $100^\circ\text{C}$  and refluxed at  $100^\circ\text{C}$  for 3 h under nitrogen. After cooling the resulting viscous mixture was poured into rapidly stirred 200 mL methanol. The precipitated product was filtered, washed with methanol and air dried. The monomer was purified by dissolving in 10 mL N,N-dimethylacetamide (DMAc) and reprecipitated by methanol. It was filtered washed dried under vacuum at  $80^\circ\text{C}$  for 8h.

Yield : 0.493 g ( 75% )

M.P. :  $230^\circ\text{C}$

Resulted (HPPTBA) was characterized by IR,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR and Mass spectroscopically.

**3.3** Synthesis of N, N'-bis[3-(2-amino-thiazol-4-yl)-phenyl]isophthalamide (ATPIPTA)

In a 100 mL three neck round bottom flask added compound (I) 0.4 g (0.001mol) and iodine 0.252 g (0.002 mol) and thiourea 1.2 g (0.004 mol) and stirred the mixture in DMAc at  $120^\circ\text{C}$  for 24 h. Then poured the reaction mixture with stirring in water, the yellow solid was obtained. The precipitate was washed successively with water and then by ethanol.

Yield 0.460 (90%).

Melting point  $>300^\circ\text{C}$

### 3.4 Synthesis of N,N',-bis [4-3-benzoylamino-phenyl]-thiazol-2-yl]4-hydroxybenzamide (BAPTHBA) (V)

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer, calcium guard tube and nitrogen gas inlet were placed 0.752 g (1mmol), N, N'- bis[3-(2-aminothiazol-4-yl)-phenyl] isophthalamide (ATPITPA) (II), 0.276 g (2 mmol) p-hydroxybenzoic acid, 0.200g lithium chloride (8 wt% based on solvent N-methyl pyrrolidine (NMP) and pyridine mixture) and 0.744g (0.63 mL, 2.4 mmol) triphenyl phosphite (TPP), 0.5 ml pyridine and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to 100°C and refluxed at 100°C for 3h under nitrogen. After cooling the resulting viscous mixture was poured into rapidly stirred 200 mL methanol. The precipitated polymer was filtered, washed with methanol and air dried. The monomer was purified by dissolving in N,N-dimethylacetamide (DMAc) and reprecipitated by methanol. It was filtered, washed and dried under vacuum at 80°C for 8 h.

Yield 0.47g ( 60%)

M.P. >300°C

IR The formation of diol from (ATPIPTA) and p-hydroxybenzoic acid is confirmed from the appearance typical characteristic OH broad band's stretching at around 3277 to 3024  $\text{cm}^{-1}$  and 1640  $\text{cm}^{-1}$  (-C=O stretching in CONH), 1288 $\text{cm}^{-1}$ , at 1070 $\pm$ 4  $\text{cm}^{-1}$  and 1059 $\pm$ 7  $\text{cm}^{-1}$  and (C-O-C symmetric and asymmetric stretch).(Figure3A.6)

Synthesis of HPPBA (VI), BSPHBA(VII) and HPBA (VIII) using corresponding amines and p-hydroxy benzoic acid was performed discussed in chapter per procedure.

### 4. Characterization of monomer synthesis

IR The formation of diol from APDPT and p-hydroxybenzoic acid was confirmed from the typical OH characteristic bands observed around 3277 to 3024  $\text{cm}^{-1}$  (broad) and 1640  $\text{cm}^{-1}$  (-C=O stretch of amide -II linkage), 1288  $\text{cm}^{-1}$ , 1070  $\text{cm}^{-1}$  and 1059  $\text{cm}^{-1}$  and (C-O-C symmetric and asymmetric stretch). (Figure 3A.1)

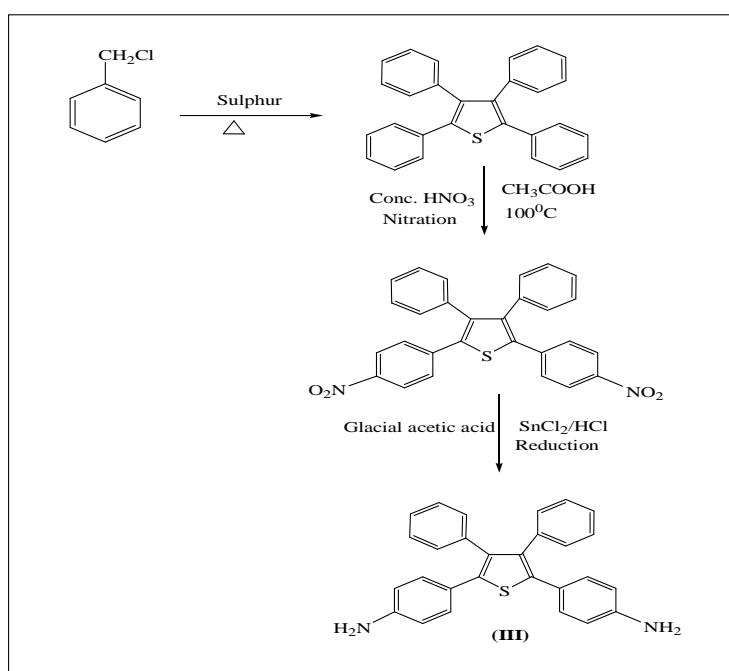
$^1\text{H}$ NMR spectra confirmed the amide linkage formation by presence of peak at 9.64 ppm the peak present in the range 7-7.89 ppm corresponding to aromatic proton.(Figure3A.2).

$^{13}\text{C}$ NMR spectra gave 14 different signals corresponding to 14 different carbons. The peak at 166 ppm was assigned to a carbon of amide linkage. The peak at 160 ppm was assigned to aromatic carbon which is directly attached to OH group. Twelve different peaks in the range 115 ppm to 139 ppm were assigned to aromatic carbons. (Figure 3A.3)

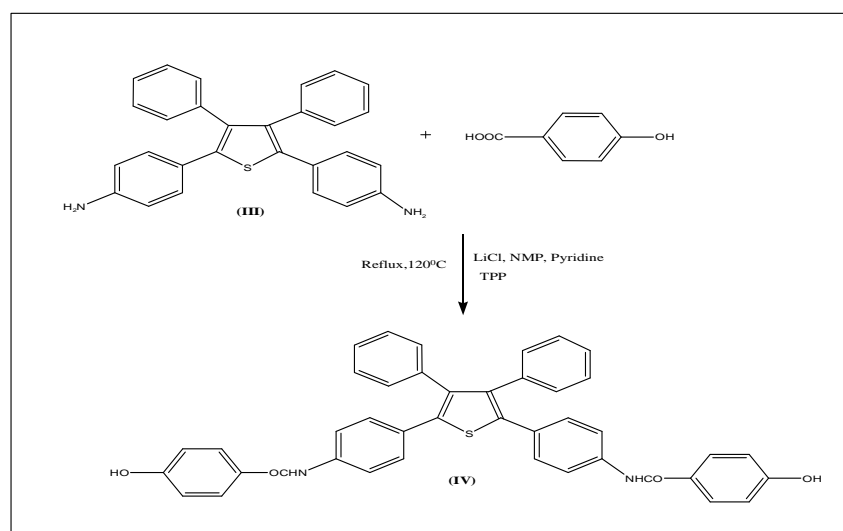
Mass spectra shows molecular ion peak at 659  $\text{m/e}^+$  was related to molecular weight of dihydrazide. The peak at 619  $\text{m/e}$  related to loss of hydroxy group (Figure 3A.4).

## RESULTS AND DISCUSSION

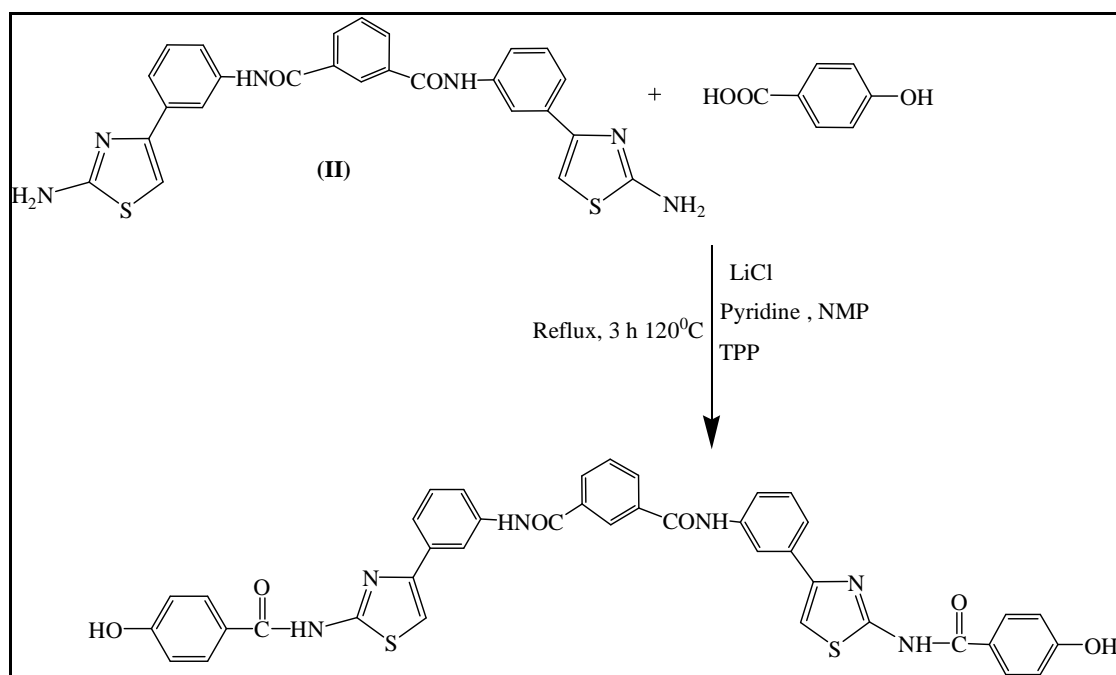
One of the successful approaches is the introduction of bulky aromatic heterocyclic pendants such as tetraphenyl thiophene and thiazole unit in polymer backbone. The rigidity, symmetry and aromaticity of these systems contribute thermal and chemical stability and enhanced mechanical properties of the resulting polymer at elevated temperatures; in addition, increase of polarisability of the nitrogen atom in the heterocyclic ring by introducing phenyl group such as tetraphenyl thiophene thiazole improves the solubility, processability, gas and water absorption as well as mechanical properties. However given the broad application space and diversity of this important class of materials, very few advances have been realized either in commercial off springs or in new synthetic methods.



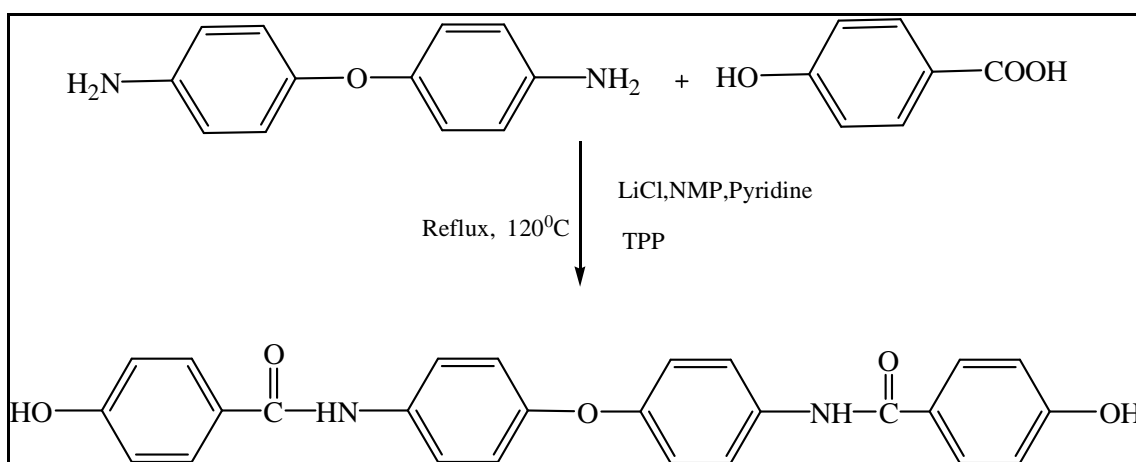
Scheme 1: Synthesis of 2,5-bis(4-aminophenyl)-3,4-diphenyl thiophene (APDPT) (III)



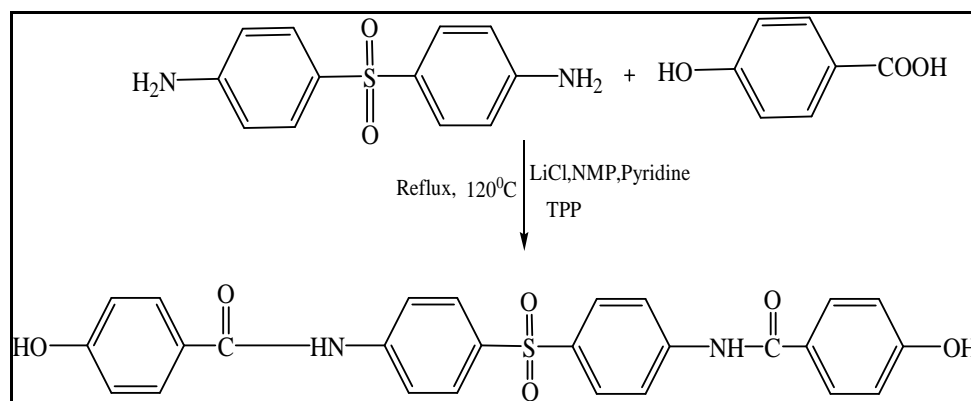
Scheme 2: Synthesis of bis N-(4-2 hydroxy-phenyl)-4-(3-phenyl-thiophen2-yl) benzamide (HPPTBA) (IV)



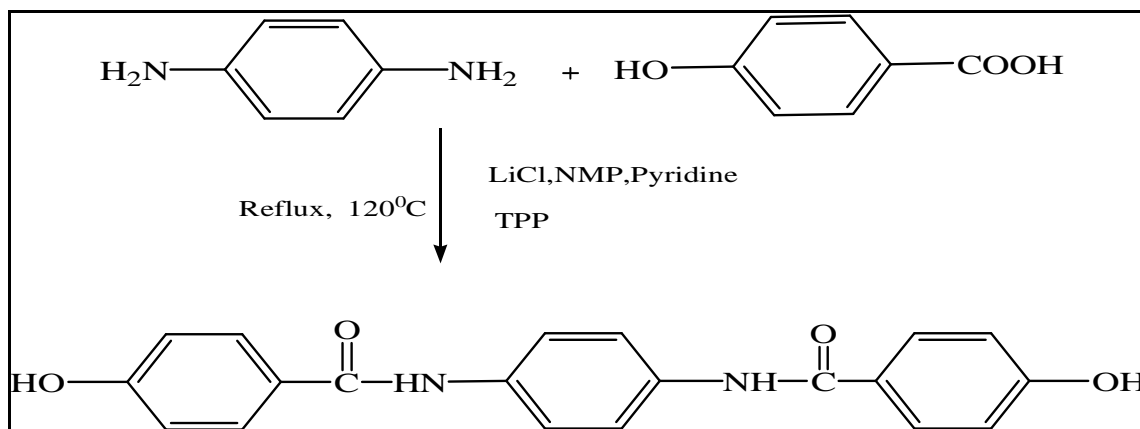
Scheme 3: N,N',-bis [4-3-benzoylamino-phenyl]-thiazol-2-yl]4- hydroxybezamide (BAPTHBA) (V)



Scheme 4: Bis 4-hydroxy- N-(4-phenoxy-phenyl)-benzamide (HPPBA) (VI)



Scheme 5: N-(4-benzenesulfonyl-phenyl)-4-hydroxy-benzamide (BSPHBA)(VII)



Scheme 6: 4-Hydroxy-N-phenyl-benzamide (HPBA) (VIII)

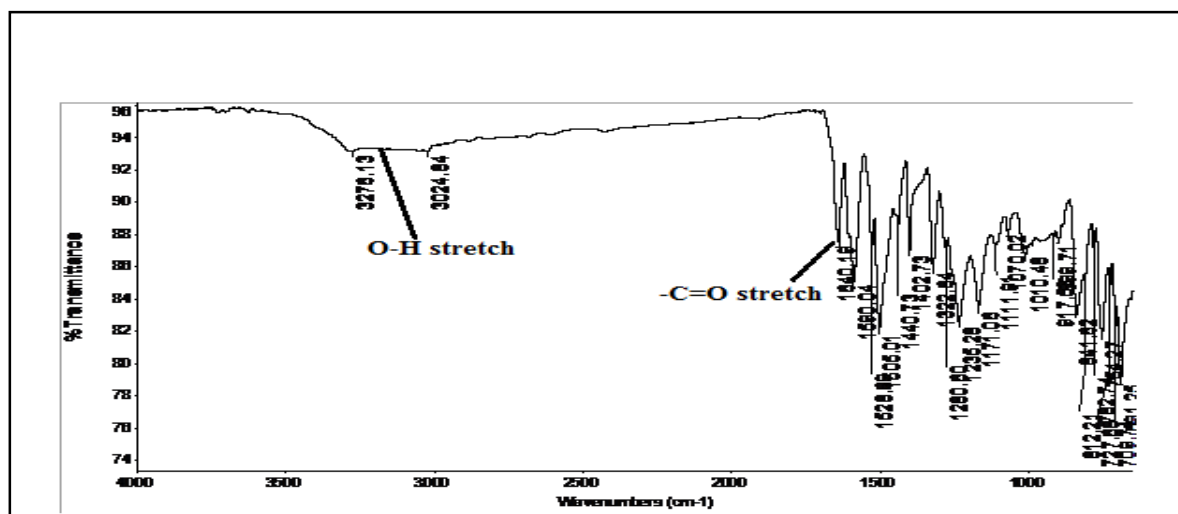


Figure 1: IR Spectra of (BAPTHBA) (V)

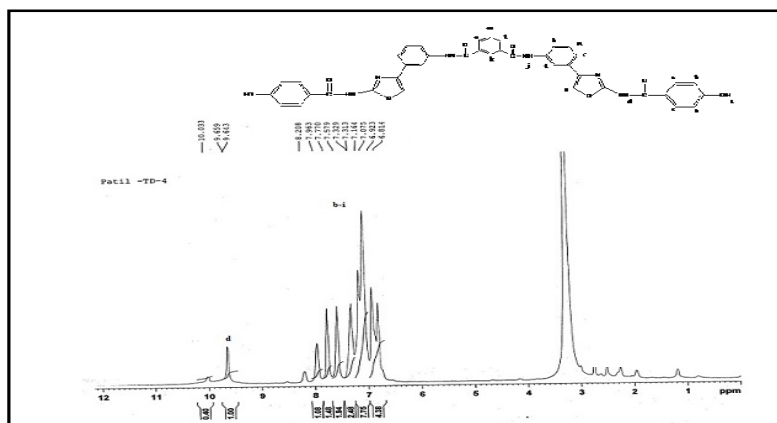


Figure 2: <sup>1</sup>H NMR Spectra of (BAPTHBA) (V)

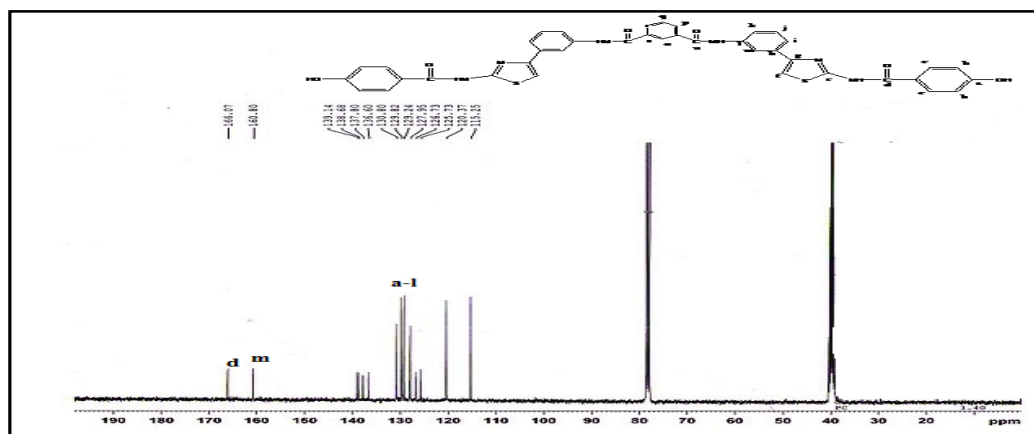
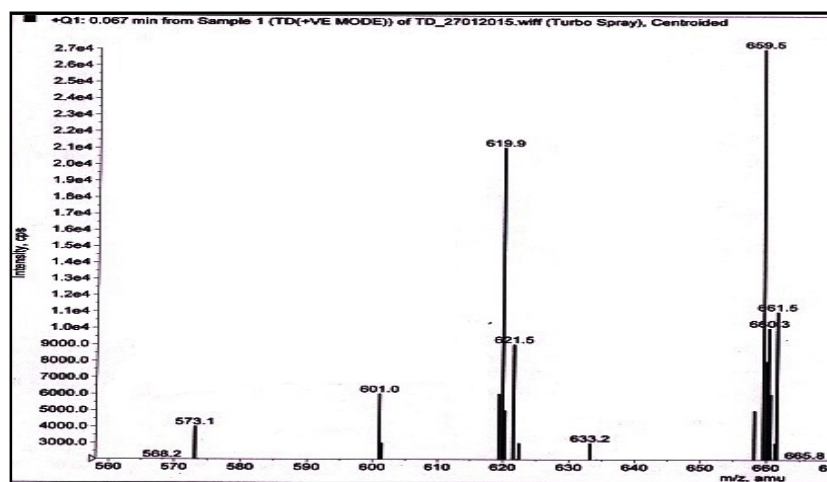
Figure 3: <sup>13</sup>C NMR Spectra of (BAPTHBA) (V)

Figure 4: Mass spectra of (HPPTBA) (IV)

## CONCLUSION

Synthesized diols were shows the good solubility in polar aprotic solvent such as DMAc, DMF, NMP, pyridine. Due to flexible linkages such as –O–, SO<sub>2</sub>, heterocyclic moiety present in polymer backbone increase the processability.

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