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# Syynthesis and characterization of aromatic-alipathic polyamides containing tetraphenylthiophene units into the backbone*

**Sudhakar S. Mahajan**, Bhimrao D. Sarwade, and Noormahmad N. Maldar*****

Division of Polymer Chemistry, National Chemical Laboratory, Pune-411 008, India

## SUMMARY

Aromatic-aliphatic polyamides were prepared from 2, 5-bis(4-carboxyethylcarbonylphenyl)-3,4-diphenylthiophene (BCDT) with few commercial diamines by using Yamazaki's phosphorylation reaction. The polymers were obtained in good yields and were characterized by solubility tests, viscosity measurements, IR spectroscopy, thermal analysis and X-ray diffraction studies. These polyamides had inherent viscosities in the range of 0.35 to 0.70 dl/g and were amorphous in nature. All the polyamides were readily soluble in solvents such as N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, N,N-dimethylformamide, nitrobenzene, hexamethylphosphoramide, *m*-cresol, sulphuric acid and did not lose weight below 300°C in air.

## INTRODUCTION

High temperature stable aromatic polymers are increasingly in demand as performance materials for industrial and aerospace applications. However, most of the high temperature stable polymers are difficult to process because of their limited solubility. A number of attempts have been made in the past to modify aromatic polyamides in order to improve their properties with a considerable emphasis on solubility enhancement (1-5). Aliphatic units have been incorporated into the polymer backbone to improve the solubility with very little influence on the thermal stability of aromatic polyamides. The introduction of pendant phenyl groups is another approach for improving the solubility.

In view of the foregoing facts, we felt that highly phenylated tetraphenylthiophene units in combination with aliphatic spacer into the polymer backbone would result in improved solubility by maintaining the thermal stability and thereby processability of resultant polyamides. In this paper we report the synthesis and characterization of aromatic-aliphatic polyamides from 2,5-bis(4-carboxyethylcarbonylphenyl)-3,4-diphenylthiophene (BCDT) with few commercial diamines.

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**To whom offprint requests should be sent

***Present address: Department of Polymer Chemistry, Shivaji University Centre for Post-Graduate Studies, Solapur 413 003, India

## EXPERIMENTAL

**Materials** : Tetraphenylthiophene was prepared according to the literature procedure(6). AR grade anhydrous aluminium chloride was used as received. Succinic anhydride, 4,4'-diaminodiphenylether (ODA),4,4'-diaminodiphenylmethane (MDA),4,4'-diaminodiphenylsulfone (SDA) and benzidene (BZD) were recrystallized prior to use. m-phenylenediamine (MPDA) was purified by vacuum sublimation. Triphenylphosphite (TPP) was purified by vacuum distillation. All the solvents were purified prior to use.

### Monomer synthesis

**Synthesis of diacid (BCDT)** : To a solution of tetraphenylthiophene (38.8g,0.1 mol), succinic anhydride (24.0g, 0.24 mol) and 400 ml dry dichloromethane at 10°C, aluminium chloride (64.0g, 0.48 mol) was added in portions with constant stirring. After 24 h at room temperature, the reaction mixture was refluxed in an oil bath for additional 75 h. Dichloromethane was distilled off. The mixture was hydrolyzed with 10% cold hydrochloric acid solution. A solid obtained was filtered and washed several times with distilled water till acid free. The crude diacid was dissolved in 10% sodium bicarbonate solution and reprecipitated from dil.hydrochloric acid and recrystallized from acetic acid: water (80:20, v/v). Yield 49.98g (85%) mp. 139-140°C.

Anal. Calcd. for $C_{36}H_{28}O_6S$ (588):
Calcd.:C,73.47%, H,4,76%, S,5.44%.
Found :C,73.30%, H,4.80%, S,5.80%.

### Polymerization

In a three-necked 50ml round bottom flask were added BCDT 0.588g (0.001 mol) and ODA 0.200g (0.001 mol) in a mixture of pyridine (4ml) and DMAC(0.5ml) containing 5% LiCl. Then TPP 0.766g (0.0025 mol) was added under nitrogen atmosphere. The reaction mixture was heated at 100°C for 4 h. The polymer was isolated by pouring the mixture into cold methanol. The solid obtained was filtered, washed several times with methanol, sodium bicarbonate solution (10%) and finally with distilled water. The polymer was dried in vacuum at 80-85°C for 4 h. The same procedure was followed for the preparation of other polyamides (PA-2 to PA-5, Table 1).

### Measurements

The IR spectra were recorded on a Pye Unicam SP-3 300 spectrophotometer. The $^1$H-NMR spectra were recorded on a Varian T-60 NMR spectrometer. The X-ray diffractograms were obtained with Phillips X-ray unit (Phillips generator, PW-1730) and a Nickel filtered CuK$_\alpha$-radiations. The thermogravimetric analyses were made with NETZSCH 409 thermal-analyser. The measurements were recorded in air at a heating rate of 10°/min. Viscosity measurements were made with 0.1% (w/v) solutions of polymers in conc. sulphuric acid at 30°C using an ubbelohde suspended viscometer.

## RESULTS AND DISCUSSION

**Monomer synthesis:** Diacid BCDT was prepared in 85% yield from tetraphenylthiophene and succinic anhydride by Friedel-Crafts reaction in dichloromethane (Scheme 1). It was characterized by IR, $^1$H-NMR spectroscopy and elemental analysis. It's IR spectrum showed characteristic absorptions at 3500-3300 cm$^{-1}$(-OH,stretching band),1710 cm$^{-1}$ (acid carbonyl band), 1680 cm$^{-1}$(keto carbonyl band). The $^1$H-NMR spectrum in tetrafluroacetic acid showed triplet at $\delta$ 2.4 (4H,- $CH_2$-COOH) a triplet at $\delta$ 2.9(4H,-$COCH_2$) and multiplet between $\delta$ 6.0-7.4 (14H,-aromatic). The Friedel-Crafts acylation of tetraphenylthiophene with succinic anhydride is expected to proceed in the similar manner as the nitration of tetraphenylthiophene, which reported to afford 2,5-bis (4-nitrophenyl)-3,4-diphenylthiophene. The selectivity of the dinitrocompound had been confirmed by X-ray investigations (7).

**Polymer synthesis** : Direct polycondensation of aromatic diamines with dicarboxylic acids using triphenylphosphite and pyridine as the condensing reagent is known to be a convenient method for the preparation of polyamides on a laboratory scale (8). In the present communication five aromatic-aliphatic polyamides have been prepared from aromatic-aliphatic diacid (BCDT), and various diamines by phosphorylation reaction (Scheme 2). Table. 1 shows diamines used, yield and viscosity of the polyamides synthesized. All the aromatic-aliphatic polyamides had inherent viscosities in the range of 0.37 to 0.67 dl/g. The low inherent viscosity in case of polyamide PA-3 may be due to the lower reactivity of the amine, since it contains electron withdrawing sulfone group in the structure. IR spectra of all the polyamides showed characteristic amide absorption band at 3300-3350 cm$^{-1}$(-NH,stretching) and 1680 cm$^{-1}$(amide as well as keto carbonyl). The polymer

**TABLE 1**

**Synthesis of Polyamides**

| Polymer | Diacid | Diamine | Yield (%) | $\eta$ inh (dl/g) |
|---|---|---|---|---|
| PA-1 | BCDT | ODA | 98 | 0.60 |
| PA-2 | BCDT | MDA | 87 | 0.55 |
| PA-3 | BCDT | SDA | 78 | 0.35 |
| PA-4 | BCDT | BZD | 85 | 0.45 |
| PA-5 | BCDT | MPDA | 83 | 0.70 |

derived from ODA showed a band 1225 $cm^{-1}$ assignable to (C-O-C) asymmetric stretching. Absorption at 1435 $cm^{-1}$ could be attributed to the characteristic of thiophene ring.

**Table.2**

**Solubilities of Polyamides**

| Polymer | Solvents | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | DMF | DMSO | NMP | DMAC | HMPA | Meta-cresol | Nitro-benzene | $H_2SO_4$ |
| PA-1 | + | + | + | + | + | + | + | + |
| PA-2 | + | + | + | + | + | + | + | + |
| PA-3 | + | + | + | + | + | ++ | + | + |
| PA-4 | + | + | + | + | + | + | + | + |
| PA-5 | + | + | + | + | + | + | + | + |

+ = Soluble at room temperature,++ = Soluble after heating.

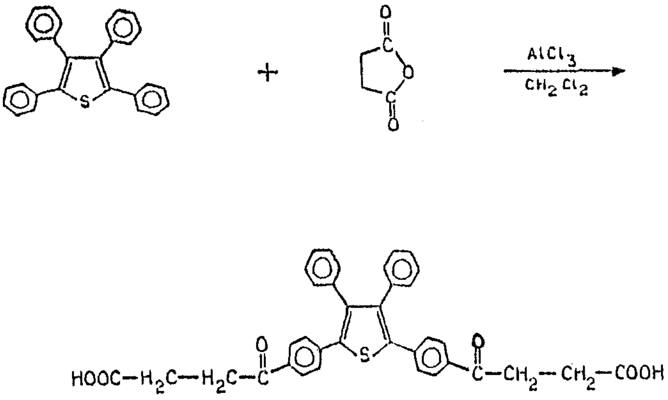
Table.2 presents the solubility characteristics of the polyamides in various solvents. A 1 % solution was taken as a criterion for solubility. All polymers were completely soluble in N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidinone(NMP), N,N-dimethylacetamide (DMAC), hexamethylphosphoramide (HMPA), m-cresol, nitrobenzene and conc. sulphuric acid and were insoluble in chloroform, acetone and benzene. The solubility behaviour of the polymers reveals that the polyamides obtained in the present case are more easily soluble. This observation could be attributed to the presence of aliphatic units and pendant phenyl groups in the backbone.

**Table.3**

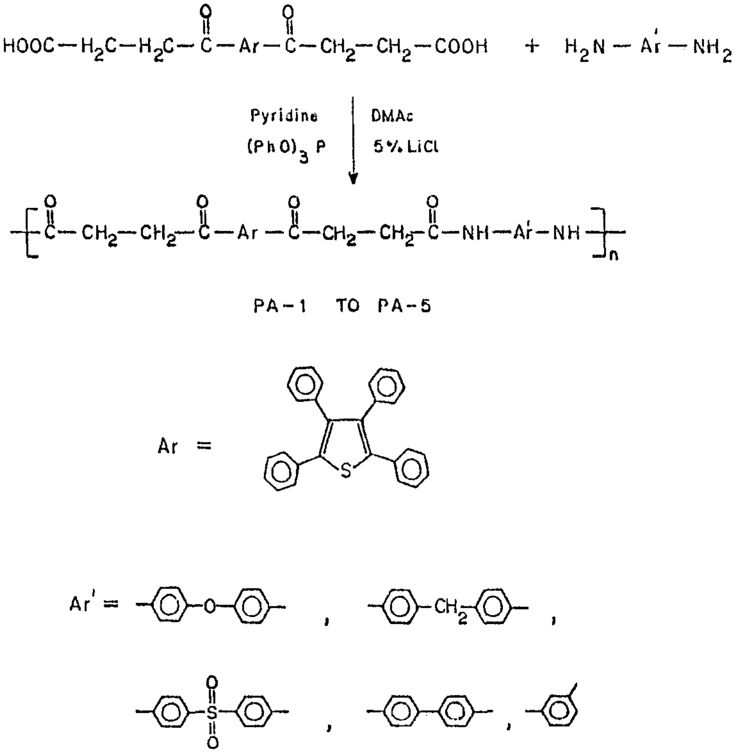
**Thermal Properties of Polyamides in air**

| Polymer | Temperature ($^{o}C$) for various % decompositions | | | | | |
|---|---|---|---|---|---|---|
| | 10 | 20 | 30 | 40 | 50 | $T_{max}{}^{a}$ |
| PA-1 | 406 | 469 | 493 | 519 | 531 | 549 |
| PA-2 | 457 | 501 | 519 | 536 | 549 | 559 |
| PA-3 | 460 | 529 | 551 | 569 | 591 | 608 |
| PA-4 | 432 | 493 | 519 | 534 | 549 | 564 |
| PA-5 | 452 | 498 | 524 | 541 | 556 | 569 |

a = Temperature of maximum exothermal peak observed in DTA.



Scheme 1



Scheme 2

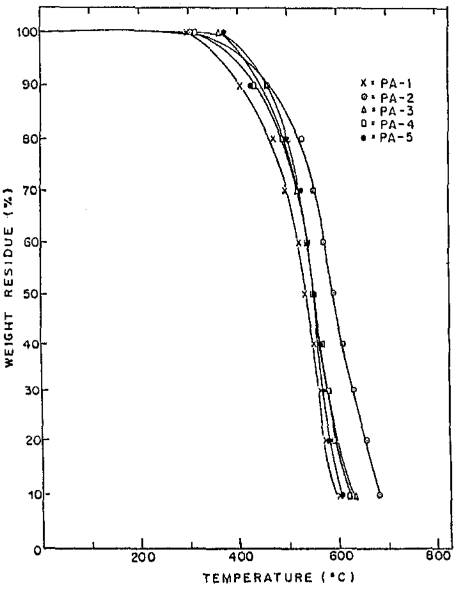


Figure 1

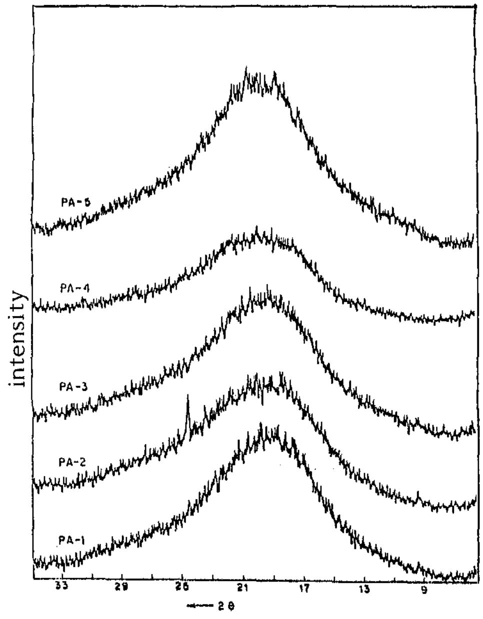


Figure 2

Thermal behaviour of these polyamides was evaluated by thermogravimetric analysis in air. TG curves are presented in (Fig.1). All the polyamides showed similar pattern of decomposition with no weight loss below 300°C. Table.3 shows the temperature for various precentage weight losses. The polymer maximum decomposition temperature ($T_{max}$) was in the range of 549-608°C.

The powder X-ray diffraction studies (Fig.2) indicated that all the polymers were amorphous in nature. The presence of aliphatic chain and pendant phenyl groups may be responsible for making these polymers less rigid.

## CONCLUSIONS

In conclusion polyamides containing tetraphenylthiophene unit with aliphatic spacers could be prepared with fairly high thermal stability and good solubility in organic solvents. These polyamides may find applications in processable high temperature polymers.

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