

Synthesis and Characterization of Aromatic–Aliphatic Polyamides

V. P. UBALE,¹ A. D. SAGAR,² N. N. MALDAR,¹ M. V. BIRAJDAR³

¹ Chemistry Department, Shivaji University Centre for Post-Graduate Studies, Solapur 413 003, India

² School of Chemical Science, SRT Marathwada University, Nanded 431 602, India

³ Polymer Chemistry Division, NCL Pune 411 008, India

Received 21 January 2000; accepted 5 April 2000

ABSTRACT: A new monomer, 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V) has been synthesized and characterized by physical and spectroscopic methods. A series of eight aromatic–aliphatic polyamides was prepared from the (V) and different aromatic diamines using Yamazaki's direct phosphorylation reaction. The polyamides were characterized by IR spectroscopy, viscosity measurements, and thermal analysis. An excellent yield of these polyamides was obtained, with inherent viscosities in the range of 0.28 to 0.67 dL/g, and the polyamide were readily soluble in aprotic polar solvents such as *N*-methyl-2-pyrrolidone, *N*-*N*-dimethyl acetamide, dimethyl sulphoxide, and so forth. Polyamides could be cast into transparent and flexible films. They had glass-transition temperatures of 225–273°C. When evaluated by thermogravimetry, thermal analysis of the polyamides showed no weight loss below 311°C, and the char yield in air at 900°C was 55%–67%. The structure–property correlation among these polyamides is also discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 566–571, 2001

Key words: 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl-thiophene; aromatic soluble polyamides; direct polyamidation; thermal properties

INTRODUCTION

Organic polymers provide one of the most versatile groups of materials and find widespread use as plastics, rubbers, fibers, adhesives, and coatings. These polymers show extreme sensitivity to temperature, most importantly, because of the intrinsic flexibility of their molecular chains, giving them very low softening points. For many years the high temperature resistance and thermal stability of polymers could be enhanced by modifying structures of the side groups, but leaving the main carbon chain unchanged, or by in-

roducing heat-resistant groups such as aromatic rings into the chain. The next step was the preparation of fully cyclic polymers. The melting and softening points of such materials were on the order of 300–400°C, while decomposition occurred at even higher temperatures. Technological application was impeded because of the unavailability of physical processes since they were difficult and sometimes impossible to process. Worldwide efforts have been devoted to improving the solubility or processability of thermally stable polymers without a remarkable change in their thermal stability. An approach was made to enhance solubility of polymers by the insertion of flexible groups, that is, ether,¹ oxyethylene,² sulfone, aliphatic linkages,^{3–5} and cardo groups in the polymer backbone. The introduction of kinked

Correspondence to: N. N. Maldar.

Journal of Applied Polymer Science, Vol. 79, 566–571 (2001)
© 2000 John Wiley & Sons, Inc.

structures and silicon moieties is one of few methods for increasing the solubility of polymers. The incorporation of pendant phenyl groups⁶⁻⁷ in the rigid polymers leads to enhancing the solubility of polymers in different solvents.

In the present investigation novel dicarboxylic acid, that is, 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V) was synthesized. It was characterized by infrared (IR), nuclear magnetic resonance (NMR), mass spectroscopy, and elemental analysis. The novel diacid (V) was used as a building block for the preparation of a series of new polyamides. The polymers were characterized by measurement of reduced viscosity, solubility, film-forming properties, IR spectroscopy, and thermal analysis. The effect of the introduction of methylene linkage and an aromatic phenylated moiety into the polymer backbone on properties of aromatic polymers has been studied in detail.

EXPERIMENTAL

Materials

Commercially available chemicals needed for this study such as sulfur and anhydrous aluminium chloride were used as received. Benzyl chloride was fractionally distilled under reduced pressure. Acetyl chloride was refluxed with phosphorus pentachloride for several hours and distilled twice. Nitrobenzene was dried with calcium chloride and distilled under pressure from phosphorus pentoxide. It was stored over calcium hydride in a brown bottle. Morpholine was dried with potassium hydroxide, fractionally distilled, then refluxed with sodium and again fractionally distilled. *N*-Methyl-pyrrolidone was distilled from calcium hydride and stored over molecular sieves before use. Pyridine was refluxed over potassium hydroxide pellets under nitrogen, distilled, and stored over 4A molecular sieves. Lithium chloride was dried under vacuum at 150°C for 6 h. The various aromatic diamines were purified prior to use. Benzidine (BZD) was recrystallized from ethanol (mp 125–126°C). *m*-Phenylene diamine (mPDA) was distilled under reduced pressure. *p*-Phenylenediamine (pPDA) was sublimed under reduced pressure. Oxydianiline (ODA) was crystallized from tetrahydrofuran and then recrystallized from alcohol. 4,4'-Methylene dianiline (MDA) was recrystallized from hot water. 2,5-Bis(4-amino phenyl)-3,4-diphenyl thiophene (TPTPDA) was recrystallized from toluene.

Measurements

Viscosity measurements were made with 0.5% (w/v) solutions of polymers at 30°C using a suspended-type Ubbelohde viscometer. The solubility of polymers was determined at 3% concentration in various solvents at room temperature or on warming, if needed. The IR spectra of samples were recorded on a Perkin-Elmer-883 IR spectrometer by KBr pellet or in nujol or as polymer film. Elemental analysis was performed with a Perkin-Elmer model 2400 C,H,N,S analyzer. Proton NMR spectra were recorded on a Varian-80. Mass spectra were recorded on a IIMS-30 double-beam mass spectrometer. The thermogravimetry was performed on a Perkin-Elmer TGA-7 at a heating rate of 10°C/min under the nitrogen gas flow or in air. Analyses of some of the polymers was done on a Rigaku Thermo Flux TG-8110 at a heating rate of 10°C/min under nitrogen for TGA and DSC-DTA simultaneously.

Synthesis of Monomer

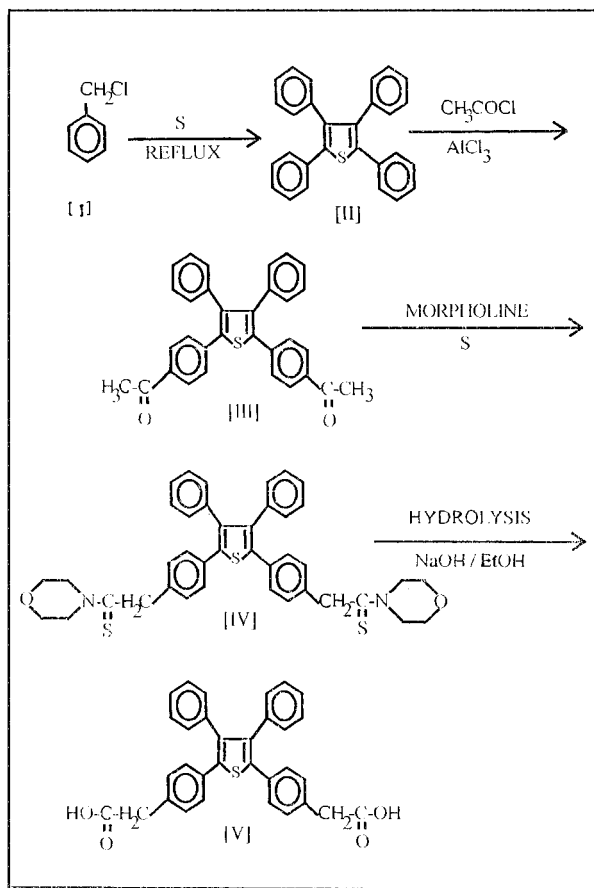
2,5-Bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V) was synthesized in four steps.

Tetraphenyl Thiophene (II) and 2,5-Bis(4-acetyl phenyl)-3,4-diphenyl Thiophene (III)

These were prepared as per an earlier procedure.⁷ (II) was recrystallized from a dichloromethane-methanol system to produce white needles (yield: 51%; mp: 184–186°C). The infrared (IR) spectrum (KBr) of (II) exhibited absorption at 3060 (aromatic C—H), 1595 (aromatic C=C), and 1435 cm⁻¹ (thiophene). (III) was recrystallized from toluene to get pure diacetyl tetraphenyl thiophene (III) as pale yellow needles (yield: 70%, mp: 255–256°C). The IR spectrum (KBr) of (III) exhibited absorption at 1680 cm⁻¹ (C=O).

2,5-Bis(4-thioacetomorpholide phenyl)-3,4 Diphenyl Thiophene (IV)

In a 500-mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer were placed 23.6 g (0.05 mol) (III), 4.6 g (0.15 mol) sulfur and 13.05 g (13 mL, 0.15 mol) morpholine. The resulting reaction mixture was stirred initially under gentle reflux until the evolution of hydrogen sulfide subsided and then stirred more vigorously for 14 h. The reaction mixture was allowed to cool, and 200 mL of ethanol was added to obtain a buff-color product that was filtered, washed with excess ethanol, and dried [Yield:



Scheme 1 Synthesis of 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V).

28.30 g (84%), mp: 120–123°C]. The IR spectrum (KBr) exhibited absorption at 1278 cm⁻¹ (C=S).

2,5-Bis(4-carboxy methylene phenyl)-3,4-Diphenyl Thiophene (V)

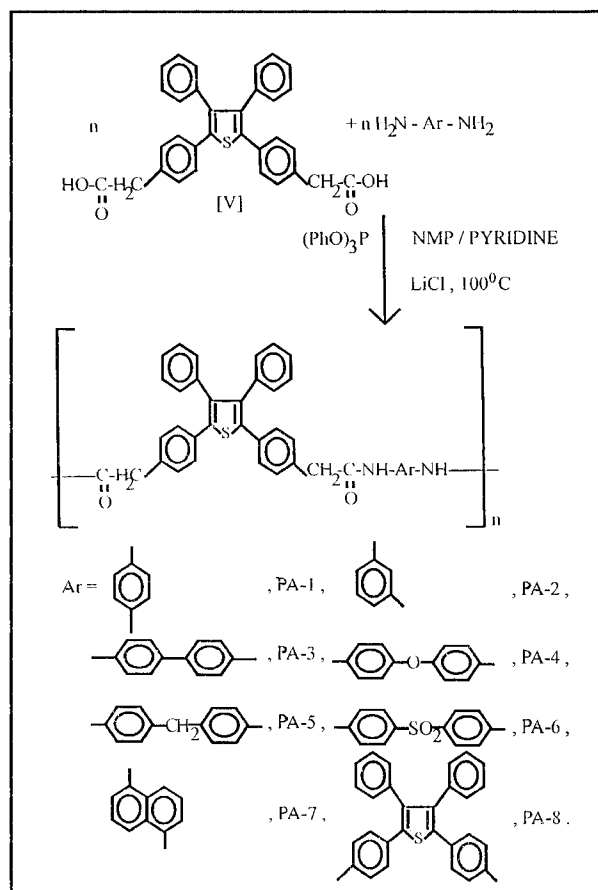
In a 1-L round-bottom flask equipped with a reflux condenser and a magnetic stirrer were placed 33.7 g (0.05 mol) (IV) and 500 mL of 10% ethanolic sodium hydroxide solution. The reaction mixture was refluxed with stirring for 12 h. Most of the ethanol was distilled out under reduced pressure. To the residual product 500 mL of hot water was added and filtered. The filtrate was acidified by 1 : 1 hydrochloric acid. The precipitated product was filtered, washed thoroughly with hot water, and dried. The product was recrystallized from ethanol to get (V) [Yield: 16.38 g (65%), mp: 238–240°C]. The IR spectrum of (V) (KBr) exhibited absorption at 3500–3250 (—OH), 1702 (C=O, indicating the presence of —COOH a carbonyl group), and 2918 and 2857 cm⁻¹ (C—H aliphatic).

Polymerization

By using the novel monomer 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V) a series of eight polyamides was prepared using Yamazaki's phosphorylation method.

Synthesis of Polyamide (PA-4)

In a 100-mL three-neck round-bottom flask equipped with magnetic stirrer, reflux condenser, calcium chloride guard tube, and nitrogen gas inlet were placed 0.504 g (1 mmol) 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V), 0.200 g (1 mmol) 4,4'-diamino diphenyl ether (ODA), 0.200 g lithium chloride [8 wt % based on solvent *N*-methyl pyrrolidone (NMP) and pyridine mixture], 0.744 g (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. The mixture was heated at 100°C for 3 h under nitrogen. After cooling, the resulting viscous mixture was poured into rapidly stirred 200 mL of methanol. The pre-



Scheme 2 Synthesis of polyamides (PA) from (V).

Table I Synthesis of Polyamides^a from (V)

Sr No	Polymer Code	Diamine	Yield (%)	Viscosity ^b
				$\eta_{sp/c}$ (dL/g)
1	PA-1	pPDA	97	0.46
2	PA-2	mPDA	98	0.35
3	PA-3	BZD	97	0.67
4	PA-4	ODA	94	0.47
5	PA-5	MDA	97	0.44
6	PA-6	SDA	92	0.28
7	PA-7	NDA	98	Ins.
8	PA-8	TPTPDA	98	0.50

^a Polymerization was carried out with 1 mmol each of diamine and diacid (V).

^b Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

cipitated polymer was filtered, washed with methanol, and air-dried. The polymer was purified by dissolving in *N,N*-dimethyl acetamide (DMAc) and reprecipitating in methanol. It was filtered, washed with methanol, and dried under vacuum at 100°C for 8 h. The yield was 94.31%, and the reduced viscosity of polymer in DMAc was 0.47 dL/g.

All other polyamides, that is, PA-1 to PA-8, were prepared by similar procedure.

RESULTS AND DISCUSSION

In the present investigation the synthesis of highly phenylated thiophene containing methyl-

ene dicarboxylic acid was performed. The monomer was characterized by IR, NMR, mass spectroscopy, and by elemental analysis.

Thus, the novel dicarboxylic acid 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V) was synthesized from benzyl chloride in four steps (Scheme 1). 2,5-Bis(4-acetyl phenyl)-3,4-diphenyl thiophene (III) was synthesized as per a procedure described in the literature. The reaction of morpholine with (III), as per the Conrad Willgerodt reaction with Kindler variation, produced (IV). The formation of an intermediate thiomorpholide derivative (IV) was confirmed by infrared spectroscopy. The infrared spectrum (KBr) of (IV) showed absorption at 1278 cm^{-1} (C=S) and the absence of a carbonyl (C=O) peak. The thiomorpholide derivative on alkaline hydrolysis yielded 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V). The elemental analyses of carbon, hydrogen, and sulfur for (V) were in good agreement with the calculated values for the molecular formula of (V). The infrared spectrum of (V) showed absorption bands at 3500–3250 (O—H stretch) and at 1702 cm^{-1} (C=O), indicating the presence of a carbonyl group. IR spectrum also showed absorption bands at 2918 and 2857 cm^{-1} , corresponding to the in-plane and out-of-plane stretching vibrations of the methylene group. The mass spectrum of (V) was consistent with the proposed structure as the peak at *m/e* 504 corresponding to the molecular ion peak of 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V) is clearly seen. The other fragmen-

Table II Solubility of Polyamides from (V)

Solvent	Polymer							
	PA-1	PA-2	PA-3	PA-4	PA-5	PA-6	PA-7	PA-8
DMAc	++	++	++	++	++	++	+-	++
DMSO	++	++	++	++	++	++	+-	++
NMP	++	++	++	++	++	++	+-	++
DMF	++	++	+-	++	++	++	-	+-
Pyridine	++	++	++	++	++	++	+-	++
<i>m</i> -Cresol	++	++	++	++	++	++	+-	++
Conc. H ₂ SO ₄	++	++	++	++	++	++	+-	++
Nitrobenzene	-	-	-	-	-	-	-	-
Chloroform	-	-	-	-	-	-	-	-
DCM	-	-	-	-	-	-	-	-
TCE	-	-	-	-	-	-	-	-
THF	-	-	-	-	-	-	-	-
EtOH	-	-	-	-	-	-	-	-

++ Soluble at room temperature.

+- Partly soluble.

- Insoluble.

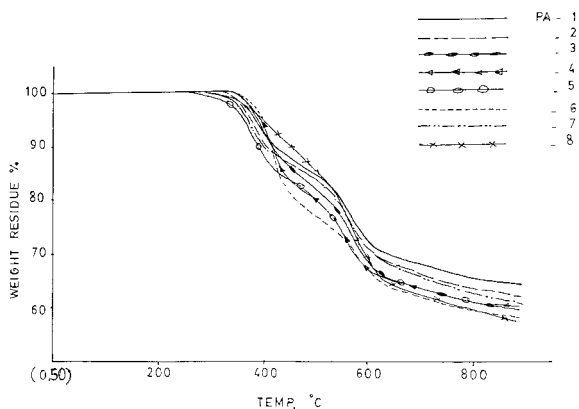


Figure 1 TG curves of PA-1 to PA-8.

tation peaks at m/e 459 and 414 indicate the loss of a carboxylic group.

The proton NMR spectrum of (V) showed the NMR signal at 2.5 δ , corresponding to a methylene (2H) group of the $-\text{CH}_2\text{COOH}$. It appeared as a singlet. The NMR signals in the range of 7.0–7.2 δ (9H) are attributed to the aromatic protons of the tetraphenyl moiety. ^{13}C -NMR showed a total of 12 peaks, corresponding to 12 different carbons of the dicarboxylic acid (V). The aliphatic carbon appearing at 39.99 PPM was due to methylene carbon, while the carbonyl carbon appeared at 185.37 PPM. Aromatic carbons showed NMR peaks in the usual range of 127–140 PPM, of which the tertiary carbons were at 140.05, 138.18, 136.54, 135.11, and 132.33, confirmed further by the absence of corresponding peaks in the relevant DEPT (distortionless enhancement by polarization transfer) NMR spectrum. Aromatic carbons to which a proton had been attached appeared at 130.96, 129.00, 128.79, 128.44, and 127.44 PPM. All these 5 NMR signals are clearly visible in the DEPT NMR spectrum.

By using 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene (V), a series of aromatic polyamides was synthesized by direct polycondensation using Yamazaki's phosphorylation method with triphenyl phosphite as a condensing agent in the mixture of *N*-methyl-pyrrolidone and pyridine (4 : 1 by volume) containing 8 wt % anhydrous lithium chloride. The polymerizations were carried out at 100°C for 3 h under nitrogen (Scheme 2). The yields and viscosities are given in Table I. All the polymers were obtained in almost quantitative yields (92–98%) as pale yellow to white fibrous materials. The reduced viscosities were in the range of 0.28–0.67 dL/g. The polyamides produced transparent and flexible films when cast from solutions in DMAc, implying a

high molecular-weight formation. The polymers were also characterized by IR spectroscopy. The IR spectrum of PA-4 showed characteristic amide absorptions at 3297 (N—H) and 1667 cm^{-1} (C=O). The disappearance of bands at 3440 and 3350 cm^{-1} indicated that all the acid and amine groups had reacted to yield high molecular-weight polyamides. The solubility characteristics were determined in different common organic solvents. A 3% solution of polymer in solvent was taken as a criterion for solubility. The polyamides showed better solubility (Table II) in solvents such as DMAc, DMSO, NMP, DMF, pyridine, *m*-cresol, and conc. H_2SO_4 but were insoluble in chlorinated solvents such as chloroform DCM, TCE, and so forth. Improved solubility character

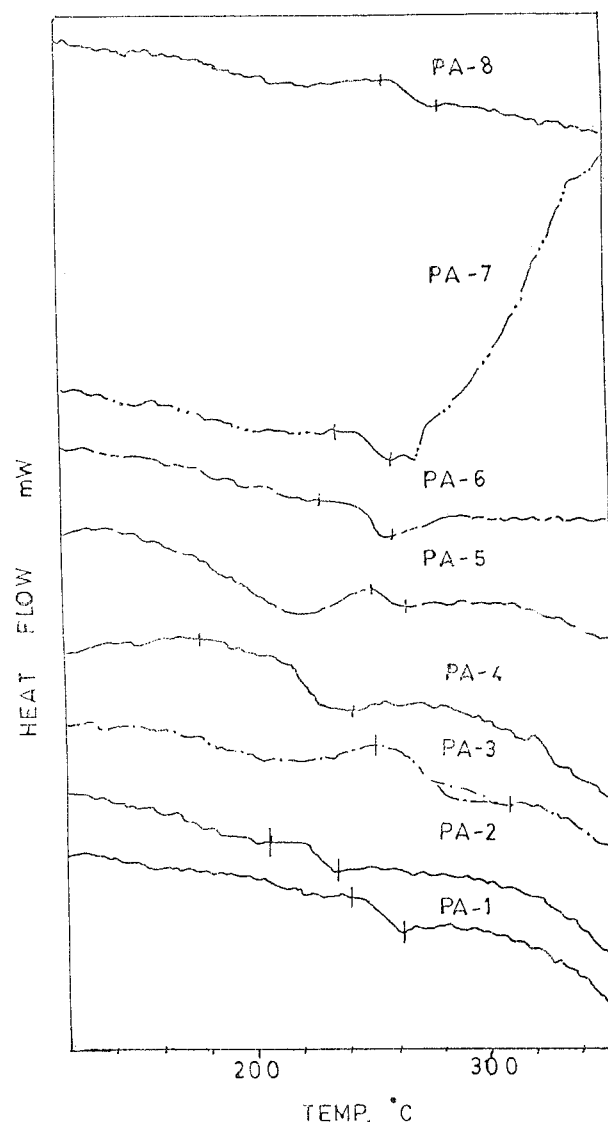


Figure 2 DSC curves of PA-1 to PA-8.

Table III Thermal Analysis^a of Polyamides

Polymer Code	Temperature (°C) for Various (%) Decomposition				Residual % wt at 900°C	T_g (°C) ^e
	T_i ^b	T_{10} ^c	T_{max} 1	T_{max} 2 ^d		
PA-1	336	428	397	567	56	251
PA-2	322	439	386	572	63	228
PA-3	344	416	405	578	56	272
PA-4	334	422	417	528	59	226
PA-5	311	406	388	569	61	227
PA-6	356	417	422	591	55	252
PA-7	317	444	375	572	67	255
PA-8	339	456	400	572	61	273

^a Thermogravimetric analysis at heating rate of 10°C/min under nitrogen.

^b Temperature at which initial loss of mass observed.

^c Temperature at which 10% loss observed.

^d Maximum decomposition temperatures from DTG.

^e Determined by DSC.

can be attributed to the introduction of a highly phenylated thiophene moiety and aliphatic methylene group in the polymer backbone.

The thermal behavior of the polymers was evaluated by means of thermogravimetry and differential scanning calorimetry (DSC). The T_G curves of polyamides are shown in Figure 1, and the DSC curves of the polyamides are shown in Figure 2. Table III incorporates the thermal data such as glass-transition temperature (T_g), initial decomposition temperature (T_i), maximum decomposition temperature (T_{max}), and residual weight at 900°C. The polyamides had glass-transition temperatures in the range of 226–273°C. The glass-transition temperature of PA-1 was 251°C and of PA-2 was 228°C. This shows that *m*-catenation lowers the glass-transition temperature. Similarly PA-3, PA-7, and PA-8 had T_g values of 272, 255, 273°C, respectively, because of their rigid structures. PA-4, PA-5, and PA-6 had T_g values of 226, 227, and 252°C, respectively. As compared to PA-1 and PA-3 they had lower T_g values. This can be attributed to the incorporation of flexible linkages such as —O—, —SO₂—, —CH₂— into the polymer backbone. All these polyamides showed a similar pattern of decomposition, with no weight loss below 311°C in air or nitrogen. The polymers showed a T_{max} between 567 and 591°C. The residual weights of the polymers were in the range of 55–67% at 900°C. This shows that the introduction of highly phenylated linkage into a polymer backbone improves solubility without having much affect on thermal stability.

CONCLUSIONS

A novel dicarboxylic acid, 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl thiophene, was synthesized and characterized by IR, NMR, mass spectroscopy, and elemental analysis. Eight polyamides were synthesized from a novel diacid using the direct polycondensation method by reacting equal moles of diacid and diamine, using triphenyl phosphite as the condensing agent. The polyamides were characterized by IR spectroscopy, viscosity, solubility, and thermal analysis. Because of the presence of a tetraphenyl thiophene moiety and aliphatic methylene linkage, the polyamides exhibited better solubility without having much of an affect on thermal stability.

REFERENCES

- Hargenrother, P. M.; Klyohaven, D. F. *Macromolecules* 1970, 3, 387.
- Dubnora, A. M.; Kotan, M. M.; Nekrasov, F. M. *Vysokomol Soedin Ser* 1977, 19, 39.
- Scariah, K. J.; Krishnamurthy, V. N.; Rao, K. V. C.; Srinivasan, M. *J Macromol, Sci Chem* 1985, 22, 1753.
- Mahajan, S. S.; Sarwade, B. D.; Maldar, N. N. *Polym Bull* 1990, 24, 143.
- Lenk, R. S.; Fellers, J. P.; White, J. L. *Polym J* 1977, 9, 9.
- Kakimoto, M.; Nagi, Y.; Imai, Y. *J Polym Sci Polym Chem* 1985, 23, 1787.
- Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Polym Chem* 1985, 23, 1797.