Partially Aromatic Polyamides Based on Tetraphenylthiophene Diamine: Synthesis and Characterization

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ABSTRACT: Tetraphenylthiophene diamine (TPTDA) was prepared through a modified three-step route to achieve an improved overall yield. TPTDA reacted with succinic, adipic, suberic, sebasic, and fumaric acids via the Yamazaki phosphorylation method to yield novel partially aromatic polyamides (TPT series). A counterpart polyamide series based on *p*-phenylene diamine (Ph series) was also synthesized under the same conditions. All of the polymers were characterized by means of spectrochemical (Fourier transform infrared spectroscopy, ^{1}H-nuclear magnetic resonance (NMR), and ^{13}C-NMR) and thermal (differential scanning calorimetry and thermogravimetric) methods of analysis. Solubility of TPT polyamides was clearly improved due to the presence of the bulky aromatic diamine as well as flexible $CH_2—CH_2$ segments. The highly phenylated thiophene diamine moiety was recognized to improve thermal stability of the TPT polyamides in comparison with Ph polyamides (integral procedural decomposition temperature (IPDT) 480–517°C against 454–485°C). A favorable balance was recognized in regard to solubility, thermostability, and melting temperature in the TPT polyamides, especially TPT4 and TPT6. Therefore, they may be considered good candidates for processable polymers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1144–1153, 2000

Key words: partially aromatic polyamide; tetraphenylthiophene diamine; synthesis; spectroscopy; thermal behavior; Yamazaki reaction

INTRODUCTION

Aromatic polyamides are characterized as high temperature resistant materials with a favorable balance of other physical and chemical properties.[1] They have aroused deep interest over the past decade due to increasing demands for thermostable polymers as substitutes for metal or ceramics in automotive, aerospace, and microelectronic industries. The thermal stability and mechanical performance of these polymers are mainly due to the presence of aromatic rings in the macromolecular backbone.

However, difficulties are encountered in processing these polymers into articles due to their high melting and/or glass transition temperature and/or their limited solubility in common organic solvents. Processable engineering plastics possessing moderately high softening temperatures and/or solubility in some organic solvents are required for practical use. Attempts to increase the solubility and processability of polyamides have been made through the introduction of some structural components such as flexible linkages (i.e., methylene, oxyethylene),[2,3] bulky pendant

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groups (i.e., phenyl, aryl, *t*-butyl), and/or synthesis of cardo polymer.[4]

Aliphatic-aromatic polyamides from aliphatic diamines and aromatic diacids have been studied in great detail, but less is known about aromatic-aliphatic polyamides because of the difficulty of preparing them from aromatic diamines and aliphatic diacids via the conventional solution or interfacial polycondensaton.[5,6] Yamazaki et al.[7,8] and Higashi et al.[9] developed a direct synthesis of aromatic polyamides and their synthetic conditions have been optimized to achieve the highest possible molecular weights.[10] Synthetic conditions developed by Yamazaki have been applied in the preparation of high molecular weight aromatic-aliphatic polyamides.[11]

2,5-Bis(4-aminophenyl)-3,4-diphenylthiophene (TPTDA) is an interesting functional monomer containing both heteroaromatic and bulky pendant components. This highly phenylated thiophene diamine is used in the preparation and development of some novel high-temperature polymers with superior properties.[12–22]

A literature survey showed that no TPTDA-based aromatic-aliphatic polyamides have been reported so far. The present study is concerned with the preparation of a series of polyamides based on TPTDA (TPT series) via the Yamazaki synthetic method and their characterization. To compare the polymer characteristics, *p*-phenylene diamine, as a reference aromatic diamine, was also used in the synthesis of another polyamide series (Ph series) under the same polymerization conditions. In the both polyamide series, succinic, adipic, suberic, sebasic, and fumaric acids were used as the linear aliphatic dicarboxylic acids. In addition to the solubility test, intrinsic viscosity as a measure of molecular weight, was determined. Structural characterization was performed by using Fourier transform infrared (FTIR), ^{1}H-nuclear magnetic resonance (NMR) and ^{13}C-NMR spectroscopies. Thermal properties were studied through the differential scanning calorimetry–thermogravimetic (DSC–TG) thermal technique.

Meanwhile, the preparative method for the synthesis of TPTDA monomer was modified to achieve a cleaner workup and higher yield.

EXPERIMENTAL

Materials

Succinic, adipic, suberic, sebasic, and fumaric acids (all from Riedel, Switzerland) were used after recrystallization. *p*-Phenylene diamine (Riedel) was twice recrystallized from hot ethanol. Triphenyl phosphite (TPP) as the ether solution (Merck, Germany) was purified by washing successively with 5 wt % aqueous NaOH, distilled water, and finally with saturated NaOH solution, followed by drying over anhydrous $MgSO_4$. The solvent was evaporated, and the purified material (mp 19°C) was stored in a container placed in a refrigerator. Pyridine (py) (Riedel) was distilled and stored over KOH pellets before used. *N*-methyl-2-pyrrolidone (NMP) (Riedel) was purified by vacuum distillation and stored over 4 Å molecular sieve. Commercially obtained anhydrous lithium chloride (Riedel) was dried under vacuum at 160°C for 13 h. A reported route for the synthesis of TPTDA monomer[12] was used after some modifications.

Measurements

The polymer solution viscosity values were measured at 30 ± 0.1°C in concentrated H_2SO_4, NMP, or HMPA (hexamethylphospharanide) using a Connon-Fenske viscometer (Technico NOMINAL CONSTANT 0.05 CS/S). FTIR spectra of the samples (as KBr disks) were obtained on a Shimadzu FT-IR-8100 spectrophotometer. An AC 80 Bruker system was used for ^{1}H-NMR and ^{13}C-NMR measurements. Tetramethylsilane was used as an internal standard in NMR analysis (solvent $CDCl_3$ or DMSO-d_6).

Thermal measurements (DSC–TG) were performed on an STA-625 PL Laboratories System at a heating rate of 20°C/min under argon atmosphere at a flow rate of 10 mL/min.

Monomer Synthesis

A three-step reported strategy for the TPTDA preparation[12] was followed with some modifications.

Step 1: Synthesis of Tetraphenylthiophene (TPT)

Into a 250-mL three-necked kettle equipped with a mechanical stirrer, an efficient reflux condenser, and a thermometer, a mixture of 63.3 g (0.5 mol) of benzyl chloride and 0.9 g (0.3 mol) of powdered sulfur was added. The content was heated at 180–200°C for 48 h with stirring. The reaction temperature was then raised to approximately 230°C, and was maintained at that temperature for 3 h. The mixture was allowed to cool to 60°C, and 50 mL of ethanol was added. The solidified bitumen-like material was filtered, washed with methanol, and then thoroughly washed with acetone. The obtained crude product was a pink-color solid, which was recrystallized from dichloromethane–methanol mixture (1 : 1 v/v) to give pure TPT as white needles; mp 183–185°C (lit.[12] 185–186°C). The yield was 37 g (76%). IR (KBr) 3054, 1600, 1492, 1437, 1077, 1030, 764, 700 cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ 6.8–7.2 (m, 20H), ^{13}C-NMR ($CDCl_3$) δ 126.0, 127.5, 128.0, 128.3, 129.0, 131.0, 134.5, 137.0, 139.0 ppm.

Step 2: Synthesis of 2,5-Bis(4-Nitrophenyl)-3,4-Diphenylthiophene (TPTDN)

Ten grams (25.8 mmol) of TPT and 200 mL of glacial acetic acid were placed in a 500-mL two-necked flask equipped with a magnetic stirrer and a condenser. The mixture was vigorously stirred at 100°C to obtain a suspension. A mixture of glacial acetic acid (20 mL) and concentrated nitric acid (14.5 mL) was added dropwise over a period of 1 h. After stirring at 100°C for an additional 0.5 h, a clear yellow solution was obtained. The solution was allowed to cool to yield a yellow crystalline product having acceptable purity to be used in the next preparative step. However, it may be recrystallized from glacial acetic acid to afford bright yellow needles; mp 213–215°C (lit.[12] 216–217°C). The yield was 7.8 g (63%). IR (KBr) 3061, 1591, 1515, 1346, 1115, 853, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.7–7.1 (m, 10H), 7.2 (d, 4H, J = 8.7 Hz), 7.9 (d, 4H, J = 8.7 Hz); ^{13}C-NMR ($CDCl_3$) δ 124.0, 127.5, 128.3, 129.5, 130.2, 135.0, 137.2, 139.8, 142.2, 146.3 ppm.

Step 3: Synthesis of TPTDA

TPTDN, 2.51 g (5.25 mmol), and 25 mL of glacial acetic acid were charged in a 250-mL round-bottom flask equipped with a reflux condenser. A solution of 12.5 g (55.4 mmol) of stannous chloride dihydrate in 4 mL of concentrated hydrochloric acid was added all at once. The mixture was magnetically stirred and refluxed at 100°C for 5 h. The mixture was cooled to −10°C in an ice-water-salt bath to give a solid. The dihydrochloride salt was collected by filtration and dissolved in 15–20 mL of hot water. Three milliliters of concentrated hydrochloric acid was added to the solution. After cooling, the produced dihydrochloride salt was collected on a vacuum filter and pressed to dry. The salt was then dissolved in water and the solution was added dropwise to an appropriate volume of stirred 40% aqueous sodium hydroxide solution, so that the pH of the solution was checked to be approximately 12. The mixture was cooled in an ice bath during the neutralization period. The resulted solid was separated by filtration and washed several times with cold water, and dried in a vacuum oven at 40°C. The solid product was recrystallized twice from hot toluene to yield 1.75 g (80%) of small, white needles; mp 270–273°C (lit.[12] 276–277°C). IR (KBr) 3423, 3338, 1631, 1508, 1292, 1185, 831, 708, 531 cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ 6.2 (d, 4H, J = 8.4Hz), 6.65 (d, 4H, J = 8.4 Hz), 6.2–7.0 (m, 10H); ^{13}C-NMR (DMSO-d_6) δ 113.7, 121.8, 126.5, 127.5, 129.8, 130.5, 131.0, 137.3, 137.6, 147.5 ppm.

Polyamide Synthesis

The following procedure was followed for the preparation of all of the polyamides. A 50-mL two-necked flask, equipped with magnetic stirrer, nitrogen inlet, and reflux condenser, was charged with 2.5 mmol of an aliphatic diacid, 2.5 mmol of an aromatic diamine, 6.25 mmol (1.65 mL, 1.94 g) of triphenyl phosphite, 3.15 mmol (0.1335 g) of lithium chloride, 1.5 mL of pyridine, and 6 mL of *N*-methyl-2-pyrrolidone. The mixture was heated for 6 h in a thermostatically controlled oil bath at 100°C under stirring and mild nitrogen purging. The reaction mixture was poured into a large amount of methanol to precipitate the polymer, which was collected by filtration. The polymer was agitated in 12.5 mL of hot ethanol for 10 min, and filtered. The washing treatment was repeated three times, and the product was finally dried under vacuum (900 mbar, 70°C, 30 h). The appearance of the reaction mixtures and final polymers, yield, and some other product specifications are tabulated in Table I.

RESULTS AND DISCUSSION

Improved Synthesis of Diamine TPTDA

A reported three-step procedure[12] was modified, especially in the first and last steps, to prepare the TPTDA, shown in Scheme 1.

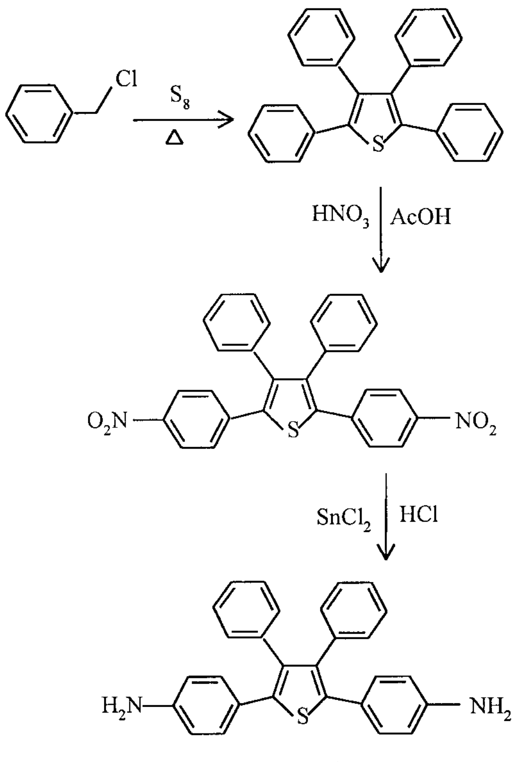
The main structural components of the monomer are constructed in the first step, in which the reaction of benzyl chloride with powdered sulfur at an elevated temperature produces TPT. Washing the crude product (a bitumen-like solid) with acetone is the key modification of the reaction workup to enhance the yield from 51%[12] to 76%.

Table I Polymerization Yield and Some Specifications of the Polyamides[a]

Polymer	Reaction Mixture Appearance	Polymer Appearance	Yield (%)	Capillary Melting Range (°C)	$[\eta]$[b] (dL/g)
TPT2	Clear, colorless	Cream-colored	69	247–253, dec.[c]	0.25
TPT4	Clear, colorless	Dark cream-colored	98	NO300,[d] dec.	0.57
TPT6	Clear, colorless	Light yellow	96	248–252	0.72
TPT8	Clear, colorless	Light yellow	94	240–243	0.62
TPTF	Yellow, emulsion-like	Yellow	100	NO300, dec.	2.30[e]
Ph2	Milky	Cream-colored	53	NO300, dec.	0.06
Ph4	Milky	Cream-colored	94	NO300	0.24
Ph6	Milky	Cream-colored	90	NO300	0.30
Ph8	Milky	Cream-colored	88	NO300, dec.	0.27
PhF	Opaque yellow, suspension-like	Dark yellow	90	NO300	0.09

[a] Reaction temperature = 100°C; reaction time = 6 h.
[b] TPT and Ph series of polyamides were measured in NMP and con. H_2SO_4, respectively; 30 ± 0.1°C.
[c] Melting followed by decomposition.
[d] Not observed up to 300°C.
[e] In hexamethylphosphoramide; 30 ± 0.1°C.

Nitration of TPT produces the possible isomers of nitro and dinitro compounds, and the desired one (TPTDN) is separated through recrystallization in acetic acid. We achieved a higher yield in this step as well.



(TPTDA)

Scheme 1

Reduction of TPTDN was accomplished with $SnCl_2$/HCl to give TPTDA. Again, a totally modified workup was designed to increase the yield to as high as 80%, much more than the reported yield, 53%.[12] Consequently, the overall yield was increased from 14%[12] to 36%. The products were characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR. Figure 1 shows the FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra of the diamine (TPTDA).

Synthesis of Polyamides

Metal salts, especially LiCl, have been found to facilitate significantly the reaction of carboxylic

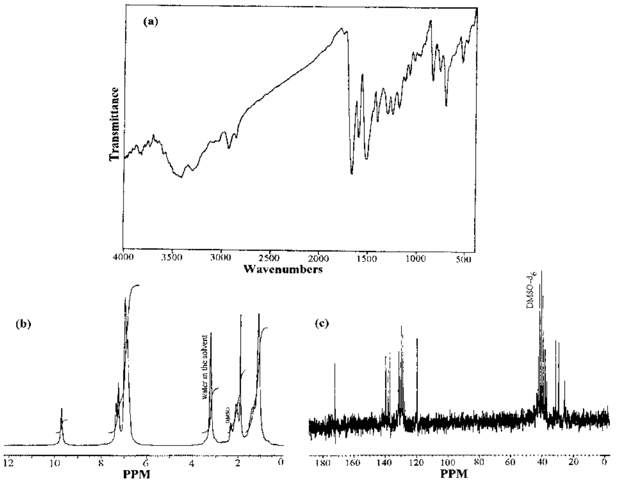
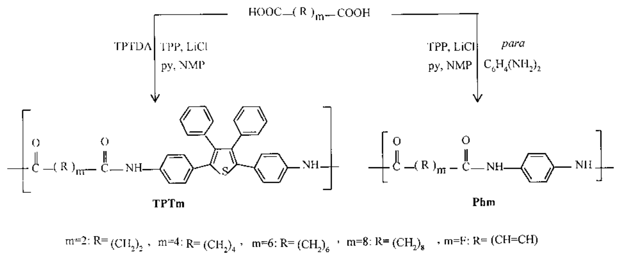


Figure 1 FTIR (a), ^{1}H-NMR (b), and ^{13}C-NMR (c) spectra of the polyamide TPT6.



Scheme 2

acids and amines promoted by $P(OPh)_3$, and the reaction has been applied successfully to direct polycondensation reaction of dicarboxylic acids and diamines.[9] The best solvent for the phosphorylation polyamidation has been found to be NMP and a small amount of pyridine as a proton scavenger. These conditions (TPP/LiCl/py/NMP), which have been usually referred to as Yamazaki conditions, were applied for the preparation of polyamides of TPTm and Phm (Scheme 2).

1,4-Phenylene diamine was chosen to prepare the similar polyamides (Phm's), to make possible the comparison between the two polyamide series properties. The results of the preparation of the polyamides are summarized in Table I. The intrinsic viscosities are 0.2–0.7 dL/g, which imply the formation of medium molecular weight polymers. The viscosity of both polysuccinamides (TPT2 and Ph2) is the lowest in the corresponding series. It may be attributed to the tendency of succinic acid to form cyclic amides with diamines; this side reaction probably interfered with higher polymer formation. This is the main fact that the two lowest yields in both series are concerned with these two polymers (69% and 53%). The viscosity values of TPTm's were measured in NMP, except TPTF, which was NMP-insoluble and measured in HMPA. Phm's viscosities were measured in con H_2SO_4, due to their limited solubility in organic solvents.

Polymer Characterization

Polymer Solubility

Solubility behavior of the polyamides is given in Table II. Clearly, the presence of the highly phenylated component in TPTm's has improved their solubility in a variety of organic solvents including amide-type solvents (DMF, DMAC), DMSO, and pyridine. All of the polymers are soluble in sulfuric acid, but insoluble in tetrahydrofuran, chloroform, formic acid, acetone, methyl ethyl ketone, chlorobenzene, toluene, aliphatic alcohols, and hydrocarbon solvents. Generally, the introduction of *p*-phenylene structure into the polymer backbone decreases solubility. However, HMPA is the only organic solvent, which can dissolve all of the polyamides (except PhF).

Spectrochemical Characterization

The synthesized polymers were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopies (Fig. 1).

Table II Solubility of Polyamides[a]

	Solvent[b]								
Polymer	con. H_2SO_4	Ch	Py	NMP	DMF	DMAC	DMSO	*m*-Cresol	HMPA
TPT2	++[c]	++	++	++	++	++	++	++	++
TPT4	++[c]	−−	++	++	++	++	++	++	++
TPT6	++[c]	+	++	++	++	++	++	++	++
TPT8	++[c]	+	++	++	++	++	++	++	++
TPTF	++	−−	+−	+−	+	+−	+−	±	++
Ph2	++	−−	+−	+−	+−	−−	+−	±	++
Ph4	++	−−	−−	−−	−−	−−	−−	±	++
Ph6	++	−−	−−	−−	−−	−−	−−	±	++
Ph8	++	−−	−−	−−	−−	−−	±	−−	++
PhF	++	−−	−−	−−	−−	±	−−	−−	±

[a] Solubility was determined at 3% (w/v) concentration. ++, soluble at room temperature; +−, partially soluble at room temperature; +, soluble on heating; ±, partially soluble on heating; −−, insoluble.

[b] Ch, cyclohexanone; Py, pyridine; NMP, *N*-methyl-2-pyrrolidone; DMF, dimethylformamide; DMAC, dimethylacetamide; DMSO, dimethylsulfoxide; HMPA, hexamethylphosphoramide.

[c] Soluble with decomposition.

The strongest absorption bands in the polyamides FTIR spectra are associated with the vibrations of the secondary amide structure (Table III). Because of the mesomerism in amide group, the required energy for stretching vibration of the corresponding carbonyl group is much lower than that for an isolated carbonyl ($\approx$1640 cm^{-1} against $\approx$1725 cm^{-1}). The υ(NH), υ(C=O) (amide band I), and a coupled vibration (υ(CN) + δ(NH): amide band II) can be regarded as reasonably positional constant group wavenumbers. Amide band III, which appears between 1263 cm^{-1} and 1238 cm^{-1}, is mainly contributed to υ(C—CO) + δ(NH). This band is less intense than I and II, but can readily be observed [Fig. 1(a)]. Amide bands γ(NH) and γ(CO) lie in the long-wavelength region at ca. 700 and 600 cm^{-1}. They are associated with vibrations out-of-plane of the amide group [δ(CONH), 1002–938 cm^{-1}; not included in Table III] and they are much more sensitive to the chemical structure of the aliphatic chain and to the arrangement of the macro-molecules within the crystal.[23] Some other important vibrational modes are also listed in Table III.

^{1}H-NMR and ^{13}C-NMR were performed to confirm the expected structure of the organic-soluble polyamides (TPTm's, m = 2, 4, 6, 8). Figure 1(b,c) show the representative NMR spectra of TPT6. The spectral data are summarized in Table IV. In the ^{1}H-NMR spectra, a deshielded singlet broad peak, attributed to the amide proton, appears in down field $\approx$ 8.9–10.0 ppm. Hydrogens of the phenylene rings at ortho position related to the amide groups (4H, 7.0–7.5 ppm; an AA′XX″ spin system, spin coupled with the meta protons; J = 8.4 Hz) are more deshielded than other protons which appeared in company with phenyl protons (14H, 6.9–7.2 ppm). The peak assignments for the ^{13}C-NMR spectra are given in Table IV. TPTF and the Ph series of polyamides cannot be characterized by solution NMR due to their limited or lack of solubility.

Thermal Characterization

Thermal properties of both polyamide series were studied by DSC and TGA analyses (Figs. 2, 3, and Table V). Polysuccinamide TPT2, polysuberamides (TPT6 and Ph6), and polysebacamides (TPT8 and Ph8) were those polymers that showed melting transitions. Meanwhile, Ph6 was the only polymer that showed second-order transition (T_g = 200.2°C). Varma et al.[5] did not observe T_m and T_g for poly(*p*-phenylene sebacamide)s obtained through interfacial polycondensation; However, Morgan and Kowlek[6] have reported T_m and T_g values for most of the polyamides obtained from phenylendiamines and aliphatic diacid chlorides through interfacial and solution methods. Therefore, the presence or absence of the melting and/or T_gs in these partially aromatic polyamides may depend on the preparation method.

An exothermal first-order transition was observed in the polysebacamide Ph8. This small peak is attributable to crystallization, which may be induced in the sample on heating during drying period. The polymer contains symmetrical *p*-phenylene units and the longest consecutive methylene spacers [$(CH_2)_8$]. So, Wander vals forces between these linear aliphatic segments, which are associated by interchain hydrogen bonding, can cause suitable orientation leads to crystalline regions. In fact, we clearly observed the regions under a cross-polarized microscope (×200) at room temperature. The polymer had already been reported as a medium crystalline polyamide.[6] The Ph8 counterpart, i.e., TPT8, did not show such an exothermic peak due to the steric hindrance of the bulky phenyl-substituted thiophene segments, which prevents proximity of the linear aliphatic segments.

In each polymer series, the corresponding polysebacamide has lower T_m than the polysuberamide due to its more CH_2—CH_2 flexible bonds. On the other hand, T_ms of TPTm's, despite the presence of five rigid aromatic nuclei in their repeating units, are much lower ($\approx$115°C) than that of Phm's. Again, the bulky phenyl groups are responsible for this differentiation. At the same time, TPT6 and TPT8 are thermally more stable than Ph6 and Ph8 (see their T_d values in Table V).

Generally, hydrogen bonds, which are formed between the carbonyl and NH groups of neighboring chains, are merely loosened, as the polyamide melts, but not ruptured; therefore, the enthalpy of fusion (ΔH_f) of the polyamides are usually low.

The presence of longer aliphatic moieties leads to smaller weight residues at high temperatures. Thus, TPT2 shows a 61.70% residue at 600°C; whereas TPT4 has a 31.66% weight residue at that temperature, and TPT6 and TPT8 show still fewer char yield than TPT2. The length of the flexible spacer played the expected role: the longer the aliphatic moiety, the lower the weight residue at high temperature.

IPDT,[24] as a means of summing up the whole shape of the normalized data curve, was calcu-

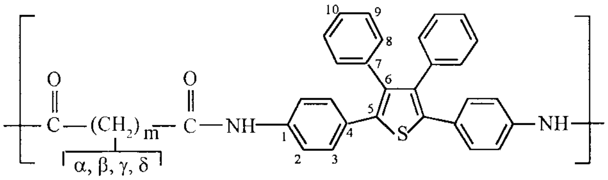
Table III FTIR Spectral Data of the Polyamides

	Wavenumber (cm^{-1}) of the Main Characteristic Bands[a]									
	Secondary-Amide Bond						Main Backbone			
Polyamide	υ (NH)[b]	υ (CO)	υ (CN) + δ (NH)	υ (C—CO) + δ (NH)	γ (NH)	γ (CO)	υ (CH_{arom})	υ (CH_{aliph})	υ (CC_{arom})	δ (CH_2)
TPT2	3405, 3316	1669 (S)	1515 (VS)	1250 (M)	707 (M)	50 (W)	3054 (M)	2860 (M)	1600 (S)	1408 (M)
TPT4	3432, 3292	1662 (VS)	1515 (VS)	1247 (M)	708 (M)	542 (W)	3031 (M)	2930 (M)	1600 (S)	1408 (M)
TPT6	3431, 3293	1662 (VS)	1515 (VS)	1246 (M)	700 (M)	540 (W)	3031 (Sh)	2931 (M)	1600 (M)	1408 (M)
TPT8	3415, 3277	1662 (VS)	1515 (VS)	1246 (M)	700 (S)	531 (M)	3031 (M)	2923 (M)	1592 (S)	1408 (M)
TPTF	3261	1669 (VS)	1531 (S)	1263 (M)	700 (S)	540 (M)	3031 (M)	2930 (M)	1600 (S)	1408 (M)
Ph2	~3500, 3292	1662 (VS)	1554 (S)	1238 (M)	700 (M)	537 (M)	3054 (M)	2937 (W)	1605 (Sh)	1408 (S)
Ph4	~3500, 3300	1662 (VS)	1554 (S), 1515 (S)	1258 (M)	700 (M)	539 (M)	3046 (M)	2938 (M)	1605 (Sh)	1408 (S)
Ph6	~3500, 3300	1662 (VS)	1554 (S), 1515 (VS)	1246 (M)	723 (M)	528 (M)	3054 (M)	2931 (M)	1605 (Sh)	1408 (S)
Ph8	~3500, 3292	1662 (VS)	1554 (S), 1515 (S)	1238 (M)	723 (M)	528 (M)	3046 (W)	2923 (S)	1605 (Sh)	1408 (S)
PhF	~3500, 3285	1654 (VS)	1554 (S), 1515 (VS)	1248 (M)	692 (M)	541 (M)	3062 (M)	2931 (M)	1598 (Sh)	1408 (S)

[a] Vibration modes: υ, stretching; δ, bending; γ, out-of-plane bending (twisting); relative intensity; W, weak; M, medium; S, strong; VS, very strong; Sh, shoulder.

[b] The peaks are broad and medium, in the TPT series. In the Ph series, the medium bands at ~ 3500 cm^{-1} are as shoulder and the strong bands at 3285–3300 cm^{-1} are broad peaks.

Table IV ^{1}H-NMR and ^{13}C-NMR Spectral Data for TPTms (m = 2, 4, 6, 8)[a]



Polyamide	Mode	Chemical Shift (ppm) from TMS, Solvent: DMSO-d$_6$
TPT2	^{1}H-NMR	8.90(2H), 7.33(4H), 7.05(14H), 2.59(4H)
	^{13}C-NMR	177.4^{CO}, 139.0^1, 138.8^5, 137.5^2, 136.0^4, 130.0^3, 128.7^6, 127.5^7, 127.4^8, 126.3^9, 119.6^{10}, $32.6^{\alpha C}$
TPT4	^{1}H-NMR	10.02(2H), 7.54(4H), 7.25(14H), 2.40(4H), 1.71(4H)
	^{13}C-NMR	171.3^{CO}, 138.8^1, 138.7^5, 137.4^2, 136.2^4, 130.0^3, 128.7^6, 127.5^7, 127.4^8, 127.0^9, 118.7^{10}, $32.5^{\alpha C}$, $25.0^{\beta C}$
TPT6	^{1}H-NMR	9.73(2H), 7.28(4H), 6.99(14H), 2.12(4H), 1.12(8H)
	^{13}C-NMR	172.0^{CO}, 140.0^1, 139.5^5, 137.5^2, 137.0^4, 131.2^3, 130.0^6, 128.7^7, 127.7^8, 127.3^9, 119.8^{10}, $31.2^{\alpha C}$, $28.8^{\beta C}$, $26.0^{\gamma C}$
TPT8	^{1}H-NMR	9.71(2H), 7.01(4H), 6.97(14H), 2.00(4H), 1.09(12H)
	^{13}C-NMR	172.2^{CO}, 138.8^1, 138.7^5, 137.5^2, 136.2^4, 130.0^3, 128.7^6, 127.5^7, 127.4^8, 126.5^9, 118.7^{10}, $28.8^{\alpha C}$, $28.7^{\beta C}$, $25.0^{\gamma C}$, $24.1^{\delta C}$

[a] Superscripts indicate the corresponding carbon atoms, according to the repeating unit chemical formula.

lated to get a more semiquantitative data regarding the relative thermal stabilities. TPT2 and TPT4 are the most stable polymers thermally. In TPT series; thermal stability decreases with increases of the CH$_2$—CH$_2$ bonds, which are susceptible to thermal scission. On the contrary, in Ph series, there is a progressive increase in IPDT values from Ph2 to Ph8, as the aliphatic spacer length is increased. Meanwhile, both polyfumaramides (TPTF and PhF) show enhanced thermal stabilities due to possible thermal crosslinking which can occur through their reactive C═C.

To achieve a better comparison between these materials in the thermal stability point of view, a useful comprehensive index of intrinsic thermal stability[24] (ITS) was also calculated (Table V). In both series, ITS values increase from polysuccinamide to polysebacamide, and the average of ITS values of the two series are approximately equal (≈0.63). But, an obvious decrease is observed in the ITS of both polyfumaramides (TPTF and PhF). It means that the fumaramides which have the highest refractoriness (high char yield), but which begin to decompose at relatively low temperatures, show higher ITS values which are a measure of their potential stabilities. Conversely, higher ITS values for other polyamides mean that they are more volatile materials (due

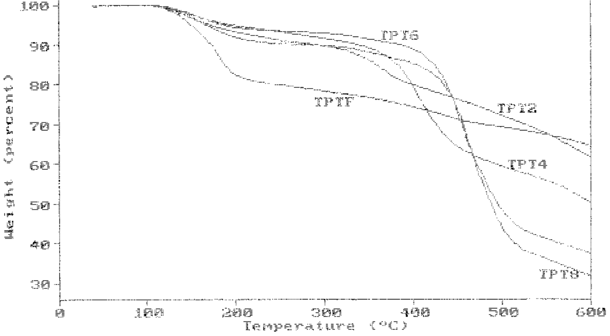


Figure 2 TGA thermograms of the TPTm polyamides.

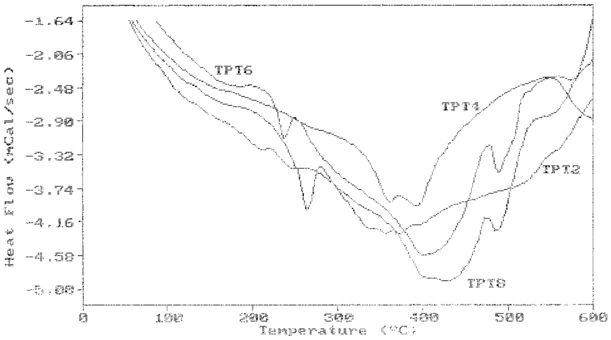


Figure 3 DSC thermograms of TPTm polyamides, m = 2, 4, 6, 8.

Table V Thermal Behavior Data of the Partially Aromatic Polyamides[a]

			TGA								
	DSC		First Wt Loss			Temperature (°C) at Various Wt % Losses					
Polymer	T_m (°C)	ΔH_f[b] (cal/g)	Wt %	T (°C)	$T_d{}^2$	5	10	30	Y[d], (Wt %)	IPDT[e] (°C)	ITS[f]
TPT2	264.90	36.80	6.0	114	320.2	170	286	524	61.70	517	0.59
TPT4	—	—	5.0	115	354.2	190	335	425	50.48	516	0.62
TPT6	238.20	8.06	5.0	121	412.4	183	382	454	33.48	495	0.67
TPT8	213.40	—[g]	8.0	113	422.6	166	264	456	31.66	480	0.68
TPTF	—	—	20.0	112	410[h]	149	172	471	64.50	487	0.42
Ph2	—	—	4.0	120	340.0	220	310	367	35.40	454	0.58
Ph4	—	—	4.5	101	390.0	169	342	406	35.30	469	0.62
Ph6[i]	354.00	28.8	4.4	116	366.3	239	365	417	31.07	471	0.66
Ph8	327.6	30.5	4.0	106	377.7	260	383	430	29.03	475	0.67
PhF	—	—	8.0	104	380[h]	167	211	411	58.50	485	0.49

[a] Thermal measurements were conducted using a DSC–TG system at a heating rate of 20°C/min under argon at a flow rate of 10 mL/min.

[b] ΔH_f values were computed by means of a nonlinear method of calculation.

[c] Onset temperature of initial decomposition.

[d] Char yield (residual weight) at 600°C in argon.

[e] Integral procedural decomposition temperature.

[f] Comprehensive index of intrinsic thermal stability.

[g] The peak was too weak to be able to take into account for calculation of ΔH_f by the instrument.

[h] There is no certainty about which weight loss is concerned with the real initial decomposition.

[i] This polyamide was shown T_g at 200.2°C.

to the scissorable CH_2—CH_2 bonds) which remain stable up to relatively high temperatures, but, finally decompose extensively and yield less residue.

It is interesting to note that char yield of TPT2 is abnormally high (61.7%), somewhat near that of TPTF (64.5%). We found that mild heating of TPT2 under an inert atmosphere leads to a very limited soluble polymer. It is probably due to the tendency of homolytic thermal cleavage of alpha protons of CO—CH_2—CH_2—CO to give free radicals, which end in crosslinking. This may happen also in the heating of TPTF (or PhF).

All of the polyamides show a small weight loss (4–8 wt %) at a temperature range of 100–120°C (TPTF, wt loss 20% at 112°C, is an exception) (see Fig. 2, Table V). These weight losses can be attributed to the loss of absorbed water (moisture) which is hydrogen-bounded with amide linkages and has not been removed in the precedent drying operation (see Experimental).

Finally, it should be pointed out that the way of synthetic method might affect the thermal stability of the product. In this respect, the poly(*p*-phenylene sebacamide), Ph8, is thermally more stable than all of those prepared by Varma et al.[5] via interfacial method (IPDT 475°C against 403–470°C).

CONCLUSION

A highly phenylated thiophene diamine (TPTDA) was prepared and its known three-step synthetic strategy was modified, so that the overall yield was improved from 14 to 36%.

Partially aromatic polyamides from linear aliphatic dicarboxylic acids and TPTDA (TPT series) or *p*-phenylenediamine (Ph series) were synthesized under Yamazaki conditions [$P(OPh)_3$/LiCl/py/NMP] at 100°C for 6 h.

TPTDA-based polyamides (TPT series) showed excellent solubility behavior, which may be attributed to the incorporation of the bulky pendant groups of tetraphenylthiophene unit into the polymer backbones. However, the introduction of *p*-phenylene structure into the polymer backbone decreases solubility.

Both polyfumaramides (TPTF and PhF) showed the highest refractoriness (ITS = 0.42 and

0.49, respectively). However, TPTDA-based polysuccinamide (TPT2) and polyadipamide (TPT4) were shown to be the most thermally stable polyamides (IPDT = 517 and 516°C, respectively).

There is a good balance of solubility, thermal stability, and melting temperature in the TPTDA-based partially aromatic polyamides (especially TPT4 and TPT6). Therefore, they may be considered as processable plastics.

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