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Synthesis and Characterization of Thianthrene-Based Polyamides

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ABSTRACT: Thianthrene-2,7- and -2,8-dicarboxylic acids plus a synthetic intermediate, 4,4′-thiobis[3-chlorobenzoic acid], have been synthesized in good yields via nucleophilic aromatic substitution of Na_2S on *N,N*-dimethyl-3,4-dichlorobenzamide. New aromatic polyamides having inherent viscosities of 1.29–2.39 dL/g were prepared by the direct polycondensation reaction of the dicarboxylic acids with 4,4′-oxydianiline and 1,4-phenylenediamine in *N*-methyl-2-pyrrolidinone (NMP) using triphenyl phosphite (TPP) and pyridine. The fused-ring thianthrene-based polyamides were more soluble than analogous poly(thioether amide)s. Polymer films were cast from either *N,N*-dimethylformamide (DMF) or *N,N*-dimethylacetamide (DMAc)/LiCl solutions and analyzed by FTIR and NMR. All prepared aramids displayed good thermal stability by DSC and TGA.

Introduction

Aromatic polyamides exhibit high thermal stability because of polymer chain stiffness and intermolecular hydrogen bonding of amide groups, although limited solubility in organic solvents also results. Introducing flexible groups and N-substituents improves aramid solubility, but usually at the expense of thermal stability and physical properties.

Incorporation of aromatic and heterocyclic rings into the polymer backbone is known to enhance thermal stability. It is also thought that thermal stability may be improved by increasing the number of double-strand heterocycles in place of single-strand connecting groups in the polymer backbone.[1] Other factors such as crystallinity, intermolecular interaction, and polymer chain packing also influence thermal behavior. Thus, polymers containing nonplanar, double-strand heterocycles should be excellent candidates for improving aramid solubility while retaining good thermal stability.

We have been investigating nucleophilic aromatic substitution as a synthetic route to thianthrene-based monomers for high-performance polymers.[2] Derivatized thianthrene molecules have been prepared by many techniques involving reactions on thianthrene[3–5] or on precursor aromatic rings used to generate thianthrenes.[6–8] The techniques cited are not practical on a large scale due to limited availability of starting materials, low reaction yields, or high material costs.

Thianthrene-based polyimides and polyamides have been reported by others using thianthrene diamines with aryl dianhydrides and aryl or aliphatic diacid chlorides, respectively.[4,8–10] Decreased thermal stability compared to similar polymers containing phenyl thioether units was attributed to reduction in crystallinity caused by the nonplanar shape of the thianthrene units disrupting packing of the polymers. However, we and others have observed good thermal stabilities for polyimides formed from thianthrene-2,3,7,8-tetracarboxylic dianhydride and aryl diamines.[2,11] Increased solubility of all thianthrene-based polymers might be expected based on the nonplanar shape of the thianthrene nucleus. For example, the single-crystal X-ray structure of the parent thianthrene shows a benzene ring–S–benzene ring dihedral angle of 128° (Figure 1).[12,13] The folding of the molecule is due to the C–S bond length and the "natural" valency angle of sulfur being 100°; this forces a bend in the central 6-membered ring to accommodate the longer bonds and bond angle change from 120°.

Thianthrene-2,7-dicarboxylic acid has previously been prepared via direct functionalization of thianthrene and investigated as a precursor to dyes and aramids.[14,15] The latter were prepared from the diacid chloride derivative and were obtained with relatively poor yields and viscosities. We report here the efficient synthesis of thianthrene-2,7- and -2,8-dicarboxylic acids via nucleophilic aromatic substitution and their polymerization with aryl diamines to high molecular weight aramids using a modification of the Yamazaki phosphorylation reaction.[16,17]

Experimental Section

All chemicals were purchased from Aldrich Chemical Co. Anhydrous sodium sulfide was prepared from the nonahydrate form by storing under vacuum in the presence of P_2O_5 and gradually increasing the temperature to 105 °C. *N*-Methyl-2-pyrrolidinone (NMP) was vacuum distilled from calcium hydride, pyridine was distilled from sodium hydroxide, and triphenyl phosphite (TPP) was vacuum distilled. LiCl and $CaCl_2$ were dried at 180 °C for 48 h under vacuum. 4,4′-Oxydianiline (ODA) and 1,4-phenylenediamine (PDA) were recrystallized from ethanol and sublimed twice.

***N,N*-Dimethyl-3,4-dichlorobenzamide (1).**[18] 3,4-Dichlorobenzoyl chloride (26.5 g, 127 mmol) was combined with 200 mL of CH_2Cl_2, 40 wt % dimethylamine in water (17.5 mL, 139 mmol), KOH (7.8 g, 139 mmol), and 50 mL of H_2O at 5 °C. After the mixture was vigorously stirred for 30 min, the organic phase was separated, washed with dilute HCl and water, dried with $MgSO_4$, and filtered, and the CH_2Cl_2 was evaporated. Recrystallization from ethanol/water (1:3) afforded white crystals in 95% yield; mp 71–72 °C; IR (KBr) 1620 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.99 (s, 3 H), 3.09 (s, 3 H), 7.26 (dd, 1 H, J = 8 and 2 Hz), 7.49 (d, 1 H, J = 8 Hz), 7.53 (d, 1 H, J = 2 Hz).

***N,N,N′,N′*-Tetramethylthianthrene-2,7- and -2,8-dicarboxamides (2 and 3).** *N,N*-Dimethyl-3,4-dichlorobenzamide (15.00 g, 68.78 mmol) and anhydrous sodium sulfide (5.64 g, 72.2 mmol, 5% excess) were refluxed in 225 mL of DMAc for 8 h. After removal of the salt and DMAc by filtration and vacuum distillation, respectively, the products were extracted with CH_2Cl_2 from a brine suspension. CH_2Cl_2 was evaporated and thin-layer chromatography showed an intensely fluores-

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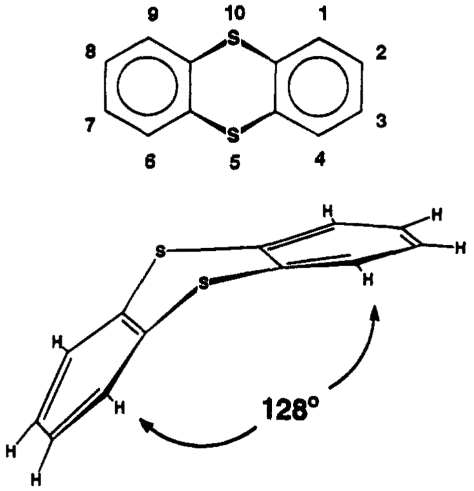


Figure 1. Thianthrene numbering system (top) and depiction of dihedral angle (bottom).

cent spot (R_f = 0.28 in ethyl acetate) corresponding to the isomeric products along with two faint impurity spots. The isomers formed an inseparable mixture which was characterized by ^{13}C NMR and FTIR for structure confirmation; IR (KBr) 1640 cm^{-1} (C=O).

Thianthrene-2,7- and -2,8-dicarboxylic Acids (4 and 5). The crude thianthrene bisamide mixture was added to 50 mL of methanol and 30 mL of a 50 wt % aqueous potassium hydroxide solution. As the solution was heated to distill off methanol, 250 mL of water was added over the first hour. When the vapor temperature reached 100 °C, the solution was cooled to ambient temperature and acidified with dilute HCl to precipitate the diacids. The products were filtered, washed with water, and dried. Thianthrene-2,7-dicarboxylic acid (**4**) was isolated by recrystallizing the isomer mixture from acetic acid and DMAc (1:2). After **4** was removed, thianthrene-2,8-dicarboxylic acid (**5**) was recrystallized from the same solvents by increasing the amount of acetic acid to DMAc (1:1). Monomer **5** required additional fractional recrystallization to remove residual monomer **4**. Yields from the thianthrene bisamide and diacid reactions are difficult to determine due to the nature of the bisamides and the side products generated. The overall yield of the thianthrenedicarboxylic acids starting from 3,4-dichlorobenzoyl chloride was 48%. Both isomers had a melting point greater than 350 °C; IR (KBr) 3300−2500 (O−H), 1690 cm^{-1} (C=O); ^{1}H NMR of **4** (DMSO-d_6) δ 7.71 (d, 2 H, J = 8 Hz), 7.89 (dd, 2 H, J = 8 and 1 Hz), 8.03 (d, 2 H, J = 1 Hz); ^{1}H NMR of **5** (DMSO-d_6) δ 7.70 (d, 2 H, J = 8 Hz), 7.89 (dd, 2 H, J = 8 and 1 Hz), 8.00 (d, 2 H, J = 1 Hz).

Anal. Calcd for $C_{14}H_8O_4S_2$ (**4**): C, 55.25; H, 2.65; S, 21.07. Found: C, 55.24; H, 2.39; S, 21.19.

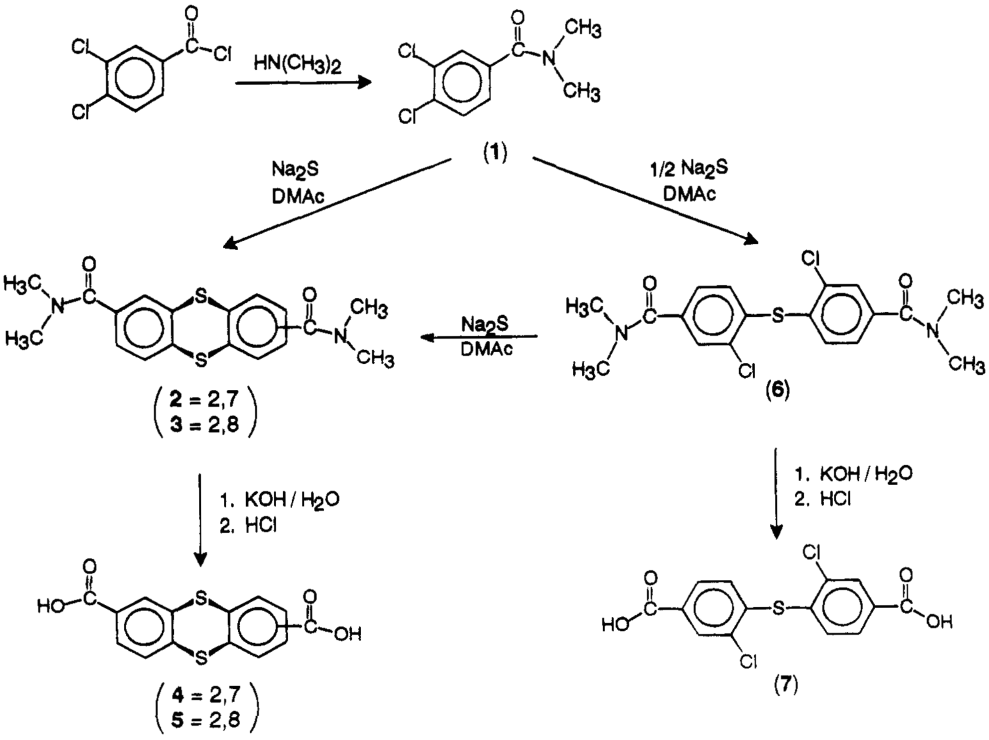
Anal. Calcd for $C_{14}H_8O_4S_2$ (**5**): C, 55.25; H, 2.65; S, 21.07. Found: C, 55.32; H, 2.45; S, 21.23.

4,4′-Thiobis[*N,N*-dimethyl-3-chlorobenzamide] (6). *N,N*-Dimethyl-3,4-dichlorobenzamide (25.23 g, 115.7 mmol) and anhydrous Na_2S (3.65 g, 46.8 mmol, 0.90 mol equiv) were heated in 250 mL of DMAc at 103 °C for 8 h. After the solution was cooled to ambient temperature, the salt and DMAc were removed by filtration and vacuum distillation, respectively. Extraction with CH_2Cl_2 from a brine solution followed by solvent evaporation gave a mixture of organic compounds. Column chromatography in ethyl acetate over silica gel followed by recrystallization from ethyl acetate gave the desired product (12.0 g, 52%): mp 129−131 °C; IR (KBr) 1640 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ 2.92 (s, 6 H), 2.98 (s, 6 H), 7.25 (d, 2 H, J = 8 Hz), 7.40 (dd, 2 H, J = 8 and 2 Hz), 7.67 (d, 2 H, J = 2 Hz).

Anal. Calcd for $C_{18}H_{18}Cl_2N_2O_2S$: C, 54.41; H, 4.57; Cl, 17.85; N, 7.05; S, 8.07. Found: C, 54.53; H, 4.68; Cl, 17.71; N, 6.90; S, 8.19.

4,4′-Thiobis[3-chlorobenzoic acid] (7). 4,4′-Thiobis[*N,N*-dimethyl-3-chlorobenzamide] (2.64 g, 6.64 mmol) was dissolved in 25 mL of methanol and 6 mL of a 50 wt % aqueous sodium hydroxide solution. The mixture was heated to distill off methanol, and an additional 150 mL of water was added during the first hour. When the vapor temperature reached 100 °C, the solution was cooled to ambient temperature and acidified with dilute HCl. The precipitate was filtered and dried. Purification of product involved dissolution in $NaHCO_3$, filtering off insolubles, reacidifying with dilute HCl, and recrystallizing from methanol/water (2:1): yield 1.93 g, 85%; mp 273−275 °C; IR (KBr) 3200−2500 (O−H), 1690 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ 7.33 (d, 2 H, J = 8 Hz), 7.87 (dd, 2 H, J = 8 and 2 Hz), 8.06 (d, 2 H, J = 2 Hz).

Scheme 1. Overall Conversion of 3,4-Dichlorobenzoyl Chloride to Thianthrene and Thioether Monomers



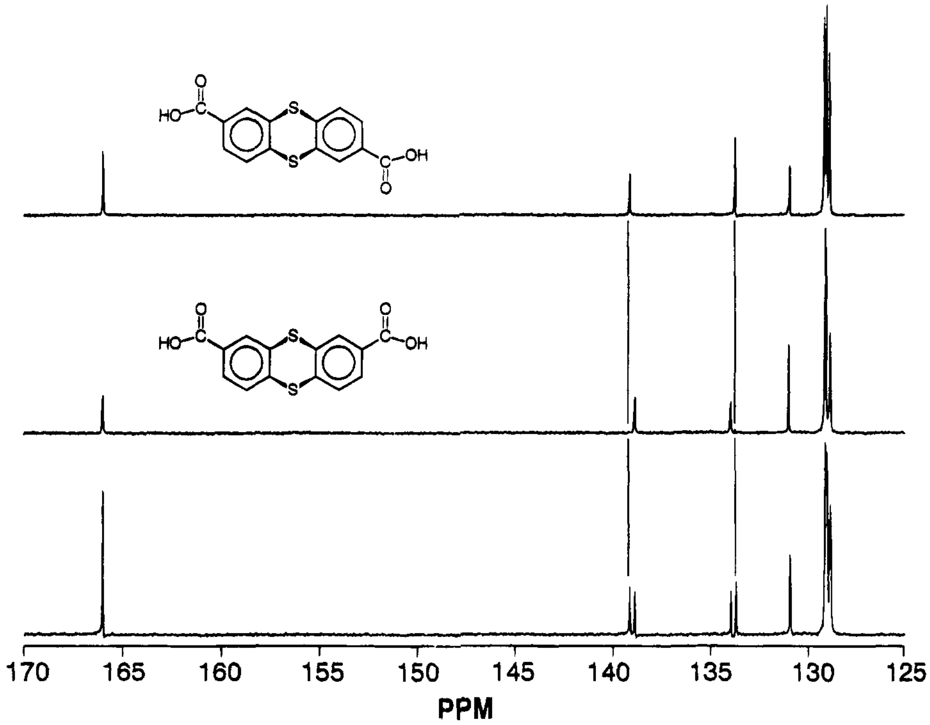


Figure 2. ^{13}C NMR spectra of thianthrene-2,7-dicarboxylic acid (upper trace), thianthrene-2,8-dicarboxylic acid (middle trace), and the crude reaction mixture (lower trace) in DMSO-d_6.

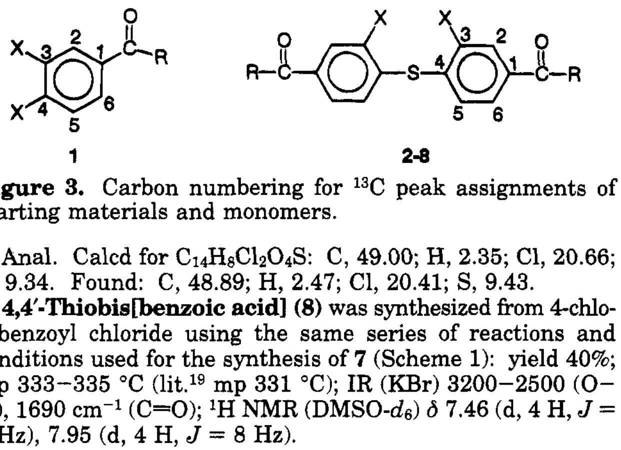


Figure 3. Carbon numbering for ^{13}C peak assignments of starting materials and monomers.

Anal. Calcd for $C_{14}H_8Cl_2O_4S$: C, 49.00; H, 2.35; Cl, 20.66; S, 9.34. Found: C, 48.89; H, 2.47; Cl, 20.41; S, 9.43.

4,4′-Thiobis[benzoic acid] (8) was synthesized from 4-chlorobenzoyl chloride using the same series of reactions and conditions used for the synthesis of **7** (Scheme 1): yield 40%; mp 333–335 °C (lit.[19] mp 331 °C); IR (KBr) 3200–2500 (O–H), 1690 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ 7.46 (d, 4 H, J = 8 Hz), 7.95 (d, 4 H, J = 8 Hz).

2,7-Bis(phenylcarbamoyl)thianthrene (9). Monomer **4** (0.79 g, 2.6 mmol), aniline (0.54 g, 5.7 mmol, 10% excess), and TPP (1.65 g, 5.3 mmol) were combined with a solvent mixture consisting of 40 mL of NMP, 8 mL of pyridine, 0.80 g of LiCl, and 2.4 g of $CaCl_2$. The mixture was reacted at 100 °C for 3 h under nitrogen. The homogeneous yellow solution was poured into methanol, and the precipitate was filtered, washed once with methanol, refluxed for an hour in methanol, filtered, and vacuum dried at 60 °C. The yield of the white crystalline solid was 1.04 g (88%): mp 321–324 °C (DSC); IR (KBr) 3280 (N–H), 1660 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ 7.12 (t, 2 H, J = 7 and 7 Hz), 7.37 (t, 4 H, J = 7 and 8 Hz), 7.77–7.79 (m, 6 H), 7.95 (dd, 2 H, J = 8 and 1 Hz), 8.18 (d, 2 H, J = 1 Hz), 10.35 (s, 2 H).

Anal. Calcd for $C_{26}H_{18}N_2O_2S_2$: C, 68.70; H, 3.99; N, 6.16; S, 14.11. Found: C, 68.52; H, 4.07; N, 6.16; S, 13.93.

2,8-Bis(phenylcarbamoyl)thianthrene (10). Monomer **5** (0.759 g, 2.49 mmol), aniline (0.511 g, 5.49 mmol, 10% excess), and TPP (1.79 g, 5.76 mmol, 15% excess) were combined with a solvent mixture consisting of 25 mL of NMP, 5 mL of pyridine, 0.50 g of LiCl, and 1.5 g of $CaCl_2$. The reaction conditions were the same as for **9**. The yield of the white crystalline solid was 1.10 g (97%): mp 281–284 °C, 295–303 °C (DSC); IR (KBr) 3280 (N–H), 1660 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ 7.12 (t, 2 H, J = 7 and 7 Hz), 7.37 (t, 4 H, J = 7 and 8 Hz), 7.78–7.80 (m, 6 H), 7.95 (dd, 2 H, J = 8 and 1 Hz), 8.19 (d, 2 H, J = 1 Hz), 10.36 (s, 2 H).

Anal. Calcd for $C_{26}H_{18}N_2O_2S_2$: C, 68.70; H, 3.99; N, 6.16; S, 14.11. Found: C, 68.93; H, 4.01; N, 6.30; S, 13.89.

Polymers. All polyamides were synthesized by the following procedure. Diacid (such as **4**, 1.500 g, 4.929 mmol) and diamine (such as ODA, 0.987 g, 4.929 mmol) were mixed with TPP (3.55 g, 11.45 mmol) in a solvent mixture of NMP (50 mL) and pyridine (10 mL) containing 1.75 wt % LiCl and 5.0 wt % $CaCl_2$. The reaction contents were heated at 100 °C for 4 h under nitrogen. The soluble polyamides formed long fibers upon precipitating the polymer mixture into methanol. Purification of the polymers involved chopping the fibers into a fine powder in the presence of methanol in a high-speed blender, washing twice and refluxing for an hour in methanol, filtering, and vacuum drying at 60 °C; yield 2.18 g, 94%. The inherent viscosity of this polymer in DMAc containing 5 wt % LiCl was 1.56 dL/g measured at a concentration of 0.5 g/dL at 30 °C. The FTIR spectrum showed absorptions at 3280 (N–H) and 1660 (C=O) cm^{-1}.

Characterization. Monomer and polymer structures were confirmed by ^{13}C and ^{1}H solution NMR (Bruker ACE 300) and FTIR (Perkin-Elmer 1600A). Differential scanning calorimetry (DSC) was conducted with a DuPont 990 thermal analyzer at a heating rate of 20 °C/min under a nitrogen atmosphere. The glass transition temperature (T_g) was taken as the inflection point of the DSC transition curve. Inherent viscosities (η_{inh}) were obtained at a polymer concentration of 0.5 g/dL in 5 wt % LiCl/DMAc at 30 °C. Thermogravimetric analyses (TGA's) were performed on a DuPont 990 thermal analyzer at a heating rate of 10 °C/min in air and nitrogen atmospheres. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Results and Discussion

Monomer Synthesis. The syntheses of the functionalized thianthrenes and the thioether intermediate are shown in Scheme 1. The thioether bonds of thianthrene and the monothioether precursor were formed by nucleophilic aromatic substitution of activated aromatic dichlorides with Na_2S in DMAc. The overall process involves incorporation of the desired aryl functionality first (the carboxylic acid group), followed by formation of the heterocycle or thioether linkage. This

Table 1. ^{13}C Chemical Shift Values (in ppm) of Precursors and Monomers[a]

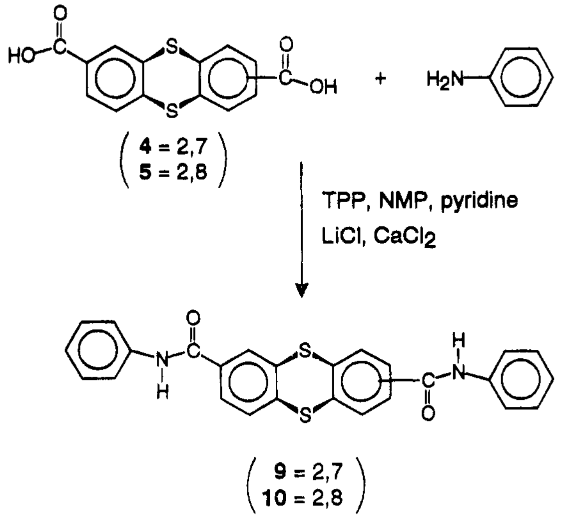
compd	R	X,X	C_1	C_2	C_3	C_4	C_5	C_6	C_{CH_3}	$C_{C=O}$
1	$N(CH_3)_2$	Cl,Cl	137.0	129.0	131.0	132.0	130.6	127.2	34.8/hidden	167.6
2 + **3**	$N(CH_3)_2$	–S–	136.1	127.1	134.1 134.2	135.2 135.2	128.6	126.9	34.8/38.9	168.5
4	OH	–S–	131.1	129.2	133.8	139.2	128.9	129.1		166.1
5	OH	–S–	131.1	129.1	134.0	138.9	128.9	129.1		166.1
6	$N(CH_3)_2$	Cl,Cl	137.7	128.6	132.8	134.0	132.1	126.9	34.8/38.9	167.8
7	OH	Cl,Cl	132.2	130.5	134.0	136.6	132.4	129.0		165.6
8	OH	H	129.8	130.4	130.4	139.5				166.7

[a] In DMSO-d_6; $\delta_c = 39.5$.

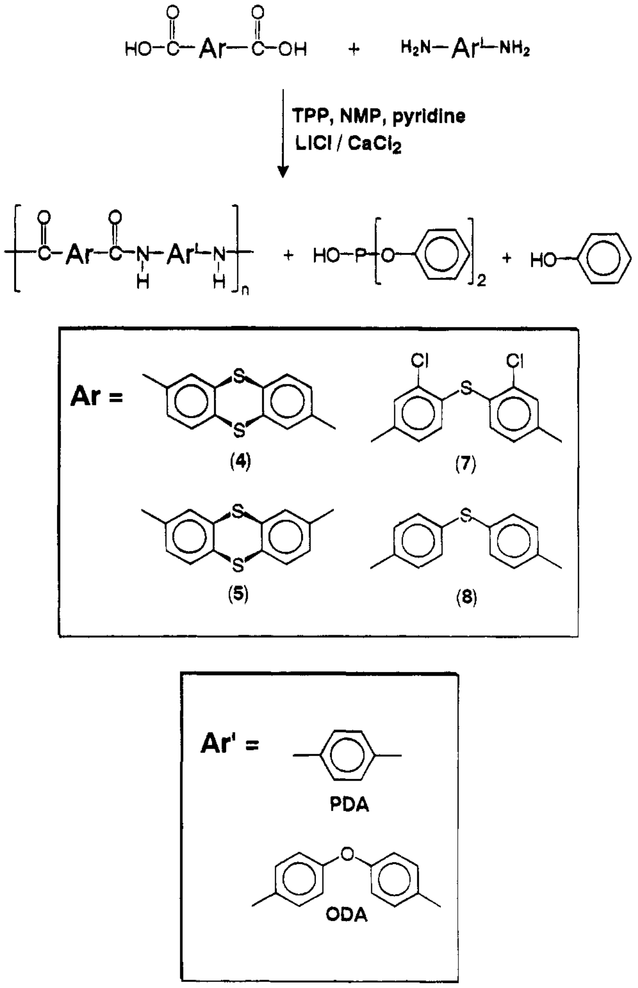
Table 2. Evaluation of Reaction Variables on Synthesis of 6

reacn no.	amide 1 (mmol)	Na_2S (mmol)	temp (°C)	reacn products (% approx from ^{13}C NMR)		
				amide **1**	Bisamide **6**	thianthrene bisamides
1	10.00	5.00	158	35	55	10
2	10.00	5.00	132	30	65	>5
3	10.00	4.75 (95%)	105	40	55	5
4	10.00	4.50 (90%)	120	40	55	<5
5	10.00	4.50 (90%)	103	30	70	<5
6	10.00	3.00 (60%)	103	65	35	<1

Scheme 2. Synthesis of Model Thianthrene Bisamides



Scheme 3. Overall Synthesis of Polyamides with Repeat Unit Structures Formed



route uses less expensive starting materials than alternatives, and the reaction yields are higher than previously mentioned techniques used for synthesizing thianthrene monomers.

The reaction giving *N,N,N',N'*-tetramethylthianthrene-2,7- and -2,8-dicarboxamides generates both isomers in essentially equivalent amounts. The first step of the reaction has been found to give predominantly the 4,4'-thiobis[*N,N*-dimethyl-3-chlorobenzamide] (**6**), as discussed later. Thioether **6** was formed first due to the amide group selectively activating the para position of **1** for nucleophilic aromatic substitution; no evidence was seen for the 3,4'- and 3,3'-isomers. Formation of the thianthrene moiety evidently involves two routes since both possible derivatives are formed in equal amounts. Displacement of the 3,3'-chlorine substituents of **6** with Na_2S directly yields thianthrene substituted in the 2,8-position. Thioether scrambling of **6** with Na_2S followed by subsequent formation of vicinal sulfide bonds is required to explain formation of thianthrene substituted in the 2,7-position. Thioether exchange in the intermediate is possible due to the activating influence of the amide functionality which strongly influences initial thioether formation. Ether exchange with various sulfur nucleophiles has been shown to be quite effective for other systems which are activated for nucleophilic aromatic substitution.[20]

The amide isomers formed an inseparable mixture which was characterized by ^{13}C NMR, FTIR, and thin-layer chromatography. Thianthrene bisamides fluoresce strongly, making TLC especially effective for product analysis. The bisamide mixture was hydrolyzed to the thianthrene-2,7- and -2,8-dicarboxylic acids (**4** and **5**), which could be separated and purified by fractional recrystallization from DMAc/AcOH. The 2,8-isomer, which was the more soluble of the two, required extensive purification to remove all of the 2,7-isomer. Single crystals of the respective isomers were not attainable for X-ray analysis, and thus the assignment of structures is based on the assumption that the pseudotrans compound (2,7-diacid) is the less soluble of the two. NMR and IR data gave no conclusive

Table 3. Polyamide Viscosities and Thermal Properties

			TGA[c] loss transitions (°C)	
polymer	η_{inh}[a] (dL/g)	T_g[b] (°C)	onset temp (N_2/air atm)	10% wt loss (N_2/air atm)
4-ODA	1.56	*d*	431/424	480/483
4-PDA	2.17	*d*	438/437	518/519
5-ODA	2.39	311	439/440	485/493
5-PDA	1.83	307	448/437	502/507
4/**5**-ODA	1.29	*d*	412/406	492/483
4/**5**-PDA	2.07	*d*	421/421	488/490
7-ODA	1.51	265	431/427	476/479
7-PDA	1.51	289	441/421	483/486
8-ODA	2.09	*d*	435/438	486/489
8-PDA	2.46	*d*	463/461	510/507

[a] Measured at a concentration of 0.5 g/dL in 5 wt % LiCl/DMAc at 30 °C. [b] Measured at a heating rate of 20 °C/min. [c] Measured at a heating rate of 10 °C/min. [d] T_g could not be detected.

information as to isomer identify. Figure 2 shows the ^{13}C NMR spectrum of the mixture of thianthrene dicarboxylic acids and the individual spectra of the purified isomers. Figure 3 and Table 1 show ^{13}C peak assignments of precursors and monomers. The carbon numbering scheme employed here is different from conventional ones for several compounds to allow following the chemical shifts of specific carbons in going from precursors to monomers, model compounds, and polymers.

By using only half the amount of Na_2S and lower temperatures, the thioether intermediate **6** was obtained as the major product. Table 2 shows reaction results for optimizing the yield of **6** by varying reactant ratios and reaction temperatures. Unreacted starting material **1** was removed by column chromatography; $R_f = 0.52$ for **1** compared to $R_f = 0.23$ for **6** in ethyl acetate. Thianthrene bisamides **2** and **3** have $R_f = 0.28$ in ethyl acetate and eluted with the desired product. Since the thianthrene bisamides were present in only small amounts, recrystallization from ethyl acetate allowed isolation of bisamide **6**. No evidence of the 3,4′- or 3,3′-thioether isomer being formed as an intermediate was found. Base hydrolysis of **6** followed by recrystallization gave 4,4′-thiobis[3-chlorobenzoic acid] (**7**). For comparison, 4,4′-thiobis[benzoic acid] (**8**) was synthesized in a similar fashion and its NMR and FTIR were spectra obtained. Reaction yields were not optimized for **8**.

Model Compound Syntheses. The syntheses of the model compounds 2,7- and 2,8-bis(phenylcarbamoyl)thianthrene (**9** and **10**) were accomplished in good yields by the reaction of 10% excess aniline with diacids **4** and **5** (Scheme 2). Reaction yields were almost quantitative when 15% excess triphenyl phosphite was used. ^{13}C NMR and FTIR spectra plus elemental analysis results were consistent with the assigned structures.

Polyamide Synthesis. The preparation of aramids by direct polycondensation of aromatic diamines with aromatic dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents has been well documented.[16,17] This method was used here to polymerize the commercially available diamines 4,4′-oxydianiline (ODA) and 1,4-phenylenediamine (PDA) with **4**, **5**, **7**, and **8** (Scheme 3). Polymers obtained with this method formed fibrous precipitates on pouring the reaction mixtures into stirring methanol. Essentially quantitative yields were obtained for all systems evaluated.

Properties of the Polyamides. High molecular weight polymers were obtained as shown by inherent viscosities in the range 1.29–2.46 dL/g (measured in 5 wt % LiCl/DMAc at 30 °C, Table 3). Lower molecular weight polymers ($\eta_{inh} < 0.5$ dL/g) were obtained when no excess triphenyl phosphite was used. Polyamide molecular weights are strongly affected by the ratio of diacid monomer to triphenyl phosphite.[17]

The polymers gave ^{13}C NMR spectra consistent with the expected structures. Figure 4 shows the ^{13}C solution NMR spectra of **4**, ODA, and the polyamide derived from them in DMSO-d_6. Peak positions for the aramids were consistent with those of model bisamides **9** and **10** (see Figure 5 and Table 4 for ^{13}C peak assignments of model compounds and polymers). Polyamide FTIR spectra also confirmed product structures. All IR spectra showed absorption bands at 3280 and 1660 cm^{-1} corresponding to the N–H and C=O amide stretching, respectively.

The thianthrene- and thioether-containing polymers were moderately more soluble than typical rigid aramids (Table 5). Although solubility depends on the structure of both monomers, the diamines appear to be the limiting factor. The ODA-based polymers have more flexibility than the rigid PDA-based polymers and were more soluble. Solubility with respect to the aromatic diacids generally decreased in the order **7** > **5** > **4** > **8**. This order was expected based on the molecular symmetry and flexibility of the diacids. The ortho-dichloro substituents of monomer **7** appear to create the greatest hindrance to polymer chain packing by causing the benzene rings to twist out-of-plane. Monomers **4** and **5**, which are pseudotrans- and pseudocis-substituted thianthrenes, respectively, emulate the solubility characteristics for linear and bent polymers synthesized from para- and meta-functionalized benzene-based monomers. However, the thianthrene-based polymers again were more soluble than typical aramids due to the dihedral angle of thianthrene disrupting polymer chain packing. The thioether monomer, which possesses the lowest amount of steric and rotational hindrance of the diacid rings, gave the *least* soluble polymers. The polymers prepared from thianthrene dicarboxylic acids have very similar solubility characteristics to those prepared from thianthrene diamines. In both cases, the pseudocis isomer was more soluble than the pseudotrans.

Only a few of these polymers displayed an obvious T_g, and these values are in the range expected for relatively rigid backbones (Table 3). More importantly, thermal stabilities of the polymers were excellent, with decomposition beginning above 400 °C in both nitrogen and air. Surprisingly, the thianthrene polyamides had degradation temperatures very close to that of the open-chain thioether analog. This behavior differs from that of polyamides synthesized from thianthrene diamines with aromatic dicarboxylic acids for which thermal degradation occurred as much as 75 °C below the thioether analogs. This behavior has also been observed for thianthrene-based polyimides prepared from thianthrene dianhydride which were thermally more stable than the polyimides prepared from thianthrene diamines.[2,4] The low thermal stability of thianthrene diamine containing polymers was attributed to the low crystallinity caused by the nonplanar thianthrene unit.[8,10] However, the polyamides prepared here also have low crystallinity as determined by wide-angle X-ray analysis (no or weak crystalline peaks seen above strong broad amorphous bases). The thermal stability of thianthrene-based polymers may depend on the basic chemi-

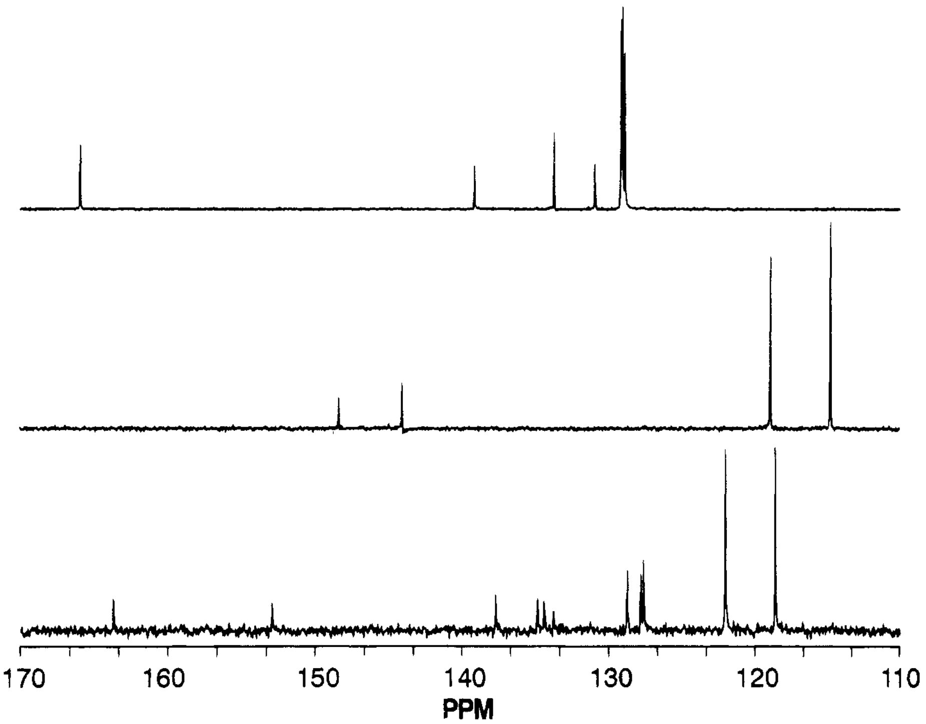


Figure 4. ^{13}C NMR spectra of **4** (upper trace), ODA (middle trace), and their polyamide (lower trace) in DMSO-d_6.

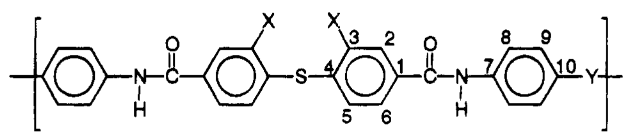


Figure 5. Carbon numbering for ^{13}C peak assignments of model compounds and polymers.

cal structure (i.e., thianthrene dicarboxylic acid derivatives give aramids which are more stable than those derived from thianthrene diamines) as well as on crystallinity, intermolecular interactions, and polymer chain packing. However, a referee has commented on the possibility that trace amounts of impurity within the thianthrene diamines could have significantly affected the onset of degradation.

Copolymers containing 1:1 mixtures of **4** and **5** had lower thermal stabilities than the corresponding homopolymers. Polyamides prepared from monomer **7** had lower degradation temperatures apparently caused by the ortho-dichloro substituents which decrease polymer chain packing and crystallization and which make available homolytic cleavage of the C−Cl bond as a degradation path.

Char yields of the polymers (from thermal degradation in nitrogen up to 700 °C) were 72−78 wt % for the thianthrene-based polyamides and 63−68 wt % for the poly(thioether amide)s. The thianthrene-containing polymers also differed by displaying two transitions during thermal degradation in air. The first transition was followed by a short plateau and then catastrophic degradation. The higher char yields combined with bimodal degradation suggest the possibility that the thianthrene-containing polymers are either cross-linked after the first thermal transition or the ladder structure of the thianthrene nucleus preserves the polymer backbone even if one of the carbon−sulfur bonds is cleaved.

Finally, polyamide films were prepared by spreading filtered solutions of the ODA-based polymers in DMF, and the PDA-based polymers in DMAc/LiCl, onto a Teflon-coated surface. The films were dried at 60−125 °C in a dust-free chamber equipped with a nitrogen gas inlet. The films prepared with LiCl were immersed in H_2O to remove residual salts and DMAc. The films were light beige, and all were tough and flexible. The DMF-prepared films were transparent and those derived from DMAc/LiCl were partially cloudy. Absence of residual solvent was demonstrated by TGA.

Conclusions

Thianthrene and thioether containing aromatic dicarboxylic acids were readily synthesized by nucleophilic aromatic substitution of *N,N*-dimethyldichlorobenzamides with sodium sulfide. Polyamides obtained from the diacids displayed good thermal stabilities. Solubility was enhanced over that of typical aramids when copolymerized with flexible diamines such as ODA. The thianthrene- and thioether-containing polymers had similar thermal degradation onsets, but the thianthrene

Table 4. ^{13}C Chemical Shift Values (in ppm) of Model Compounds and Soluble Polymaides[a]

	X,X	Y	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	$C_{C=O}$
9	−S−	nil	134.9	127.9	133.8	137.8	128.8	127.7	138.9	120.4	128.6	123.4	163.9
10	−S−	nil	134.9	127.8	133.9	137.6	128.6	127.7	138.9	120.4	128.6	123.9	163.9
4 + ODA	−S−	−O−	134.9	127.9	133.8	137.7	128.8	127.7	134.5	122.1	118.7	153.0	163.8
5 + ODA	−S−	−O−	134.8	127.6	133.9	137.7	128.7	127.6	134.4	122.0	118.6	152.9	163.9
4,**5** + ODA	−S−	−O−	134.9	127.8	133.8 133.9	137.6 137.7	128.7	127.7	134.4	122.1	118.6	153.0	163.7
7 + ODA	Cl,Cl	−O−	135.2	129.1	134.3	136.0	132.2	127.6	134.0	122.1	118.7	153.0	163.2

[a] In DMSO-d_6; δ_c = 39.5.

Table 5. Solubility of Polyamides in Various Solvents[a]

polymer	DMAc	DMSO	*m*-cresol	acetone	H_2SO_4
4-ODA	+	+	±	−	+
4-PDA	−	−	−	−	+
5-ODA	+	+	±	−	+
5-PDA	−	−	−	−	+
4/5-ODA	+	+	±	−	+
4/5-PDA	−	−	−	−	+
7-ODA	+	+	±	−	+
7-PDA	+	±	±	−	+
8-ODA	−	±	±	−	+
8-PDA	−	−	−	−	±

[a] (+) Soluble at room temperature; (±) partially soluble at room temperature; (−) insoluble.

moiety appeared to keep the polymers intact longer. In addition, the polymers prepared from the acid derivatives of thianthrene have higher thermal stabilities than analogous polymers prepared from thianthrene diamines. Films of the polyamides obtained here displayed good toughness and flexibility, consistent with high molecular weight and low crystallinity for these novel polymers.

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