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Synthesis and Characterization of Polyimides from 3,7-Diaminophenothiazinium Chloride (Thionine)

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ABSTRACT: A new series of thermally stable, organic solvent soluble polyimides has been synthesized by reacting the tricyclic heterocyclic molecule 3,7-diaminophenothiazinium chloride, thionine, with four different dianhydrides. With the exception of the polyimide obtained from pyromellitic dianhydride and thionine, the polyimides were synthesized by a single-stage polymerization reaction at an elevated temperature. For these polymers, the conditions necessary for the polymerization to proceed did not permit the isolation of the intermediate poly(amic acid). To assess the reactivity of the primary amine groups of the thionine molecule, model compounds were prepared by reacting thionine with phthalic anhydride. This reaction was studied in different solvents and under various experimental conditions so that the intermediate diamic acid could be isolated. Subsequent treatment of the bis(phthalic diamic acid) at elevated temperatures yielded the bis(phthalic diimide). The polyimides obtained from thionine and the dianhydrides 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were soluble in many of the common organic solvents, whereas the polyimides obtained from the dianhydrides pyromellitic dianhydride (PMDA) and naphthalenetetracarboxylic dianhydride (NTCDA) were soluble in fewer organic solvents but dissolved completely in strong acids without decomposition. The differences in solubility of these polyimides are attributed to the differences in the dianhydride flexibility and polarity. Differential thermal analyses and thermogravimetric studies established that these polyimides were thermally stable up to 500 °C in air. The polyimides prepared with pyromellitic dianhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, or 1,4,5,8-naphthalenetetracarboxylic dianhydride exhibited a 10% weight loss in the region of 507 °C in air. The polyimide synthesized with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride exhibited a 10% weight loss at 539 °C in air. All four polyimides exhibited improved thermal stability ranging from 10 to 80 °C in a nitrogen atmosphere. Characterization of the polyimides by X-ray diffraction showed that the polyimide obtained from thionine and PMDA had a greater degree of crystallinity than the other polyimides. Computer simulations of the geometry of each polyimide indicated a preference by that polyimide for its own unique helical structure conformation.

Introduction

Studies of the synthesis and properties of polymers that incorporate the tricyclic heterocycle phenothiazine and its derivatives are a significant research component in this laboratory.[1-3] The incorporation of phenothiazine derivatives into a variety of polymer systems has an extensive literature, but there are no reports of phenothiazine polyimides. Although polyimides comprise an extensively studied class of thermally stable polymers and a large number of different polyimides have been synthesized and their thermal stabilities investigated,[4-6] only a few polyimides that incorporate tricyclic heterocycles have been studied.[7-10] Various industrial applications of the common polyimides as neat resins as well as matrix resins for composites for high-temperature use have been developed. Several polyimides[11-15] have excellent properties of use as structural adhesives and coatings or as thin films. These are applications where adhesion to the substrate and not the joining of two materials of prime importance. The synthesis and properties of high-temperature polymers have been reviewed.[16,17] Many of these polymers retain their properties at 300 °C for months and even withstand temperatures greater than 400 °C for a few minutes. The incorporation of a ladder structure that utilizes aromatic or heterocyclic rings in the main polymer chain frequency confers enhanced thermal stability to the polymer. Such structures are inherently more stable than a single-stranded chain.[18,19] On the basis of this rationale, we have synthesized four new polymers that incorporate a tricyclic, six-membered fused ring containing two different heterocyclic atoms in the center ring of the tricyclic system.

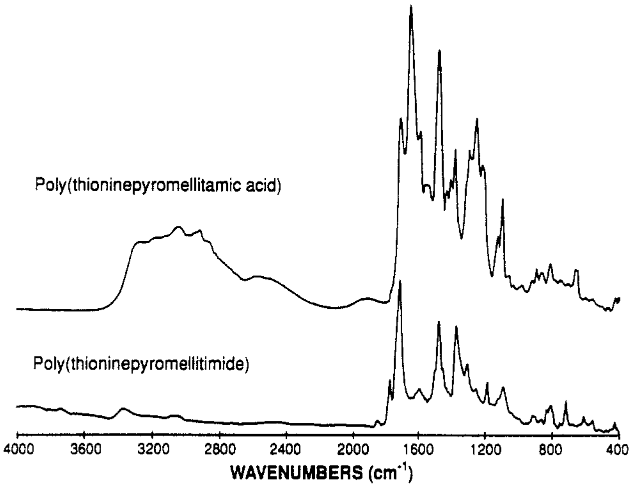

Figure 1. FTIR spectra of poly(thioninepyromellitamic acid) and poly(thioninepyromellitimde).

Some tricyclic, six-membered heterocyclic polyimides containing dibenzo-*p*-dioxin, thianthrene, and phenoxatiin have been reported.[7-9] These polymers, when characterized under a nitrogen atmosphere, were reported to exhibit good thermal stability up to ca. 400 °C. Our literature search did not find references to any polyimides that contained a completely conjugated phenothiazine moiety in a polymer system. Molecular modeling studies that we have carried out have indicated that thionine should be

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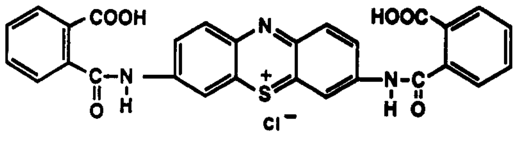
approximately planar as a consequence of resonance throughout the molecule, although phenothiazine itself is nonplanar with a reported dihedral angle between the benzene planes of 158.5°[21] Substituted phenothiazines typically show a smaller dihedral angle between planes. For the thionine polymers, the phenothiazine moiety in the backbone carries a delocalized charge, and the electron delocalization should result in enhanced heat stability and good mechanical properties as well as good solubility characteristics.

To assess the facility of the reaction of thionine toward organic diacids, model compounds 1 and 2 were synthesized.



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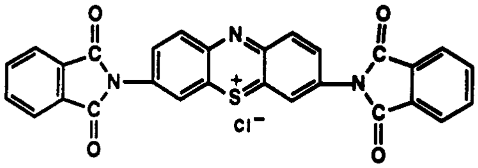

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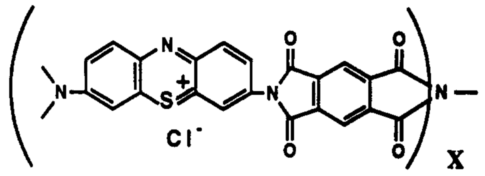
The synthesis of these compounds yielded the optimum conditions for the preparation of the model compounds and provided the experimental conditions for the condensation polymerization of thionine with pyromellitic dianhydride, compound 3, and the other dianhydrides.



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In this paper we report our results for the synthesis of the polymers, and their spectral, thermal, and X-ray characterization, and computer simulations of their structures.

Experimental Section

Materials. Thionine hydrochloride (Eastman Kodak Co.) was recrystallized twice from distilled water. Zone-refined pyromellitic dianhydride (Aldrich Chemical Co.), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (PCR Inc.) (6FDA) were used without further purification. The 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (Aldrich Chemical Co.) (BTDA) was purified by sublimation under reduced pressure. The 1,4,5,8-naphthalenetetracarboxylic dianhydride (Aldrich Chemical Co.) was recrystallized from nitrobenzene. All solvents used were freshly distilled and were stored over washed and dried, grade 514GT-4 A molecular sieves.

Measurements. NMR, UV–vis, FTIR, and Mass Spectra. All NMR spectra were obtained on a Bruker 360-MHz spectrometer. UV spectra were taken on a Varian DMS 300 UV–visible spectrophotometer. Infrared spectra were obtained with a Nicolet 5-DX FTIR spectrophotometer. Mass spectra and elemental analysis were carried out by the Analytical Laboratory of the Chemistry Department at The University of Michigan.

Viscosity Determinations. Viscometric measurements were performed using Ubbelohde viscometers kept at a constant temperature of 25.0 ± 0.2 °C. Solvent efflux time through the viscometer capillary was greater than 100 s, thereby avoiding any kinetic energy corrections. Solvents were methanesulfonic acid for thionine + PMDA, sulfuric acid for thionine + NTCDA, and *N*-methyl-2-pyrrolidinone for thionine + BTDA and also for thionine + 6FDA. The lowest solution concentration was 0.25%. At lower concentrations the polyelectrolyte effect became pronounced. This could be avoided by the addition of LiCl to the solution.

DSC and TGA. Differential scanning calorimetric measurements were obtained using a Perkin-Elmer 7 series thermal analyzer. Thermogravimetric analyses were obtained either on a Shimdazu TGA-50 thermogravimetric analyzer in air at a heating rate of 20 °C/min or on a Perkin-Elmer 7 series thermogravimetric analyzer in air or in nitrogen.

Computer Modeling of Polyimide Structures. The calculation of the energy minimization of computer-simulated structures for the four thionine-containing polyimides was carried out using the POLYGRAF program available from Molecular Simulations Inc., Burlington, MA.

Synthesis. Synthesis of the Bis(phthalic diamic acid) (1) from Thionine and Phthalic Anhydride. Recrystallized thionine (0.206 g, 0.78 mmol) was dissolved in 5 mL of dried, freshly distilled *N*-methyl-2-pyrrolidinone by stirring at room temperature in the dark for 2 h. Upon dissolution, the temperature was raised to 38 °C with an oil bath, and 0.459 g (3.10 mmol) of finely ground phthalic anhydride was added at once to the stirred thionine solution. After 24 h of stirring at 38 °C in the dark, the reaction product was precipitated in 60 mL of cold, well-stirred distilled water. The light green precipitate was filtered, washed twice with cold water, and dried in a vacuum oven at room temperature for 2 days. The dirty green product did not melt on heating up to 350 °C and was obtained in quantitative yield.

Mass Spectrum: EI 489; FAB 525. Proton NMR (DMSO-d_6): δ 10.1 (s, broad, 2H, COOH), 8.47 (broad, 2H, NH), 7.84 (doublet, 2H, J = 7.62 Hz), 7.62 (triplet, 2H), 7.55 (doublet, 2H, J = 8.85 and 1.32 Hz), 7.52 (triplet, 2H), 7.36 (singlet, 2H, J = 1.88), 7.22 (doublet, 2H, J = 8.62 and 2.1 Hz), 6.63 (doublet, 2H, J = 8.59 Hz). IR (KBr pellet): 1711 (m), 1658, 1598, 1535, 1483, 1434, 1295, 1259, 1216, 792, 716 cm^{-1}.

Synthesis of the Bis(phthalic diimide) (2) from 1. Compound 1 (0.2 g, 0.357 mmol) was dissolved in 2 mL of *N*-methyl-2-pyrrolidinone in a 10 mL two-neck flask equipped with a mechanical stirrer. A pinch of sodium acetate was added, followed by the addition of 1.5 mL or acetic anhydride. The solution was heated to 145 °C, with continuous stirring for 22 h. The product was precipitated by pouring the mixture into 80 mL of stirred, distilled water, allowing the precipitate to settle and then collecting it by filtration. The product was repeatedly washed with boiling distilled water and then dried in a vacuum desiccator at room temperature for 2 days. The bis(phthalic dimide) was obtained in quantitative yield and did not melt on heating up to 350 °C.

Proton NMR (DMSO-d_6): δ 7.98 (multiplet, 8H), 7.82 (doublet, 2H, J = 8.48 Hz), 7.72 (doublet, 2H, J = 1.89), 7.53 (doublet of doublets, 2H, J = 8.51 and 1.54 Hz), 2.24 (singlet, 3H, $COOC\mathit{H}_3$). IR (KBr pellet): 1720 (vs), 1649, 1612 cm^{-1}. Mass spectrum: EI 531; FAB 532. Elemental Anal. Calcd for $C_{30}H_{17}O_6N_3S$: C, 65.81; H, 3.13; N, 7.67. Found: C, 64.53; H, 3.86; N, 8.14.

Synthesis of Poly(amic acid) (PAA, 3) from Thionine and Pyromellitic Dianhydride (PMDA) and Synthesis of the Polyimide. In a dry 25-mL round-bottom flask containing 8 mL of dried, distilled *N*-methyl-2-pyrrolidinone, 0.501 g (1.90 mmol) of recrystallized thionine was dissolved by stirring in the dark for 3 h at 30 °C. Finely ground PMDA (0.414 g, 1.90 mmol) was added to the solution, followed by the addition of 1 mL of dried *N*-methyl-2-pyrrolidinone to dissolve any material stuck to the wall of the flask. The reaction was allowed to run for a total of 26 h. Part of the solution (4 mL) was precipitated in 100 mL of cold distilled water, and the collected precipitate was washed with a small quantity of cold distilled water. The poly(amic acid) that was obtained was dried in a vacuum oven.

Proton NMR (DMSO-d_6): δ 10.3 (broad, multiplet, COOH), 8.83 and 8.57 (broad, singlets, NH), 8.25 (singlet), 8.11 (singlet), 7.9 (singlet), 7.73 (singlet), 7.66 (singlet), 7.37 (singlet), 7.21 (doublet), 6.98 (doublet), 6.92 (singlet), 6.72 (doublet), 6.68

(doublet). IR (KBr pellet): 1716, 1652, 1610, 1540, 1480, 1299, 1258, 1215, 815 cm^{-1}.

To the remaining 5 mL of the reaction mixture were added 0.3 g of anhydrous sodium acetate and 5 mL of acetic anhydride, and the solution was heated at 155 °C for 24 h. The resulting brown solution was poured into 100 mL of stirred distilled water. The dispersed precipitate was heated for a few minutes to remove strongly adhering *N*-methyl-2-pyrrolidinone and allowed to settle. The product was collected by vacuum filtration and washed with 100 mL of boiling distilled water and finally with a small quantity of acetone. The bis(phthalimide) was dried in a vacuum oven at room temperature for 48 h.

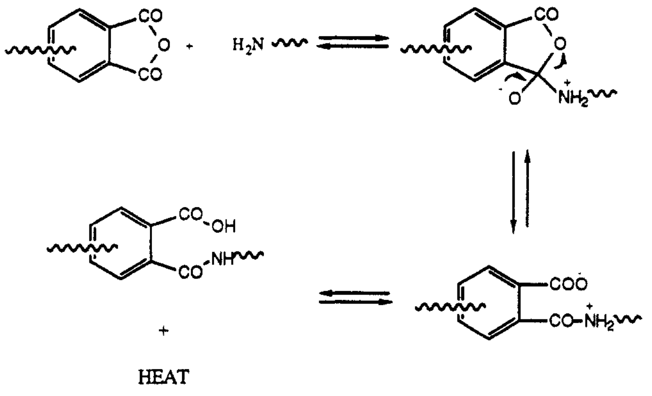
IR (KBr pellet): 1722, 1712, 1658, 1631 cm^{-1}.

Synthesis of Polyimides from Thionine and Dianhydrides at Elevated Temperature by a Single-Step Reaction. Recrystallized thionine (0.242 g, 0.917 mmol) was mixed with 0.2 g (0.916 mmol) of pyromellitic dianhydride in a 25 mL round-bottom flask equipped with a magnetic stirrer. Freshly distilled *N*-methyl-2-pyrrolidinone was added to the mixture to make a solution containing 20% solids. This solution was refluxed at 185–187 °C for the identical time (the time for each reaction was varied and is noted in the Results and Discussion), and then 0.05 g (0.34 mmol) of phthalic anhydride was added to end cap the polymer. The end-capping reaction was continued for 1 h at that elevated temperature. The resulting dark, viscous liquid was poured into 500 mL of hot distilled water, and the mixture was boiled and filtered while hot. The precipitated polyimide was washed repeatedly with 200 mL of boiling distilled water and finally with 10 mL of acetone. The polymer was dried in a vacuum oven at 50 °C for 20 h. Yield 85–87%.

All of the thionine polyimides were prepared using the protocol described above.

Results and Discussion

The experimental results obtained for the synthesis of the poly(amic acid) at a lower temperature from thionine and different dianhydrides can be explained by considering the following reaction mechanism.



This reaction scheme requires that an equilibrium exist between reactants and products, thereby making the propagation reaction reversible.[20,22] The forward reaction is believed to start with the formation of the charge transfer complex between the dianhydride and the diamine.[23,24] Propagation occurs immediately via a nucleophilic substitution at one of the anhydride carbonyl carbon atoms. Thus, the amine nucleophile attacks the sp^2 carbon and displaces the adjacent carboxylate moiety. As a result of this attack, the carboxyl group is chemically attached to the product and cannot be removed. However, by using polar aprotic solvents, the carboxyl groups can be stabilized by formation of strong hydrogen-bonded complexes, thereby driving the reaction in the forward direction. Also, since the forward reaction is bimolecular and the reverse reaction is unimolecular, increasing the concentration of the reactants results in an increase in the reaction rate and the molecular weight of the polymer.

Since the forward reaction should be exothermic at ambient temperature, the equilibrium should shift in the reverse direction and the product's molecular weight should decrease when the reaction temperature is increased. Conversely, decreasing the reaction temperature should result in shifting the equilibrium in the forward direction, and higher molecular weight polymeric product should be obtained.

As expected, the rate of polymerization was found to increase when the concentration of the reactants was increased. However, the rate of the polymerization reaction was also found to increase with an increase in temperature. This type of exception to the general trend is possible when two different, very unreactive monomers do not condense exothermically with each other at ambient temperature. In these cases, the molecular weight of the poly(amic acid) increases as the temperature is increased.[24-26] The present result demonstrates that relatively sluggish reactivity of the diamino groups in thionine. However, the amino groups do react with a very reactive dianhydride such as PMDA at ambient temperature. When dianhydrides like NTCDA, 6FDA, and BTDA were used instead of PMDA, no reaction occurred at room temperature. Raising the temperature promoted the reaction of thionine with these dianhydrides. However, at elevated temperatures the amic acid functional group was immediately converted to the imide function. The lower reactivity of these dianhydrides can be attributed to their lower values of electron affinity (EA) compared to PMDA.[24]

The poly(amic acid) obtained from thionine and PMDA can be converted to a polyimide by thermal or chemical means. Imide linkage formation by heat does not change the chloride counterion of thionine, but the chemical cyclization using acetic anhydride replaces the chloride counterion by an acetate counterion, as shown by the NMR and mass spectral characterization of the model compound.

Characterization of the model compounds using mass spectroscopy also indicated that the diamic acid (1) is, as expected, unstable to heat and is converted to the relatively stable diimide (2). The fast atom bombardment (FAB) technique gave the expected mass of 525 for model compound 1. However, the same diamic acid when subjected to mass spectroscopy by the electron impact (EI) technique cyclizes to the more stable diimide by the loss of two molecules of water at the elevated temperature within the mass spectrometer. This results in the detection of a mass of 489 instead of 525.

The kinetics of the thermal conversion of a poly(amic acid) film of thionine and PMDA was studied using infrared spectroscopy. A film was prepared by dissolving the poly(amic acid) (reduced specific viscosity 0.2 dL/g at the concentration of 1 g/dL in *N*-methyl-2-pyrrolidinone) in dimethylformamide at room temperature and evaporating the solvent in a vacuum oven at room temperature on a silver chloride plate. The resulting poly(amic acid) film on silver chloride gave the infrared spectrum shown in Figure 1. The silver chloride plate was then heated in a conventional oven at 167 °C for 210 min and then at 200 °C for 35 min. Infrared spectra were obtained at various time intervals. Normalized absorbance was obtained by taking the ratio of the absorbance of a particular peak to the absorbance of the 819-cm^{-1} peak (a peak corresponding to the 1,2,4,5-tetrasubstituted benzene ring). Peaks typical of amic acid decreased as the film was heated, and peaks corresponding to the imide linkage appeared. The rate of cyclization at 167 °C was initially rapid but decreased with time. However, the rate increased again when the

Table I. Characterization Parameters of the Four Thionine-Containing Polyimides

polymer	reactn time[a] (h)	intr. vis. (dL/g)	solvent used for viscosity measurements	imide group peak positions (cm^{-1}) asym str	imide group peak positions (cm^{-1}) sym str	elem anal.	C	H	N	refr index	permittivity
thionine + PMDA	4.17	0.384	methanesulfonic acid	1776	1719	calcd	59.27	1.81	9.42	1.84	
						found	58.89	2.40	9.31		
thionine + NTCDA	7.25	0.959	sulfuric acid	1786	1714	calcd	62.97	2.03	8.47		
						found	62.19	3.12	8.30		
thionine + BTDA	10.00	0.380	*N*-methyl-2-pyrrolidinone	1780	1720	calcd	63.34	2.20	7.64	1.73	2.993
						found	61.15	2.89	7.56		
thionine + 6FDA	10.00	0.207	*N*-methyl-2-pyrrolidinone	1785	1724	calcd	55.41	1.80	6.25		
						found	54.84	2.59	6.66		

Table II. Summary of Solubility Behavior of the Four Thionine Polyimides[a]

polymer	condition	acet	MeOH	DMF	DMAc	NMP	DMSO	HCOOH	MSA	H_2SO_4
thionine + PMDA	RT(im)	−	−	−	+ −	+ −	+ −	−	+ + −	+ + −
	RT(10 min)	−	−	−	+ −	+ −	+ −	+ −	+ + −	+ + −
	heat	−	−	−	+ + −	+ + + −	+ + −	+ + −	+ + + +	+ + + +
thionine + NTCDA	RT(im)	−	−	+ −	+ −	+ −	+ −	−	+ + + −	+ + + −
	RT(10 min)	−	−	+ + −	+ + −	+ + −	+ + −	+ −	+ + + −	+ + + −
	heat	−	−	+ + −	+ + −	+ + + −	+ + −	+ + −	+ + + +	+ + + +
thionine + BTDA	RT(im)	−	−	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +
	RT(10 min)	−	−							
	heat									
thionine + 6FDA	RT(im)	+ −		+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +	+ + + +
	RT(10 min)	+ −								
	heat	+ −								

[a] RT(im) = room temperature, immediately after addition of solvent; RT(10 min) = room temperature, 10 min after addition of solvent; heat = result after heating the solution. Solvents used: MeOH = methanol, DMAc = dimethylacetamide, DMSO = dimethyl sulfoxide, DMF = dimethylformamide, NMP = 1–methyl–2–pyrrolidinone. Symbols: − = insoluble, + − = slightly soluble, + + − = increasing solubility, ++++ = completely soluble.

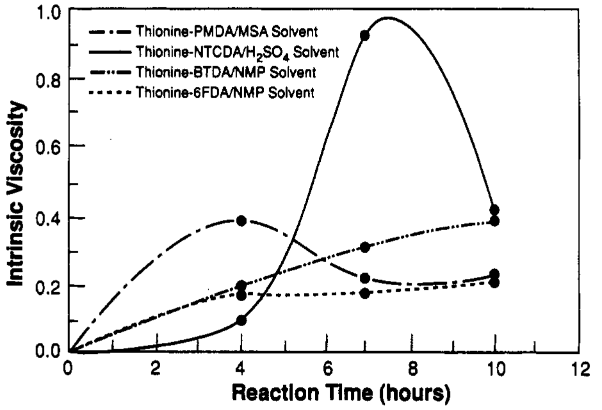


Figure 2. Intrinsic viscosity of the polyimides plotted against the reaction of thionine and the selected dianhydride.

temperature was raised to 200 °C. The FTIR spectrum also revealed that the polymer contained an anhydride end group, and this was confirmed by NMR spectroscopy.

This method of quantitatively following the imidization reaction failed at the later stage of reaction. The method was not sufficiently sensitive to the changes in the concentration of the imide groups in the late stages of the reaction. It was therefore necessary to use the method of Oishi et al.[27] for a quantitative assessment of the imidization reaction. This approach permits the degree of imidization to be determined using the following equation:

$$\text{degree of imidization } (x) = \frac{[A(1386)/A(1490)]_t - [A(1386)/A(1490)]_{t=0}}{[A(1386)/A(1490)]_{t=\infty} - [A(1386)/A(1490)]_{t=0}}$$

where the 1386-cm^{-1} peak represents the appearance of the imide moiety and the 1490-cm^{-1} peak represents the reference peak.

The conversion of the poly(amic acid) to polyimide can be considered as a first-order reaction, since it proceeds between two functional groups belonging to the same precursor fragment. Accordingly, if the degree of imidization is x at the heating time t, the rate of imidization dx/dt can be expressed as

$$dx/dt = k(100 - x)$$

where k is the first-order rate constant. This equation can be transformed to

$$\ln[100/(100 - x)] = kt$$

When the left-hand side of the above equation was plotted against time for this imidization reaction, linear plots were obtained, showing that the imidization process follows first-order kinetics. The first-order rate constant (k) for all three temperatures were determined, and from the rate constants the energy of activation for the conversion of poly(amic acid) to polyimide was found to be 17.2 kcal/mol.

Thermogravimetric analysis indicated that the thermally cyclized polyimide with chloride counterions is ca. 80 °C more stable than the chemically cyclized polyimide with acetate counterions.

Synthesis of Polyimides at Elevated Temperatures. All four thionine-containing polyimides were synthesized by reacting thionine with each of the dianhydrides PMDA, NTCDA, 6FDA, and BTDA at the appropriate elevated temperature. To reduce the reactivity of the resulting polyimides and thereby avoid possible cross-linking reactions at the elevated temperatures, the polyimides were end capped with phthalic anhydride. As in the two-step polyimide synthesis, reactions carried out in *N*-methyl-2-pyrrolidinone yielded a polymer of the highest molecular weight. Thermogravimetric analysis indicated that the maximum rate of cyclization of the poly(amic acid) obtained from thionine and pyromellitic dianhydride occurs in the region of 200 °C so that a temperature of 185 °C was used for the polyimide syntheses.

Effect of Reaction Time on the Molecular Weight of the Polymer. The results of a series of time-controlled

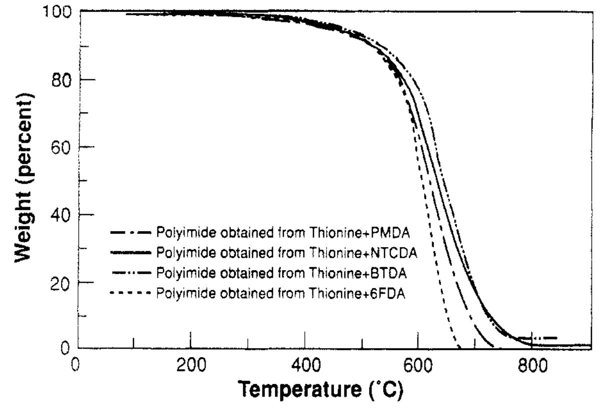


Figure 3. Comparison of the TGA curves for the four polyimides in air showing the excellent thermal stability of these polymers.

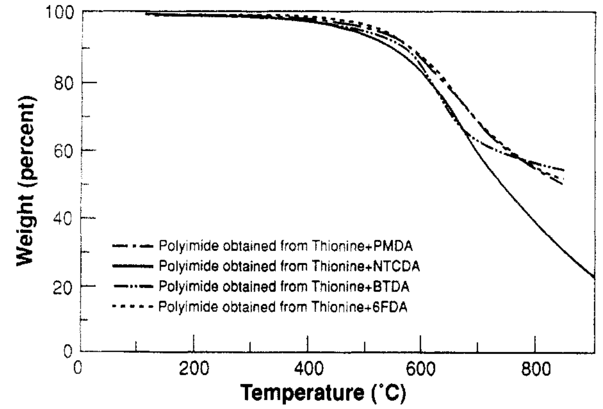


Figure 4. Comparison of the TGA curves for the four polyimides in nitrogen showing the improvement in the thermal stability of the same four polyimides.

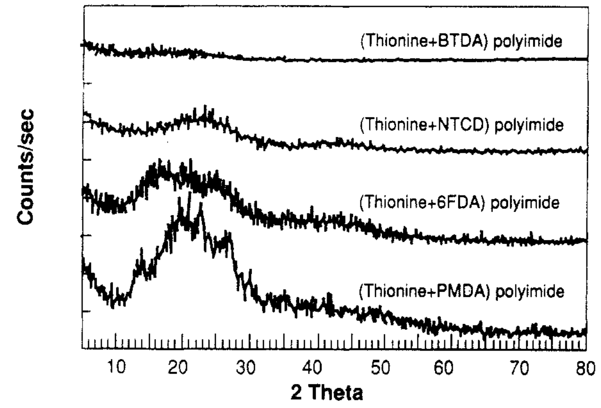
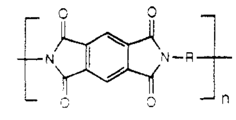


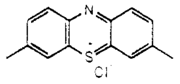
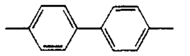
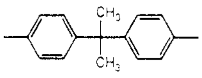
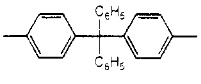
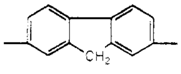
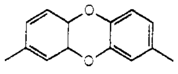
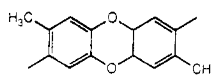
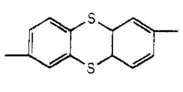
Figure 5. X-ray diffraction of the four polyimides prepared from thionine and the noted dianhydrides.

reactions run under identical conditions revealed that some degree of time-dependent polyimide degradation did occur (Figure 2). The optimum reaction times and corresponding intrinsic viscosity values are reported in Table I. The polyimide obtained from NTCDA had the highest intrinsic viscosity, whereas the polyimide obtained from 6FDA had the lowest intrinsic viscosity. However, any conclusions regarding the polyimide molecular weights based on their intrinsic viscosity values would probably not be valid. The polyimides containing the rigid dianhydrides NTCDA and PMDA will behave like a rigid rod whereas the polyimides obtained from the flexible dianhydrides BTDA and 6FDA may be able to form coiled structures. Consequently, the low molecular weight, rigid polyimides may exhibit a higher intrinsic viscosity than the intrinsic viscosities of the highly flexible, higher molecular weight, coiled polyimides obtained from BTDA and 6FDA. Furthermore, a strict comparison of the intrinsic viscosity values is not justified because only two of the solution viscosities were obtained in *N*-methyl-2-pyrrolidinone. One of the viscosities was obtained in methanesulfonic acid and the other in sulfuric acid.

Table III. Temperatures at Which a 10% Weight Loss in Air Occurs for Various Tricyclic, Biphenyl, and Bibenzyl Polypyromellitimides

General formula:



R	T°C	Ref.
	510	-
	530	16
	470	16
	460	16
	510	16
	490	7
	470	7
	420	7

Characterization and Solubility Properties of Thionine-Containing Polyimides. The presence of imide groups in the polymers was confirmed by IR absorption bands in the regions of 1720 and 1780 cm^{-1}. The IR absorptions and the elemental analyses of these polymers are reported in Table I. The elemental analysis results conform to the theoretically expected values except for the hydrogen percentages. The higher value for the hydrogen percentages is attributed to strongly absorbed moisture.

The polyimide containing thionine and 6FDA was the only one found to be soluble in tetrahydrofuran and could be analyzed by gel permeation chromatography. The number-average molecular weight by gel permeation chromatography was 3496. The weight-average molecular weight was 6118, and the polydispersity was 1.75. These values are relative to polystyrene standards in tetrahydrofuran.

A qualitative determination of the solubility of the four polymers in various solvents is summarized in Table II. The polyimides containing the benzophenone unit or fluorine atoms have enhanced solubility in common organic solvents, whereas polyimides containing PMDA or NTCDA components are sparingly soluble in common organic solvents. The PMDA and NTCDA polymers were fully soluble in strong acids like methanesulfonic acid and sulfuric acid. This solubility behavior is explicable in terms of the polymer chain rigidity. Polymers containing BTDA and 6FDA will have a flexible linking moiety that can also participate in hydrogen bonding and solvation. In contrast, the polyimides prepared from the dianhydrides

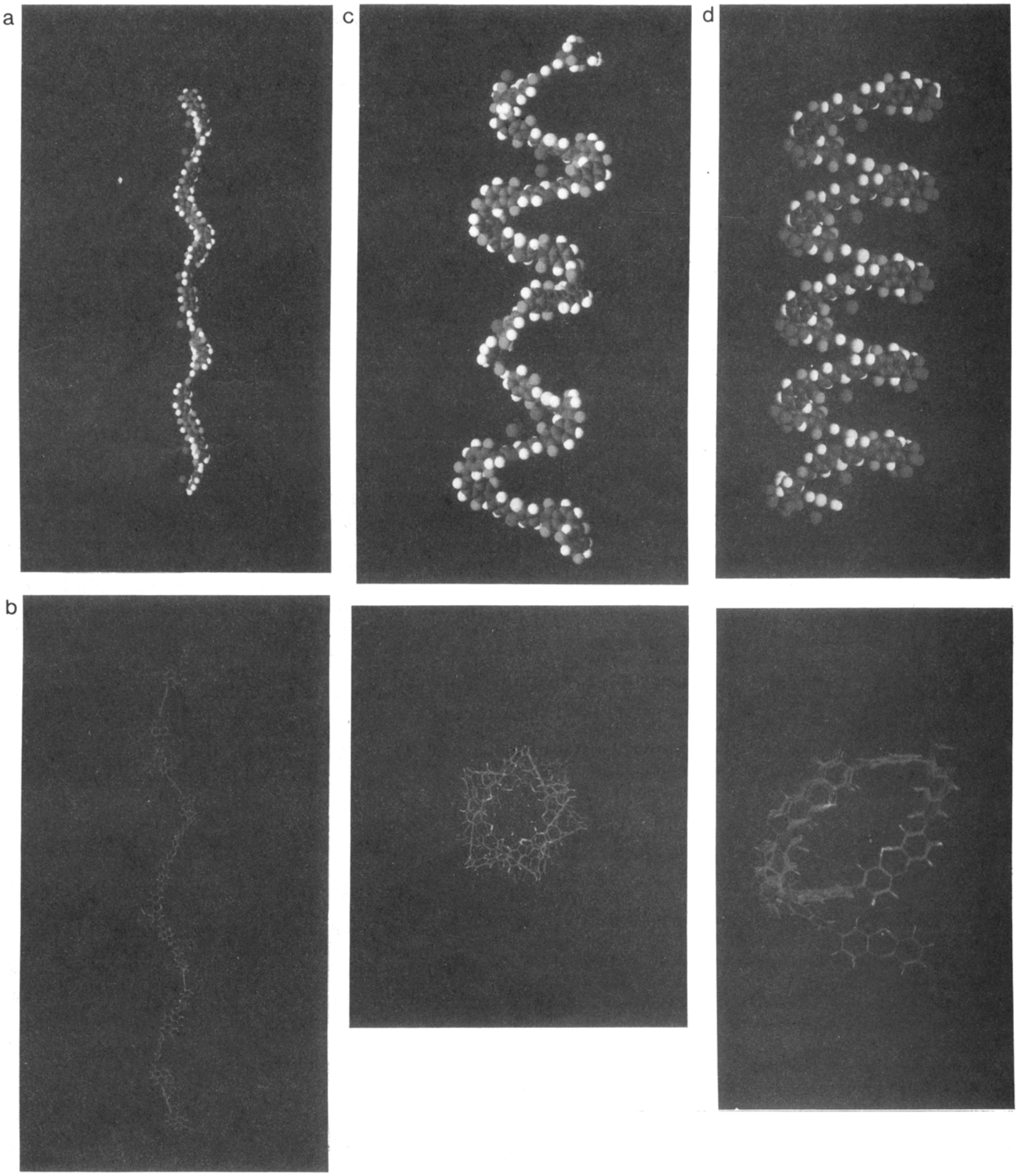


Figure 6. Computer-simulated structures of the polyimides obtained from thionine and (a) PMDA, (b) NTCDA, (c) BTDA, and (d) 6FDA. The top views in (c) and (d) are front views showing the polymer coil, and the bottom views show the polymer cavity.

PMDA and NTCDA will lack functional groups that can participate in hydrogen bonding and solvation, thereby diminishing their solubility in the usual organic solvents.

Thermal Properties of the Thionine Polyimides. The thermal properties of the polyimides were studied by thermogravimetric analysis. Results of thermogravimetric analysis in air are given in Figure 3, and the curves for heating in a nitrogen atmosphere are given in Figure 4.

For thermogravimetric analysis, the maximum rate of decomposition was determined by plotting the first derivative (% wt/min) against temperature. The number of peaks in the derivative plot indicated the number of possible degradation steps.

Thermogravimetric analysis of the thionine–PMDA polyimide indicates that the polyimide can be completely dried by conventional drying techniques at room temperature. The polymer shows a 10% weight loss at 507 °C, with a maximum rate of degradation occurring at 615 °C. This polymer was completely degraded at 745 °C, with no residue remaining at 850 °C. The thionine–PMDA

Table IV. Energy Minimization of Computer Simulated Structures for the Four Thionine-Containing Polyimides[a]

polymer	total energy	internal energy			nonbonding		end-to-end dist (Å)
		bond	angle	torsion	VDW	electro	
thionine + PMDA	651	54.7	401.7	117.7	429.5	−353.4	156
thionine + NTCDA	791	123.7	43.6	168.4	806.8	−352.3	152.6
thionine + BTDA	917	83.1	410.1	197.6	578.9	−352.8	85
thionine + 6FDA	1001	157.2	467.9	131.3	631.0	−389	27.9

[a] The calculation was carried out using the POLYGRAF program available from Molecular Simulations Inc. Energy values are reported in units of kilocalories/mole.

polymer undergoes three competing degradation steps, with maximum degradation occurring at 615 °C. This polyimide when prepared by the reduced temperature, two-step sequence has a slightly reduced thermal stability versus the polymer synthesized via the single step reaction. This difference may be attributed to the difference in the molecular weights of the two polyimides and to the difference in the thermal history of the two polymers. When the polymer was heated under a nitrogen atmosphere, a 10% weight loss was observed at 570 °C, and the maximum rate of decomposition occurred at 665 °C. At a temperature of 850 °C the polymer left a residue amounting to 49% of the starting weight.

Thermogravimetric analysis of the dried thionine–NTCDA polymer indicated that a 10% weight loss of the polymer occurs at 505 °C in air. This polymer also appears to degrade by three closely related degradation steps as indicated by the rate of weight loss curve as a function of temperature. The polymer shows a maximum rate of degradation at 613 °C, with complete degradation at 790 °C. When the thionine–NTCDA polymer was heated under a nitrogen atmosphere, it showed slightly improved stability. The polymer undergoes a 10% weight loss at 527 °C in a nitrogen atmosphere, with a maximum rate of decomposition at 662 °C. A 29% weight loss is undergone by this polyimide at 850 °C in a nitrogen atmosphere.

The thermogravimetric analysis of the thionine–BTDA polyimide showed a 10% weight loss at 539 °C in air. The maximum rate of polymer degradation occurred at 635 °C, with complete degradation at 765 °C and no residue at 850 °C. The curve of polymer degradation as a function of temperature indicated that this polymer degrades by two competitive degradation steps. When the thionine–BTDA polymer was heated in a nitrogen atmosphere, the thermal degradation was slightly retarded. The polymer showed a 10% weight loss at 546 °C, with a maximum rate of decomposition at 679 °C. A 52% solid residue was left when the polymer was heated to 850 °C in a nitrogen atmosphere.

The thionine–6FDA polymer showed a 10% weight loss at 507 °C, with the maximum rate of decomposition in air occurring at 604 °C. The polymer degraded completely at 675 °C, leaving no residue. This polymer also undergoes decomposition by two competitive steps. Initially, a sharp single-step degradation occurs, and then a second slow degradation step commences, with complete degradation occurring by 675 °C. When the thionine–6FDA polymer was heated in a nitrogen atmosphere, a 10% weight loss was observed at 587 °C, with a maximum rate of decomposition at 607 °C. This polymer in a nitrogen atmosphere at 850 °C left a 53% residue. Table III shows the temperature at which a 10% weight loss in air occurs for five tricyclic polypyromellitimides and three other aromatic pyromellitimides. This permits a comparison of the thermal stability of the poly(thioninepyromellitide) with other aromatic polypyromellitimides.

Study of Structure–Property Relationship of Different Polyimides of Thionine. An assessment of the four polyimides containing thionine, with a chloride counterion, and different dianhydride moieties reveals that each polymer has unique solubility characteristics but nearly the same thermal stability. The polyimides having flexible linkers to the dianhydride moieties show better solubility as in the case thionine–BTDA and thionine–6FDA polymers. The polyimide with the 6FDA moiety showed the best solubility characteristics. The polyimide obtained by the reaction of thionine and pyromellitic dianhydride under single-stage polymerization conditions shows poor solubility but better thermal stability than the two-stage chemically cyclized polyimide, in which the chloride ion is replaced by the acetate counterion.

Wide-Angle X-ray Diffraction. The wide-angle X-ray scattering patterns of all these polyimides were taken on powders. The results are shown in Figure 5. The scattering curve for the PMDA-based polyimide showed the highest degree of crystallinity of the four polyimides. The next level of crystallinity, which was somewhat lower, was ascribed to the polyimide incorporating 6FDA. This flexible polyimide was slightly more crystalline than the rigid polyimide obtained from NTCDA. Of the four polyimides, the least crystalline was the one prepared with BTDA.

Computer simulations for all these polyimides were performed using the POLYGRAF program. The energy minimization calculations utilized the Dreiding II force-field parameters. The results are shown in Figure 6a–d and Table IV. We interpret these results as indicating that the four polyimides prefer to organize into a helical type of structure. The polyimides obtained from 6FDA and BTDA have a tendency to assume a geometry with a cavity that can accommodate small molecules, whereas PMDA and NTCDA polyimides assume geometries with effectively no cavity. The calculation for the polyimide obtained from 6FDA assigned it the highest total energy, whereas the calculation for the polyimide obtained from PMDA resulted in an assignment of the lowest total energy. Computer simulation on the polyimide of degree of polymerization of 8 indicated that the polyimide obtained from 6FDA has the lowest value of the end-to-end distance, followed by the BTDA polyimide, the NTCDA polyimide, and finally the PMDA polyimide. This result supports an assignment for the polyimides obtained from PMDA and NTCDA as being nearly rigid rods, whereas the polyimides obtained from 6FDA and BTDA are considered to be highly coiled and flexible.

Refractive Index and Permittivity Determination. The determination of the refractive index and the permittivity of these polyimides required that thin, optically uniform films of these materials be cast on silicon wafers by spin coating. Such films could only be prepared from thionine–PMDA and thionine–BTDA polyimides. Other polyimides formed films that exhibited a characteristic rainbow pattern irrespective of the solvent used. The refractive index of the thionine–PMDA polymer was 1.84, and for the thionine–BTDA polymer it was 1.73. The permittivities for these polymers were 3.386 and 2.993, respectively.

Conclusions

Four new thermally stable polyimides have been synthesized from 3,7-diaminophenothiazinium chloride (thionine) and pyromellitic dianhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, and 1,4,5,8-naphthalenetetracarboxylic dianhydride. Optimum conditions for the synthesis of each polyimide were determined, and the resulting polymers were characterized by solution viscosity, NMR, FTIR, DSC, and TGA studies. The refractive index and permittivities for two of the polymers were determined. These new polymers represent a new class of polyimides with significantly improved thermal stability and solubility over most state-of-the-art polyimides.

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