Synthesis and Characterization of 3,6-Diaminoacridine (Proflavine) Containing Polyimides[†]

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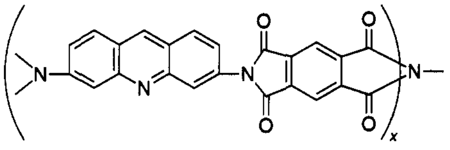
ABSTRACT: The tricyclic heterocyclic molecule 3,6-diaminoacridine (proflavine) has been reacted with the dianhydrides pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and naphthalenetetracarboxylic dianhydride (NTCDA) to yield a new series of polyimides in which the aromatic tricyclic component contains a ring nitrogen atom at position 10. The synthesis of the four polymers was achieved within the temperature range of 185–195 °C and each of the polyimides was characterized with respect to solubility, thermal properties, infrared and UV–visible spectra, refractive index, and permittivity. Uniform, light yellow films of the four polyimides could be cast from appropriate solvents. TGA analysis of these polyimides showed that they were thermally stable up to 600 °C in a nitrogen atmosphere. These polymers exhibited low permittivity values and high refractive indices. All four polymers were soluble in dilute formic acid, in addition to several common organic solvents. Formic acid solutions of the polyimide from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and proflavine exhibited birefringent behavior upon orientation by repeated passage through a viscometer capillary. In contrast to the polymer prepared from 3,7-diaminophenothiazine (thionine) and pyromellitic dianhydride, in which the intermediate poly(amic acid) could be isolated and characterized, the reaction of proflavine and pyromellitic dianhydride did not proceed at sufficiently low temperatures to permit the isolation of the intermediate poly(amic acid).

Introduction

We have previously reported the synthesis and characterization[1] of polyimides from the aromatic tricyclic heterocycle component 3,7-diaminophenothiazine (thionine) and the dianhydrides pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and naphthalenetetracarboxylic dianhydride (NTCDA). The present study reports the synthesis and characterization of a series of polyimides based upon the aromatic tricyclic system 3,6-diaminoacridine, commonly called proflavine, in which the thionine moiety with its ring nitrogen and sulfur atoms in the previous polymers has been replaced by a proflavine molecule containing only the ring nitrogen atom at position 10. The absence of the sulfur atom in the present ring system should decrease the out-of-plane distortion of the three fused rings, facilitating the system conjugation and resulting in facile electron delocalization throughout the molecule. The presence of the lone pair of electrons on the ring nitrogen should promote the solubilization of the polymer in acidic solvents, and the extended conjugation of the system should confer enhanced thermal stability and mechanical properties on these polymers over polyimides that have a less extended aromatic system.

As detailed in our previous publication,[1] the primary amine groups at positions 3 and 6 in proflavine, were allowed to react with phthalic anhydride under a variety of conditions in which temperature and concentration were varied. These experiments provided the most effective reaction conditions for the condensation of proflavine with the anhydride and were subsequently utilized to prepare the polymers from the dianhydrides. The structure for the polymer from proflavine and PMDA is given in structure **I**.



structure **I**

In this paper we report the synthesis and characterization of new polyimides prepared from proflavine and the following dianhydrides: pyromellitic dianhydride (PMDA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA).

Experimental Section

Materials. Proflavine, 3,6-diaminoacridine free base, was prepared from 3,6-diaminoacridine hydrochloride (Aldrich Chemical Co.) by neutralization with a sodium hydroxide solution at 0 °C under a nitrogen atmosphere. The free diamine was then recrystallized from a 70:30 (v/v) ethanol/water mixture and yielded light yellow, needle-shaped crystals; mp 284–5, reported 277 (sealed),[2] and 288 °C.[3] Phthalic anhydride (Mallinckrodt Chemical Co.) was used without further purification. Pyromellitic dianhydride, zone refined grade (Aldrich Chemical Co.), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (PCR Inc.) were used without further purification. The 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (Aldrich Chemical Co.) was purified by sublimation under reduced pressure. The 1,4,5,8-naphthalenetetracarboxylic dianhydride (Aldrich Chemical Co.) was recrystallized from nitrobenzene. All solvents were freshly distilled and were stored over washed and activated, grade 514GT, 4-Å molecular sieves.

Measurements. NMR. All NMR spectra were obtained on a Bruker 360-MHz spectrometer.

UV–VIS, FTIR, and Mass Spectra. UV spectra were recorded on a Varian DMS 300 UV-visible spectrophotometer. FT-IR spectra were recorded on a Nicolet 5-DX FTIR spectro-

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Table 1. Summary of Data Characterizing the Proflavine Polyimide Polymers

									imide group peak positions (in KBr)	
		% C	% H	% N	reaction time (h)	intrinsic viscosity	refractive index	permittivity	asymmetric stretch (cm^{-1})	symmetric stretch (cm^{-1})
proflavine + PMDA	calcd	66.70	3.40	10.78						
$C_{23}H_9O_4N_3 + H_2O + 0.5C_5H_9ON$	found	66.22	3.36	10.07	9	0.213	1.7283	2.987	1777	1724
proflavine + NTCDA	calcd	70.60	2.85	9.15						
$C_{27}H_{11}O_4N_3 + H_2O$	found	70.20	3.35	9.34	10	0.410	1.7866	3.192	1787	1715
proflavine + BTDA	calcd	67.80	3.22	7.91						
$C_{30}H_{13}O_5N_3 + 2H_2O$	found	68.05	3.60	7.90	6	0.105	1.8513	3.427	1781	1728
proflavine + 6FDA	calcd	58.81	2.62	6.43						
$C_{32}H_{13}O_4N_3F_6 + 2H_2O$	found	59.32	3.01	6.43	6	0.123	1.6050	2.576	1786	1729

photometer. Mass spectra and elemental analysis were determined by the analytical laboratory of the Chemistry Department at The University of Michigan.

Viscosity Determinations. Viscometric measurements were performed using Ubbelohde viscometers at a constant temperature of 25.0 ± 0.1 °C. Solvent efflux times through the capillary viscometer were greater than 100 s so that kinetic energy corrections were not required.

TGA Studies. Thermogravimetric analysis was performed either on a Shimadzu thermogravimetric analyzer Model TGA-50 in air at a heating rate of 20 °C/min or on a Perkin-Elmer 7 series thermogravimetric analyzer in air or in nitrogen.

Refractive Index Measurements. Uniform films of approximately 3000–4000 Å were cast on a silicone wafer by spin coating from formic acid solutions for each of the polyimides. The refractive index of the film was measured by ellipsometry using a HeNe laser with the wavelength set at 632 nm.

Computer Modeling of Polyimide Structures. The calculation of the energy minimization of computer-simulated structures for the four proflavine-containing polyimides was carried out using the POLYGRAF program originally available from Molecular Simulations Inc., Burlington, MA, and now merged into Serius[2] at the same address.

Synthesis. Synthesis of 3,6-Diaminoacridine Diphthalimide. Recrystallized 3,6-diaminoacridine (0.318 g, 1.52 mmol) was dissolved in 5 mL of dry, freshly distilled *N*-methyl-2-pyrrolidinone, and phthalic anhydride (0.45 g, 3.04 mmol) was added to this continuously stirred solution. The solution temperature was raised to 195 °C and kept at that temperature for 5 h. The reaction mixture was poured into 150 mL of distilled water. The resulting precipitate was filtered and washed with 100 mL of boiling distilled water and then with acetone, air dried, and then dried in a vacuum oven; yield 87%. The product was recrystallized from dimethylformamide; the mixture darkens at 340 °C and becomes completely brown and melts at 350–353 °C. ^{1}H NMR (DMSO-d_6): δ 7.79 (dd, J = 1.62 and 10.62 Hz), 8.29 (s), 8.35 (d, J = 9.14 Hz), 9.27 (s), 8.00 (multiplet, overlapping phthalimide protons). Infrared spectroscopy: 1786.3 and 1719.9 cm^{-1}. MS: EI 469; partial solubility in methanol, soluble in DMF, DMAc, NMP, and DMSO.

Preparation of the Polyimide. Recrystallized proflavine (0.192 g, 0.917 mmol) was mixed with pyromellitic dianhydride (0.200 g, 0.916 mmol) in a 25-mL round-bottomed flask equipped with a magnetic stirrer. Freshly distilled *N*-methyl-2-pyrrolidinone was added to the mixture to give a solution containing 20% solids. The solution was heated under reflux at 185–187 °C. After the requisite time had elapsed, phthalic anhydride (0.05 g, 0.34 mmol) was added to endcap the polymer. The solution was heated and stirred for an additional hour. The dark-colored viscous liquid was poured into 500 mL of well-stirred, hot distilled water. The mixture was boiled and filtered while hot, and the collected precipitate was repeatedly washed with 200-mL portions of boiling water. A final wash with 10 mL of acetone removed any adhering water. The polymer was dried in a vacuum oven at 50 °C for 20 h; yield 87%.

The polyimides from proflavine and the other dianhydrides were prepared using the procedure given above.

Results and Discussion

The reactivity of the amino groups at positions 3 and 6 of proflavine with anhydrides was assessed by reacting proflavine free base with phthalic anhydride to give the bis(phthalic diimide). Under the initial low-temperature reaction conditions, all attempts at preparing the bis(amic acid) intermediate failed. The NMR spectra of the reaction products prepared at lower temperatures of 4 and 45 °C revealed that only one of the two amino groups had reacted with the phthalic anhydride. At higher temperatures of 100 and 145 °C the reaction yielded a small quantity of the bis(phthalic diimide). At a temperature of 185 °C the bis(phthalic diimide) was obtained in 87% yield.

This behavior differs significantly from that observed in the reaction of thionine with phthalic anhydride and with pyromellitic dianhydride.[1] We can rationalize, in part, the unequal reactivity of one of the two amino groups of the proflavine molecule on the basis of the respective pK_a values[4] of the conjugate acids. The reported value for the dissociation of the first proton from an amino group in proflavine is 1.5, demonstrating that this proton behaves like a semistrong acid. The pK_a value for the second proton is 9.65, demonstrating that this amino group functions as a moderate base. These values indicate that, after reaction at the first amino group, the resulting product is a weak base, making it very difficult for the second amino group to react. Raising the temperature forces the second amino group to react with the anhydride, but the elevated temperature does not permit the isolation of the amic acid. It drives the reaction to completion and results in the formation of the bis(phthalic diimide). In our studies with thionine, the reaction with phthalic anhydride or with pyromellitic dianhydride occurred at a lower temperature, and the intermediate amic acid could be isolated.

Synthesis of Polyimides from Proflavine. The synthesized polyimides were end capped with phthalic anhydride in order to reduce the reactivity of the polymers and to avoid the introduction of cross-linking reactions that occur at elevated reaction temperatures. All of the polymerizations were carried out in *N*-methyl-2-pyrrolidinone as the solvent. In order to avoid side reactions, a minimum amount of solvent was used, and because of the increase in viscosity as the polymerization proceeded, optimum mixing of the reactants peaked at a 20% solids content.

Effect of Reaction Time on the Polymer Molecular Weight. A significant factor contributing to maximizing the molecular weight of the polyimides was the reaction time. By studying the polymerization at four different reaction times but under otherwise identical conditions, it was possible to establish the length of time during which the polymerization yielded the highest molecular weights. Table 1 summarizes the optimum reaction times and the corresponding polymer intrinsic viscosity values. In our previous study, using thionine as the diamine and PMDA or NTCDA as the anhydride, it was possible to run the reaction for a shorter period

Table 2. Tabulation of the Results of the Energy Minimization Runs on the Proflavine Polyimides[a]

polymer	total energy	internal energy bond	angle	torsion	nonbonding VDW	end-to-end distance (Å)
proflavine + PMDA	1028	76.5	383.6	82.5	484.6	145.2
proflavine + NTCDA	1196	144.1	17.5	157.6	875.8	138.4
proflavine + BTDA	1320	96.8	379.5	219.6	623.6	47.2
proflavine + 6FDA	1379	165.7	436.0	140.8	635.0	27.8

[a] All energy values are in kcal/mol. Energy minimization was performed using POLYGRAF Program by Molecular Simulations, Inc.

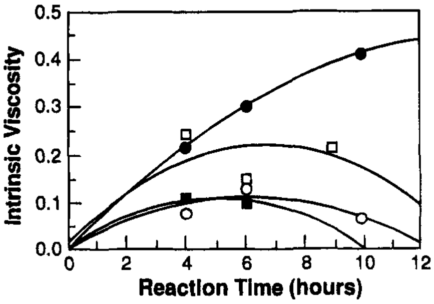

Figure 1. Effect of reaction time on the intrinsic viscosity of proflavine polyimides: (□) proflavine + pyromellitic dianhydride; (●) proflavine + naphthalenetetracarboxylic dianhydride; (■) proflavine + benzophenonetetracarboxylic dianhydride; (○) proflavine + 4,4′-(hexafluoroisopropylidene)diphthalic anhydride.

of time, 4.25 and 7.5 h, and obtain intrinsic viscosities significantly greater than those obtained with proflavine. A plot of intrinsic viscosity versus reaction time reveals a reduction in the intrinsic viscosity after exceeding a specified reaction time (Figure 1). This is interpreted as indicating that some depolymerization of the polymer has occurred. This factor limited the reaction time of proflavine with BTDA and 6FDA to 6 h in contrast to the 10 h that was possible when thionine was the diamine. As a consequence, the intrinsic viscosities were lower for the proflavine–BTDA and –6FDA polymers relative to the analogous thionine polymers. The polyimide obtained from NTCDA and proflavine had the highest intrinsic viscosity of the four polymers prepared in the present study. This polymer is considered to behave as a rigid rod, whereas polyimides obtained from BTDA and 6FDA have much lower intrinsic viscosities since they are more flexible and can approach a coiled structure. The polyimide from proflavine and PMDA had an intrinsic viscosity of half that of the NTCDA-containing polymer but twice as large as the BTDA and 6FDA polymer. A search of the literature on the viscosity of polyimide solutions resulted in the finding that in those instances where a viscosity was reported it was an inherent viscosity taken at a single concentration that varied from polymer to polymer with respect to the concentration and solvent used. Our reported values of intrinsic viscosity are not inconsistent with the reported inherent viscosities for other tricyclic polyimides with heteroatoms at positions 9 and 10. The polyimide synthesized from 4,4′-diaminodiphenyl ether and benzophenonetetracarboxylic dianhydride in a poly(phosphoric acid) solvent at 160 °C had an inherent viscosity in a concentrated sulfuric acid solvent of 0.04 dL/g. Increasing the polymerization temperature resulted in a polymer with an increase in its inherent viscosity.[10]

The polymer structures were modeled using the POLYGRAF computer simulation program. Simulations were performed using a hypothetical oligomeric chains of degree of polymerization 10 and using Dreiding II force field parameters. Results of computer simulations are reported in Table 2. All of the polymer model structures had a preference toward helical forms. More flexible polyimides obtained from proflavine and 6FDA or proflavine and BTDA preferred to model as helices with a central empty core, whereas more rigid polyimides, viz., proflavine–PMDA or proflavine–NTCDA tend to model as helices without a central cavity. These results parallel our findings with the thionine polyimides.[1]

Table 3. GPC Results of 6FDA and NTCDA Polyimides[a]

mol wt[b]	6FDA polyimide	NTCDA polyimide
number average	35807	22587
weight average	75315	52283
Z average	101582	66632
viscosity average	75315	52283
Z + 1 average	126180	75580
peak mol wt	75754	65183
dispersity	2.103	2.315
Z avg/wt avg	1.349	1.274
Z + 1 avg/wt avg	1.675	1.446

[a] Solvent: 1,1,1,3,3,3-hexafluoro-2-propanol. [b] With reference to poly(ethylene terephthalate) standards.

The prediction of chain conformation is possible using intrinsic viscosity data and molecular weight values. As indicated above, the intrinsic viscosities obtained for highly rigid polyimides were larger than the intrinsic viscosities of the flexible and coiled polyimides. It was possible to obtain estimates of the molecular weights for the proflavine–NTCDA and proflavine–6FDA polyimides in 1,1,1,3,3,3-hexafluoro-2-propanol using a GPC column calibrated to a poly(ethylene terephthalate) standard. These results are given in Table 3. When comparing the molecular weights obtained from the GPC data with the values of intrinsic viscosity, it is necessary to keep in mind that the GPC was run in a hexafluoro-2-propanol solvent whereas the viscosities were determined in a formic acid solvent and also that the calibration of the GPC was based on poly(ethylene terephthalate) standards. The anticipation of larger intrinsic viscosity values for these polymers relative to the GPC molecular weight values is observed for the proflavine–NTCDA polymer but not for the more flexible proflavine–6FDA polymer. However, the viscosity values that were observed are not inconsistent with values reported for a pregel type polymer system reported by Aharoni.[5] Formic acid is known to be a strong protonating reagent for many amide type polymer systems. If these polymers tend to be in coiled structures in formic acid and more extended and rodlike structures in hexafluoro-2-propanol, then the apparent discrepency can be rationalized. At concentrations above 1.5% the polymer chain orientation is imposed as the solution flows through the viscometer capillary. However, the viscosity measurements are made below this concentration and the polymer remains largely in a spherical shape, leading to diminished values of intrinsic viscosity.

Characterization and Solubility Properties of Polyimides. FTIR spectroscopy of the polymers revealed the presence of bands in the region of 1720 and 1780 cm^{-1}, confirming the presence of imide groups. The

Table 4. Tabulation of the Solubility Behavior of the Proflavine Polyimides in Various Solvents[a]

polymer	condition	acet	MeOH	DMF	DMAc	NMP	DMSO	HCOOH	MSA	H_2SO_4
proflavine + PMDA	R.T. (immed)	insol	insol	sl sol	sl sol	sl sol	sl sol	im sol	im sol	im sol
	R.T. (10 min)	insol	insol	sl sol	sl sol	sl sol	sl sol	en sol	en sol	en sol
	heat	insol	insol	sl sol	sl sol	sl sol	sl sol			
proflavine + NTCDA	R.T. (immed)	insol	insol	sl sol	sl sol	sl sol	sl sol	sl sol	sl sol	sl sol
	R.T. (10 min)	insol	insol	sl sol	sl sol	sl sol	sl sol	en sol	en sol	en sol
	heat	insol	insol	sl sol	sl sol	sl sol	sl sol	sol	sol	sol
proflavine + BTDA	R.T. (immed)	insol	insol	sl sol	sl sol	sl sol	sl sol	im sol	im sol	im sol
	R.T. (10 min)	insol	insol	sl sol	sl sol	sl sol	im sol	en sol	en sol	en sol
	heat	insol	insol	sl sol	sl sol	sl sol	im sol	sol	sol	sol
proflavine + 6FDA	R.T. (immed)	sl sol	sl sol	sol	sol	sol	sol	sol	sol	sol
	R.T. (10 min)	sl sol	sl sol							
	heat	sl sol	sl sol							

[a] sol = soluble; sl sol = slightly soluble; im sol = improved solubility; en sol = enhanced solubility. sol > en sol > im sol> sl sol > insol. R.T. (immed) = room temperature, immediately after addition of solvent. R.T. (10 min) = room temperature, 10 minutes after addition of solvent. heat = solubility after heating polymer and solvent. acet = acetone; MeOH = methanol; DMAc = dimethylacetamide; DMSO = dimethyl sulfoxide; DMF = dimethylformamide; NMP = 1-methyl-2-pyrrolidinone; HCOOH = formic acid; MSA = methanesulfonic acid.

absence of bands in the regions of 1802–1812 and 1692–1709 cm^{-1} suggests the absence of a measureable concentration of isoimide bonds.[6] The asymmetric and symmetric band frequencies are provided in Table 1.

A qualitative solubility table for these polymers in various solvents is given in Table 4. The polyimide containing the fluorine atoms in the molecule of dianhydride has enhanced solubility in many common organic solvents, relative to the three other polyimides. In contrast, the polyimides synthesized with PMDA or NTCDA and proflavine are sparingly soluble in common organic solvents and dissolve completely only in formic acid, methanesulfonic acid, and sulfuric acid. The polyimide prepared from BTDA and proflavine dissolves to a slightly greater degree in some common organic solvents than do the polyimides obtained from PMDA or NTCDA and proflavine. However, complete dissolution occurs only in formic and sulfuric acids. The reduced solubility of the proflavine polyimides in many of the common organic solvents relative to the thionine polyimides was unexpected. This behavior is rationalized, in part, to the presence of charge on the thionine moiety and to the rigidity of the polymeric chains. Polymers prepared with 6FDA have a flexible aliphatic isopropyl group, with the fluorine atoms contributing to the polymer chain flexibility and possibly entering into hydrogen-bonding interactions via the keto groups in the polymer and hydrogens of the solvent. Chain flexibility facilitates solvation, whereas polyimides synthesized with PMDA or NTCDA are very rigid, solvation of the polymer chain is not facile, and the solubility is poor. Another contrast between the proflavine and thionine polymer systems is that the proflavine polyimides are completely soluble in formic acid, whereas the charge-bearing thionine polyimides were insoluble in this weak acid solvent.

Solution Behavior. Upon passage of the polymer solution through the narrow bore capillary of the Ubbelohde viscometer, it was observed that the polyimide obtained from benzophenonetetracarboxylic dianhydride and proflavine exhibited anomalous solution behavior. For a 1.4% solution of the polymer in formic acid, the solution initially showed normal behavior upon flowing through the viscometer capillary. When the process was repeated several times at each particular concentration, the reduced specific viscosity value increased each time the measurement was made. When the experiment was repeated at higher polymer concentrations, the same behavior was observed. In order to determine the flow time for a polymer solution, repetition of the flow through the viscometer at the same concentration was repeated until three consecutive constant readings were obtained. The results indicated that, as the concentration is reduced, the reduced specific viscosity rises to a maximum at a concentration of 1.5% and then begins to decrease. Several explanations for this behavior are possible. Such behavior is consistent with a polyelectrolyte effect, the formation of aggregates, or the formation of a lyotropic liquid crystalline system. When a viscosity measurement was performed with a 2% polymer solution, the solution formed a gel in the upper viscometer bulb after a single passage through the viscometer capillary. The measurement of the viscosity in a very dilute formic acid solution of the same polymer resulted in uniform, but low, reduced viscosity readings.

Films cast from a highly viscous, gellike solution presented a greater number of birefringent areas in the film than the film cast from the dilute polymer solution (<0.5%), indicative of a strong orientation of the molecules either in a linear fashion or into crystalline domains in the gelled sample. The behavior is explicable by the following argument:

The polyimide obtained from benzophenonetetracarboxylic dianhydride and proflavine in a formic acid solvent, at any concentration, is an isotropic solution. The solution at concentrations less than 1% remains isotropic. A solution at a concentration greater than 1% is only partially isotropic but becomes anisotropic as a consequence of polymer chain alignment upon evaporation of the solvent and further organization of the polymer chains giving rise to strain birefringence as the film dries. It is also possible for such a structure to organize itself to achieve a liquid crystalline state which would also account for the observed birefringence. The presence in various polyimides of crystallinity and spherulites is documented in the literature.[7,8]

TGA Assessment of Proflavine Polyimides. All four proflavine polyimides showed good thermal stability in air and under nitrogen as revealed by TGA studies (Figures 2 and 3). The proflavine–pyromellitic dianhydride polymer showed a 10% weight loss in air at 539 and 619 °C in nitrogen, while the contrasting polymer containing thionine had a 10% weight loss at 507 °C in air and at 570 °C under nitrogen. Similarly the proflavine–naphthalenetetracarboxylic dianhydride polymer showed a 10% weight loss at 590 °C in air and 629 °C under nitrogen, while the analogous thionine polymer showed a 10% weight loss at 505 °C in air and at 527 °C under nitrogen. The proflavine polyimides containing 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride

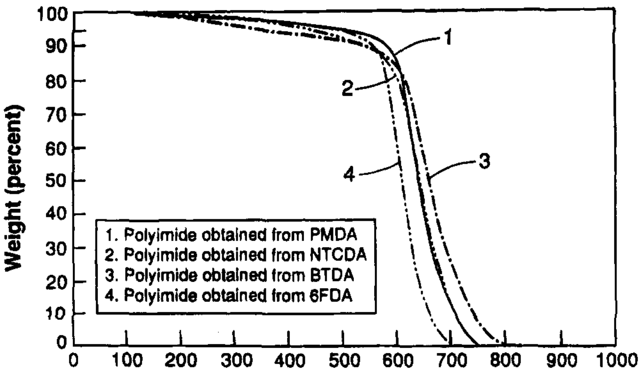

Figure 2. TGA curves of the four proflavine polyimides in an air atmosphere.

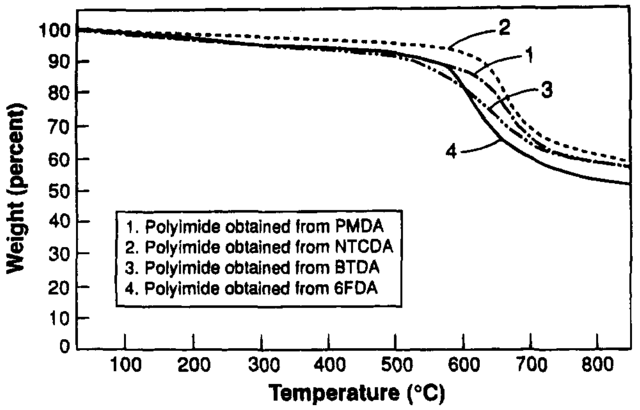

Figure 3. TGA curves for the four proflavine polyimides in a nitrogen atmosphere.

showed 10% weight loss at 535 and 559 °C in air and at 590 and 592 °C under nitrogen. The equivalent thionine polymer temperatures for 10% weight loss were 539 and 507 °C in air and 546 and 582 °C under nitrogen. For most of the proflavine polymers the temperature at which a 10% weight loss occurred in air or under nitrogen was significantly higher. The temperature at which the maximum weight loss occurred tended to be much closer and centered at about 625 °C in air and at 660 °C under nitrogen, but the proflavine polymers still tended to be somewhat more stable. Even at 850 °C under nitrogen the residual residue for the proflavine polyimides ranged from 3% to 25% higher than that for the thionine polyimides. This is a further indicator of the somewhat enhanced thermal stability for these polyimides. A reasonable explanation for the enhanced stability is that the carbon–sulfur bond in thionine is a weaker bond than the carbon–carbon bond in proflavine and fragments at a lower temperature. This begins the degradation and the fragmentation of the thionine-containing polymer chains at a lower temperature than the proflavine-containing polymers. In a reported study[11] of polyimides containing 2,7-diaminothianthrene and 2,8-diaminothianthrene units with pyromellitic dianhydride and benzophenonetetracarboxylic dianhydride the temperature at which a 10% weight loss occurred was in the region of 465–468 °C. This temperature is between 125 and 150 °C lower than that of the polyimides with the same dianhydride and proflavine. The authors attributed the reduced thermal stability to the out-of-plane distortion between the two aromatic rings caused by the sulfur heteroatom and the reduced bond stability that results from the reduced electron delocalization through the heteroatom center ring.

Refractive Index and Permittivity Measurements. The results of the refractive index and dielectric constant determinations by ellipsometry are summarized in Table 1. The results obtained showed that the proflavine–6FDA polyimide had the lowest refractive index of 1.6050 and a permittivity of 2.576, whereas the proflavine–BTDA polyimide had the highest refractive index of 1.851 and a permittivity of 3.427. The analogous thionine–BTDA polyimide had a refractive index of 1.73 and a permittivity of 2.993 which was comparable to the proflavine–PMDA polyimide. These values of permittivity are comparable to the dielectric constant values of other commercially available polyimides.[9]

Conclusion

In an extension of an earlier study, four new polyimides based on proflavine and the dianhydrides pyromellitic dianhydride, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, and naphthalenetetracarboxylic dianhydride were synthesized and characterized. These polyimides were found to have an improved thermal stability over similar polyimides containing the thionine moiety. This improved stability is attributed in part to the greater degree of planarity of the tricyclic ring system that has only a single ring nitrogen atom and to the absence of the weaker carbon–sulfur bond relative to the carbon–carbon bond in the center ring. The easier carbon–sulfur bond cleavage and possible generation of an additional fragment from thionine compared to proflavine would increase the entropy for the fragmentation reaction and help to drive the polymer decomposition. The polyimide of PMDA and diaminothianthrene is reported[10] to show a 10% weight loss in air at 420 °C. This is 90 °C lower than the polyimide from PMDA and thionine.

Computer modeling of the polyimides suggests that the proflavine–PMDA and –NTCDA polyimides have stiff, extended chain type structures, while the BTDA AND 6FDA polyimides form rather loose helices possessing a cavity down its central axis. The low values of the permittivity and the high refractive indices suggest that these materials may find application in the area of nonlinear optics and high-temperature electrical insulation.

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References and Notes

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