Polyimides Based on 9,9-Disubstituted Xanthene Dianhydrides

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ABSTRACT: The preparation of a range of 9,9-disubstituted xanthene dianhydrides is discussed, as is their use in the preparation of poly(amic acid)s and polyimides. Groups in the 9,9-positions include various combinations of phenyl, substituted phenyl, methyl, ethyl, butyl, trifluoromethyl, perfluoroethyl, perfluoropropyl, cyclotetramethylene, cyclopentamethylene, hydroxy, and acetoxy. Polyimide films prepared from some of these new dianhydrides exhibit good mechanical properties, lower dielectric constant, lower moisture absorption, and low coefficient of thermal expansion, demonstrating their potential use in electronic applications. In addition, these new materials may find use in other film, fiber, and part applications.

Introduction

In previous publications we have disclosed our work in the field of rigid, fluorinated dianhydrides.[1-3] The goal of this work has been to prepare fluorinated polyimides with a nearly rodlike backbone structure in order to obtain materials with an ideal combination of low dielectric constant, low moisture absorption, and low coefficient of thermal expansion. Such materials are prime candidates for electronics applications like interlayer dielectrics in integrated circuits because the combination of improved electrical properties and low stress allows for further miniaturization and higher speed in devices. Our earlier work largely involved rigid xanthene dianhydrides which were substituted in the 9-position with either trifluoromethyl groups or phenyl and trifluoromethyl groups. Combination of these dianhydrides with rigid fluorinated diamines indeed showed the ability to achieve a good combination of the desired properties mentioned above.

As a follow-up to this work, we were interested in exploring the nonfluorine-containing analogs of these xanthene dianhydrides, as well as other fluorinated and partially fluorinated analogs of this basic structure. It was also of interest to compare the properties of the polyimides from these nonfluorinated and partially fluorinated xanthene dianhydrides to the fluorinated ones of the earlier work and determine their suitability for electronics applications. A fair number of new dianhydrides and their precursors was prepared, and the thermal, physical, and electrical properties of polyimides derived from some of these dianhydrides were investigated.

Experimental Section

Materials. The synthesis of the rigid dianhydrides 9,9-bis(trifluoromethyl)xanthenetetracarboxylic dianhydride (6FCDA) and 9-phenyl-9-(trifluoromethyl)xanthenetetracarboxylic dianhydride (3FCDA) was described in previous publications.[1,2] The acronyms for these dianhydrides (and others within the text) were chosen to be consistent with the known nonrigid 6FDA and 3FDA compounds. The 4,5,4′,5′-dioxydiphthalic anhydride[4] was graciously provided by Oxychem. All dianhydrides were dried at 150-180 °C under vacuum/N_2 bleed prior to use.

The diamines 4,4′-oxydianiline (ODA), *p*-phenylenediamine (PPD), diaminodurene (DAD), and 2,2′-dimethylbenzidine (DMB) were obtained in high purity from sources within DuPont. The 2,2′-bis(trifluoromethyl)benzidine (TFMB; Marshallton) was sublimed and recrystallized from toluene prior to use. Bis(4-aminophenyl)hexafluoropropane (6FDAm, Chriskev) and 3,3′,5,5′-tetramethylbenzidine (TMB; Aldrich, 99+%) were used without further purification. All the diamines were dried at 50-80 °C under vacuum/N_2 bleed prior to use.

Dixylyl ether (DXE) was prepared by a literature method.[5] Perfluoroalkyl phenyl ketones were purchased from Fairfield Chemical Co. and the other ketones from Aldrich. *N*-Methylpyrrolidinone (NMP) was anhydrous grade from Aldrich. *N*-Cyclohexylpyrrolidinone (CHP; Aldrich) was distilled from CaH_2. Tetrachloroethane (TCE; Kodak) was used as received. Other solvents/reagents were reagent-grade materials and were used as received.

9,9-Diphenyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (PPXDA) and Its Derivatives. a. 9,9-Diphenyl-2,3,6,7-tetramethylxanthene (TMPPX). A mixture of 90.4 g (0.4 mol) of dixylyl ether (DXE), 72.9 g (0.4 mol) of benzophenone, and 160 g (8 mol) of HF was heated in a shaker tube for 8 h at 90 °C. After cooling and aspirating off excess HF, the tube contents were transferred to a 4-L polyethylene jar, half-filled with ice and containing 500 mL of a 50% sodium hydroxide solution. The mixture was extracted with 3 L of methylene chloride, the extracts were filtered through a 5-cm bed of basic alumina, and methylene chloride was distilled out. The still-hot, pastry orange residue was stirred with 500 mL of hexane, and the product was isolated by filtration. It was washed thoroughly with hexane and was air-dried, yielding a total of 98 g (62.8%) of a pale yellowish solid. The product was purified by sublimation, followed by recrystallization from octane. Mp: 228-229 °C. The NMR spectrum was correct for the structure: a multiplet at 7.22 ppm, a doublet of doublets at 7.03 ppm, and singlets at 6.91, 6.62, 2.23, and 2.12 ppm in a 6:4:2:6:6 ratio. Anal. Calcd for $C_{29}H_{26}O$: C, 89.2; H, 6.67. Found: C, 89.2; H, 6.96.

In another experiment, when the reaction was run at 140 °C, no TMPPX was obtained, and the only product isolated was 9-phenyl-9-hydroxy-2,3,6,7-tetramethylxanthene.

When the reaction was run at 120 °C, TMPPX was obtained, but it was contaminated with 9-phenyl-9-hydroxy-2,3,6,7-tetramethylxanthene, 9-phenyl-2,3,6,7-tetramethylxanthene, and 9-phenyl-9-methoxy-2,3,6,7-tetramethylxanthene (the last compound was obtained when methanol was used during the workup).

b. 9,9-Diphenyl-2,3,6,7-xanthenetetracarboxylic Acid (PPXTA) and 9,9-Diphenyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (PPXDA). *Note*: The oxidation procedure described below is the one used throughout the subsequent experiments. It is based on the procedure published by Marvel and Rassweiler[6] and will be referred to as the "Marvel/Rassweiler" method.

A sample of 78 g (0.2 mol) of 9,9-diphenyl-2,3,6,7-tetramethylxanthene was refluxed in a mixture of 1600 mL of pyridine and 800 mL of water with rapid mechanical stirring, and 210 g (1.33 mol) of potassium permanganate was added in portions through the top of the condenser. After addition was complete, the mixture was refluxed for 1 h. It was then filtered through Celite, and the filtrate was concentrated down to about 300-400 mL. Then 700 mL of water and 250 mL of a 50% sodium hydroxide solution were added, and the solution was brought to reflux and oxidized again with 200 g of potassium permanganate. After the

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second oxidation, excess permanganate was destroyed by the addition of isopropyl alcohol, the mixture was filtered through Celite, and the filtrate was acidified with concentrated sulfuric acid. This produced a white precipitate which was filtered, washed thoroughly with copious amounts of water, and air-dried overnight. It was obtained in a 100-g (98%) yield and was converted directly to the dianhydride PPXDA.

All the above PPXTA was boiled for 10 min in 500 mL of acetic anhydride, and the solution was then stripped to dryness at house vacuum. The cooled residue was dissolved in 500 mL of methylene chloride, stirred with two spoonfuls of Darco, and filtered through Celite. The filtrate was added dropwise to 400 mL of boiling toluene, so that most of the methylene chloride distilled out, and a crystalline solid separated. It was isolated by filtration and was washed with toluene and finally with hexane. After drying there was obtained 72.5 g (76.5%, based on TMPPX) of crystalline material with anhydride peaks at 1850 and 1780 cm^{-1} in the IR. The NMR was confirmatory with singlets at 7.85 and 7.68 ppm and multiplets at 7.36 and 7.87 ppm in a 1:1:3:2 ratio. By DCS the purity was 99.5%, and mp was 316 °C. Anal. Calcd for $C_{29}H_{14}O_7$: C, 73.4; H, 2.95. Found: C, 73.1; H, 3.30.

In a scale-up of the above reaction, three runs like the one above were combined and processed together, yielding a total of 232 g of dried PPXDA (82% based on TMPPX). As an additional structure confirmation and proof of ease of imidization, three bisimide derivatives were prepared.

c. 9,9-Diphenyl-2,3,6,7-xanthenetetracarboxylic Bis(*p*-anisidylimide). A mixture of THF solutions of 4.74 g (0.01 mol) of PPXDA and 3.0 g (excess) of *p*-anisidine was stripped to dryness, and the residue was heated progressively to 245 °C and kept there for 1 h. After cooling, the product was extracted with methylene chloride, and the extracts were chromatographed on alumina. The yellow eluate was stripped, yielding the bis(anisidylimide) as a pale yellow solid, which was very insoluble and did not melt up to 310 °C. The NMR (ppm) was confirmatory: 7.78 (s), 7.58 (s), 7.34 (m), 7.32 (d), 7.03 (d), 6.96 (m), and 1.62 (b s) in a 1:1:3:2:2:2:3 ratio. Anal. Calcd for $C_{43}H_{28}N_2O_7$: C, 75.4; H, 4.05; N, 4.05. Found: C, 75.0; H, 4.16; N, 4.00.

d. 9,9-Diphenyl-2,3,6,7-xanthenetetracarboxylic Bis(butylimide). A mixture of THF solutions of 4.74 g (0.01 mol) of PPXDA and 2 g (excess) of butylamine was stripped to dryness, and the residue was heated gradually to 245 °C. After cooling, the residue was taken up in methylene chloride and was chromatographed on alumina. The eluate was stripped and triturated with isopropyl alcohol, yielding a white solid which was isolated by filtration and was obtained after air-drying in a 4.3-g (74%) yield. IR: 1765, 1715 (vs) cm^{-1}. NMR 7.66 (s), 7.46 (s), 7.31 (m), 6.92 (m), 3.67 (t), 1.65 (sextet), 1.37 (sextet), 0.94 (t) ppm in a 1:1:3:2:2:2:2:3 ratio. Mp: 237–238 °C. Anal. Calcd for $C_{37}H_{32}N_2O_5$: C, 75.6; H, 5.45; N, 4.77. Found: C, 75.2; H, 5.47; N, 4.87.

e. 9,9-Diphenyl-2,3,6,7-xanthenetetracarboxylic Bis(*p*-tolylimide). This derivative was prepared as above, but using *p*-toluidine, and it was obtained as a pale creamy solid, not melting up to 345 °C. IR: 1775, 1720 (vs) cm^{-1}. NMR: 7.78 (s), 7.30 (s, compressed A_2B_2 pattern), 7.25–7.40 (m), 6.97 (m), 2.40 (s) ppm in a 2:2:8:6:4:6 ratio. Anal. Calcd for $C_{43}H_{28}N_2O_5$: C, 79.1; H, 4.29; N, 4.29. Found: C, 77.6; H, 4.45; N, 4.08.

9-Phenyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (MPXDA) and Its Derivatives. a. 9-Phenyl-2,3,6,7,9-pentamethylxanthene. A mixture of 113 g (0.5 mol) of DXE, 60 g (0.5 mol) of acetophenone, and 200 g (10 mol) of HF was heated in an autoclave, for 8 h at 75 °C. After distilling off excess HF, the autoclave contents were transferred to a 4-L polyethylene jar, half-filled with ice water and containing excess sodium hydroxide. The product was extracted with methylene chloride, the extracts were filtered through Celite and then through a bed of alumina, and the eluate was stripped to dryness. Boiling of the residue with isopropyl alcohol and cooling gave the product, mp 185–187 °C (from heptane), in a 73-g (45%) yield. NMR: 7.10–7.35 (m), 6.86 (s), 6.55 (s), 2.20 (s), 2.05 (s), 1.89 (s) ppm in a 5:2:2:6:6:3 ratio. Anal. Calcd for $C_{24}H_{24}O$: C, 87.8; H, 7.32. Found: C, 87.9; H, 7.14.

b. 9-Phenyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Acid and 9-Phenyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (MPXDA). A 65.6-g (0.2-mol) batch of 9-phenyl-2,3,6,7,9-pentamethylxanthene was oxidized by the Marvel/Rassweiler method. Crude 9-phenyl-9-methyl-2,3,6,7-tetracarboxylic acid was obtained, after drying, in a 63-g (76%) yield. It was boiled in 350 mL of acetic anhydride until a clear solution resulted, which was filtered to remove a small amount of solid. The filtrate was stripped at reduced pressure down to a thick slurry, which was boiled with 250 mL of toluene and then cooled, and the dianhydride was obtained in a 47.8-g yield (58.0% based on the tetramethyl precursor) as a pale creamy solid. It was recrystallized from anisole. Mp: 280 °C (by DSC at 99.1% purity).

In another experiment, the dianhydride was obtained in 65.3% yield by treating the dried tetraacid with thionyl chloride in chloroform. The dianhydride is soluble in chloroform, yielding a confirmatory NMR spectrum: 7.82 (s), 7.52 (s), 7.48–7.58 (m), 7.51 (dd), 2.02 (s) ppm in a 2:2:3:2:3 ratio. It was characterized as the bis(propylimide) and bis(*p*-tolylimide).

c. 9-Phenyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Bis(propylimide). Mp: 215–217 °C. IR: 1760, 1705 (vs), 1620 cm^{-1}. NMR: 7.63 (s), 7.30–7.45 (overlapped by m, phenyl), 3.61 (t), 2.01 (s), 1.67 (sextet), 0.94 (t) ppm in a 2:2:5:4:3:4:6 ratio.

d. 9-Phenyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Bis(*p*-tolylimide). Mp: 302–303 °C. IR: 1770, 1715 (vs) cm^{-1}. NMR: 7.66 (s), 7.47 (s), 7.28 (s, compressed A_2B_2 pattern), 7.2–7.4 (m), 2.39 (s), 2.02 (s) ppm in a 2:2:8:5:6:3 ratio. Anal. Calcd for $C_{38}H_{26}N_2O_5$: C, 77.3; H, 4.41; N, 4.73. Found: C, 76.4; H, 4.57; N, 4.61.

9,9-Dimethyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (MMXDA) and Its Derivatives. a. 2,3,6,7,9,9-Hexamethylxanthene. A mixture of 45.2 (0.2 mol) of DXE, 14 g (0.24 mol) of acetone, and 80 g (4 mol) of HF was heated in an autoclave for 8 h at 90 °C. After removal of excess HF, the residue was transferred to a 4-L polyethylene jar half-filled with ice water and containing excess sodium hydroxide. The product was extracted with methylene chloride, and the extracts were passed through a bed of Celite and alumina and were stripped and distilled in vacuo, collecting a material with bp 130–162 °C (0.9 Torr). After recrystallization from octane the product melted at 126–128 °C and was obtained in a 9.6-g (18%) yield. NMR: 7.12 (s), 6.80 (s), 2.22 (s), 2.19 (s), 1.59 (s) ppm in a 2:2:6:6:6 ratio. Anal. Calcd for $C_{19}H_{22}O$: C, 85.7; H, 8.27. Found: C, 85.5; H, 8.24.

In another experiment, where the reaction temperature was 95 °C, the product [bp 160–180 °C (2.5 Torr)] was obtained, after recrystallization from isopropyl alcohol, in 35.5% yield.

b. 9,9-Dimethyl-2,3,6,7-xanthenetetracarboxylic Acid and 9,9-Dimethyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (MMXDA). The oxidation of 2,3,6,7,9,9-hexamethylxanthene was done by the Marvel/Rassweiler method. The crude tetraacid was converted directly to the dianhydride by refluxing in excess acetic anhydride. The first crop was obtained as a white solid in 30% yield; from the filtrate another 15% was isolated. MMXDA had mp 391 °C (by DSC at 98.2% purity) with a sharp IR [1845, 1770 (vs, br) cm^{-1}]. It was characterized as the bis(propylimide) and bis(*p*-tolylimide) derivatives.

c. 9,9-Dimethyl-2,3,6,7-xanthenetetracarboxylic Bis(propylimide). This compound was prepared from the crude dianhydride by refluxing it with excess propylamine in THF, stripping the solvent and heating the residue to 240 °C, cooling to room temperature, dissolving the residue in methylene chloride, and chromatographing on alumina. The white solid had mp 228–229 °C. IR: 1765, 1705 (vs) cm^{-1}. NMR: 7.98 (s), 7.56 (s), 3.67 (t, NCH_2), 1.78 (s, 9-CH_3), 1.73 (sextet, $CH_2\mathit{CH_2}CH_3$), 0.97 (t, CH_3) ppm in the correct 2:2:4:6:4:6 ratio.

d. 9,9-Dimethyl-2,3,6,7-xanthenetetracarboxylic Bis(*p*-tolylimide). This compound was prepared similarly, using *p*-toluidine; no mp up to 340 °C. IR: 11770, 1715 (vs) cm^{-1}. NMR: 8.07 (s), 7.62 (s), 7.30 (s, compressed A_2B_2 pattern), 2.42 (s), 1.78 (s) ppm in a 2:2:8:6:6 ratio. Anal. Calcd for $C_{33}H_{24}N_2O_5$: C, 75.0; H, 4.55; N, 5.30. Found: C, 73.5; H, 4.59; N, 5.14.

9-Ethyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (EMXDA) and Its Derivatives. a. 9-Ethyl-2,3,6,7,9-pentamethylxanthene. A mixture of 113 g (0.5 mol) of DXE, 36 g (0.5 mol) of 2-butanone, and 200 g (10 mol) of HF was kept in an autoclave at 105 °C for 6 h. After the usual processing, the product [bp 165 °C (1.3 Torr)] was obtained in a 32-g (23%) yield. Mp: 144–146 °C (from octane). NMR: 7.03 (s), 6.79 (s), 2.22 (s), 1.86 (q), 1.63 (s), 0.52 (t) ppm in a 2:2:12:2:3:3 ratio. Anal. Calcd for $C_{20}H_{24}O$: C, 85.7; H, 8.57. Found: C, 84.9; H, 8.22.

b. 9-Ethyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Acid and 9-Ethyl-9-methyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (EMXDA). The pentamethyl precursor from the preceding experiment (41 g, 0146 mol) was oxidized by the Marvel/Rassweiler method, and the crude tetraacid was obtained, after air drying, in a 35-g (60%) yield. It was refluxed briefly in 500 mL of acetic anhydride, and then the slurry was cooled and filtered. The solid was boiled in toluene, filtered, and dried, yielding 18.6 g of the dianhydride. IR: 1850, 1770 (vs, br) cm^{-1}.

It was characterized as the bis(*p*-tolylimide). Mp: 323–324 °C. IR: 1770, 1715 (vs) cm^{-1}. NMR: 8.00 (s), 7.64 (s), 7.32 (s, compressed A_2B_2 pattern), 2.22 (s), 2.09 (q), 1.82 (s), 0.62 (t) ppm in a 2:2:8:6:2:3:3 ratio.

9,9-Diethyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (EEXDA) and Its Derivatives. a. 9,9-Diethyl-2,3,6,7-tetramethylxanthene. A mixture of 90.4 g (0.4 mol) of DXE, 35 g (0.4 mol) of 3-pentanone, and 160 g (8 mol) of HF was kept in an autoclave at 100 °C for 6 h. After standard processing and trituration of the residue with isopropyl alcohol, there was obtained 11 g (9.4% yield) of the product. Mp: 226–227 °C (from xylene). NMR: 6.95 (s), 6.78 (s), 2.22 (s), 1.90 (q), 0.50 (t) ppm in a 2:2:12:4:6 ratio. Anal. Calcd for $C_{21}H_{26}O$: C, 85.7; H, 8.84. Found: C, 84.6; H, 8.63.

b. 9,9-Diethyl-2,3,6,7-xanthenetetracarboxylic Acid and 9,9-Diethyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (EEXDA). During the oxidation of the tetramethyl precursor by the Marvel/Rassweiler method, about 25–30% of the precursor remained undissolved and was lost with the MnO_2 precipitate. The tetraacid was converted to the dianhydride by boiling in acetic anhydride. The product (mp 392.5 °C by DSC, at 98% purity) was obtained in 40% yield. IR: 1845, 1780 (vs, br) cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_7$: C, 66.7; H, 3.70. Found: C, 65.5; H, 3.85. It was characterized as the bis(*p*-tolylimide).

c. 9,9-Diethyl-2,3,6,7-xanthenetetracarboxylic Bis(*p*-tolylimide). Mp: 314–315 °C. IR: 1765, 1710 (vs) cm^{-1}. NMR: 7.94 (s), 7.64 (s), 7.32 (s, compressed A_2B_2 pattern), 2.42 (s), 2.15 (q), 0.61 (t) ppm in a 1:1:4:3:2:3 ratio. Anal. Calcd for $C_{35}H_{28}N_2O_5$: C, 75.5; H, 5.04; N, 5.04. Found: C, 75.0; H, 5.15; N, 4.85.

9,9-Dibutyl-2,3,6,7-tetramethylxanthene and Its Derivatives. A mixture of 113 g (0.5 mol) of DXE, 75 g (0.5 mol) of 5-nonanone, and 220 g (11 mol) of HF was kept in an autoclave at 110 °C for 6 h. After standard processing, there was obtained 45.9 g (26.4%) of a solid. Mp: 171–172 °C (from octane). NMR: 6.97 (s), 6.75 (s), 2.23 (s), 1.85 (m), 1.12 (sextet), 0.83 (m), 0.71 (t) ppm in a 2:2:12:4:4:4:6 ratio. Anal. Calcd for $C_{25}H_{34}O$: C, 85.7; H, 9.71. Found: C, 84.3; H, 9.74.

9,9-Dibutyl-2,3,6,7-xanthenetetracarboxylic Acid and 9,9-Dibutyl-2,3,6,7-xanthenetetracarboxylic Dianhydride. A 35 g (0.1 mol) of a sample of 9,9-dibutyl-2,3,6,7-tetramethylxanthene was oxidized by the Marvel/Rassweiler method. Low solubility in the oxidizing medium resulted in about 10% recovery of the starting material. The tetraacid was boiled in 500 mL of acetic anhydride, and the solution was filtered and stripped. The residue was boiled with 200 mL of toluene. Part of the residue dissolved, and part remained as a sticky resin. The solution was decanted and gave on cooling crystals in a 9.2-g (24%) yield. Mp: 228–234 °C. IR: 1845, 1775 (vs) cm^{-1}. NMR: 8.03 (s), 7.74 (s), 2.11 (m), 1.20 (sextet), 0.76 (m), 0.73 (t) ppm in a 2:2:4:4:4:6 ratio. Anal. Calcd for $C_{25}H_{22}O_7$: C, 69.1; H, 5.07. Found: C, 67.7; H, 5.08.

This dianhydride was characterized as the bis(*p*-tolylimide) derivative. Mp: 286–288 °C. IR: 1765, 1720 (vs, br) cm^{-1}. NMR: 7.95 (s), 7.62 (s), 7.32 (s, compressed A_2B_2 pattern), 2.43 (s), 2.09 ("t"), 1.18 (sextet), 0.85 (m), 0.73 (t) ppm in a 2:2:8:6:4:4:4:6 ratio.

9,9-Cyclotetramethylene-2,3,6,7-xanthenetetracarboxylic Dianhydride (C4XDA) and Its Derivatives. a. 9,9-Cyclotetramethylene-2,3,6,7-tetramethylxanthene. A mixture of 115 g (0.51 mol) of DXE, 45 g (0.53 mol) of cyclopentanone, and 200 g (10 mol) of HF was kept in an autoclave at 100 °C for 6 h. After standard processing and boiling of the residue with a 50/50 mixture of methanol and isopropyl alcohol, 89.1 g (59.8%) of product was obtained. Mp: 144–146 °C (from heptane). NMR: 7.04 (s), 6.79 (s), 2.21 (s), 2.19 (s), 2.14 (m), 1.96 (m) ppm in a 2:2:6:6:4:4 ratio. Anal. Calcd for $C_{21}H_{24}O$: C, 86.3; H, 8.22. Found: C, 85.1; H, 8.17.

b. 9,9-Cyclotetramethylene-2,3,6,7-xanthenetetracarboxylic Acid and 9,9-Tetramethylene-2,3,6,7-xanthenetetracarboxylic Dianhydride (C4XDA). 9,9-Cyclotetramethylene-2,3,6,7-tetramethylxanthene (60 g, 0.2 mol) was oxidized by the Marvel/Rassweiler method, yielding 58 g (77%) of crude dianhydride, after treatment of the tetraacid with refluxing acetic anhydride. It was recrystallized from diphenyl ether and washed with boiling toluene. Mp: 396 °C (DSC). IR: 1850, 1775 (vs, br) cm^{-1}. Anal. Calcd for $C_{21}H_{12}O_7$: C, 67.0; H, 3.19. Found: C, 66.2; H, 3.42.

C4XDA was characterized as the bis(*p*-tolylimide). Mp: 319–320 °C. IR: 1766, 1720 (vs) cm^{-1}. NMR: 7.97 (s), 7.67 (s), 7.33 (s, compressed A_2B_2 pattern), 2.43 (s), 2.33 ("t"), 2.13 (m) ppm in a 1:1:4:3:2:2 ratio. Anal. Calcd for $C_{35}H_{26}N_2O_5$: C, 75.8; H, 4.69; N, 5.05. Found: C, 74.8; H, 4.78; N, 4.84.

9,9-Cyclopentamethylene-2,3,6,7-tetramethylxanthene and Its Derivatives. A mixture of 113 g (0.5 mol) of DXE, 49 g (0.5 mol) of cyclohexanone, and 200 g (10 mol) of HF was kept in an autoclave at 100 °C for 6 h. After removal of solvents and of lower boilers up to 150 °C (1.1 Torr), the residue was chromatographed on alumina, yielding 61 g (40%) of a yellowish glass, which was very soluble in hydrocarbons. NMR: 7.30 (s), 6.90 (s), 2.24 (s), 2.22 (s), 1.97 (t), 1.72 (m), 1.58 (m) ppm in a 2:2:6:6:4:4:2 ratio.

9,9-Cyclopentamethylene-2,3,6,7-xanthenetetracarboxylic Acid and 9,9-Cyclopentamethylene-2,3,6,7-xanthenetetracarboxylic Dianhydride (C5XDA). The crude product from the above experiment was dissolved in pyridine and oxidized with permanganate by the Marvel/Rassweiler method. Final acidification yielded a tacky material, which was boiled with excess acetic anhydride, and then the solution was stripped in vacuo. The residue was difficult to crystallize, but ultimately 10 g of the anhydride was crystallized from acetic anhydride. IR: 1850, 1780 (vs br) cm^{-1}.

9,9-Pentamethylene-2,3,6,7-xanthenetetracarboxylic dianhydride was characterized as the bis(*p*-tolylimide). Mp: 277–278 °C. IR: 1766–1720 cm^{-1}. NMR: 8.20 (s), 7.76 (s), 7.31 (s, compressed A_2B_2 pattern), 2.22 (s), 2.14 (t), 1.77 (m), 1.64 (m) ppm in a 2:2:8:6:4:4:2 ratio.

9-Methyl-9-(trifluoromethyl)-2,3,6,7-xanthenetetracarboxylic Dianhydride (MTXDA) and Its Derivatives. a. 9-(Trifluoromethyl)-2,3,6,7,9-pentamethylxanthene. A mixture of 202 g (0.89 mol) of DXE, 100 g (0.89 mol) of 1,1,1-trifluoroacetone, and 260 g (13 mol) of HF was heated in a shaker tube for 8 h at 125 °C. After venting off excess HF, the contents were transferred to a 4-L polyethylene jar half-filled with ice water and containing excess sodium hydroxide. The product was extracted with methylene chloride, the extract was filtered through a bed of Celite and alumina, and the filtrate was stripped to dryness. The residue was stirred with hexane and was filtered, yielding 179 g (63%) of an off-white, granular product. Mp: 184–185 °C (from octane). The material was sublimable in vacuo. NMR: singlets at 7.25 (H1), 6.91 (H4), 2.25 (2,3-CH_3), and 1.96 (9-CH_3) in a 2:2:12:3 ratio. Anal. Calcd for $C_{19}H_{19}F_3O$: C, 7.12; H, 5.94; F, 17.8. Found: C, 70.4; H, 5.99; F, 17.4.

b. 9-(Trifluoromethyl)-9-methyl-2,3,6,7-xanthenetetracarboxylic Dianhydride (MTXDA). Several 52-g (0.16-mol) batches of 9-(trifluoromethyl)-2,3,6,7,9-pentamethylxanthene (0.16 mol) were oxidized with potassium permanganate in a pyridine/water mixture by the Marvel/Rassweiler method. The product was moderately soluble in hot aqueous sulfuric acid, but it precipitated on cooling as shiny white platelets. The yields of 9-(trifluoromethyl)-9-methyl-2,3,6,7-xanthenetetracarboxylic acid averaged 45–46 g (64%). It was converted directly to the dianhydride.

To a rapidly stirred slurry of 66 g (0.15 mol) of 9-(trifluoromethyl)-9-methyl-2,3,6,7-xanthenetetracarboxylic acid in 500 mL of chloroform was added slowly 60 mL (large excess) of thionyl chloride, and the slurry was refluxed for 12 h. The solid was filtered off and washed with chloroform, yielding 49 g (81%) of 9-(trifluoromethyl)-9-methyl-2,3,6,7-xanthenetetracarboxylic dianhydride. In another run, a 91% yield was obtained. This dianhydride has a low solubility in chloroform, but it is sufficient for obtaining a confirmatory NMR spectrum: 8.30 (s(b), H1), 7.88 (s, H4), 2.22 (s, CH_3) ppm in a 2:2:3 ratio. By DSC it was

99.88% pure and had a melting point of 307.7 °C. Its structure was confirmed by preparing the bis(propylimide) and bis(tolylimide) derivatives.

c. 9-(Trifluoromethyl)-9-methyl-2,3,6,7-xanthenetetracarboxylic Bis(propylimide). This derivative was prepared as described in previous experiments, and it was obtained in 80% yield as a white solid. Mp: 209–210 °C after recrystallization from toluene/octane. NMR: 8.12 (s(b), H1), 7.69 (s, H4), 3.69 (t, NCH_2), 2.22 (s, 9-CH_3), 1.72 (m, $-CH_2-$), 0.98 (t, propyl CH_3) ppm in a 2:2:4:3:4:6 ratio. Anal. Calcd for $C_{25}H_{21}F_3N_2O_5$: C, 61.7; H, 4.32; N, 5.76. Found: C, 60.9; H, 4.42; N, 5.60.

d. 9-(Trifluoromethyl)-9-methyl-2,3,6,7-xanthenetetracarboxylic Bis(*p*-tolylimide). The bis(*p*-tolylimide) was prepared as above, using *p*-toluidine instead of propylamine, and was purified by chromatography. Mp: 321–322 °C. IR: 1775, 1730 (vs), and 1630 cm^{-1}. NMR: 8.24 (s(b), H1), 7.80 (s, H4), 7.32 ("s", compressed A_2B_2 pattern), 2.42 (s, tolyl methyl), 2.22 (s, 9-methyls) ppm in a 2:2:8:6:3 ratio. Anal. Calcd for $C_{33}H_{21}F_3N_2O_5$: C, 68.0; H, 3.61; N, 4.81. Found: C, 66.6; H, 3.68; N, 4.62.

9-(Pentafluoroethyl)-9-(trifluoromethyl)-2,3,6,7-xanthenetetracarboxylic Dianhydride (8FCDA) and Its Derivatives. a. 9-(Pentafluoroethyl)-9-(trifluoromethyl)-2,3,6,7-tetramethylxanthene. A mixture of 45.2 g (0.2 mol) of DXE, 41 g (0.2 mol) of trifluoromethyl pentafluoroethyl ketone, and 50 g (2.5 mol) of HF was heated in a shaker tube at 140 °C for 8 h. After venting residual HF, the reaction mixture was transferred to a polyethylene jar containing ice water plus excess sodium hydroxide. The product was extracted with methylene chloride, the extracts were run through a bed of alumina and then stripped, and the residue was stirred with methanol and filtered. There was obtained a total of 18 g (21%) of white solid. The product was very soluble in toluene and chloroform but insoluble in methanol. It was purified by sublimation and then by recrystallization from heptane. Mp: 139–140 °C. The NMR spectrum was confirmatory: 7.57 (s(b)), 6.93 (s), 2.27 (s) ppm in the correct 1:1:6 ratio. Anal. Calcd for $C_{20}H_{16}F_8O$: C, 56.6; H, 3.77; F, 35.8. Found: C, 56.8; H, 3.77; F, 35.0.

b. 9-(Pentafluoroethyl)-9-(trifluoromethyl)-2,3,6,7-xanthenetetracarboxylic Dianhydride (8FCDA). A 71.4-g (0.168-mol) batch of 9-(pentafluoroethyl)-9-(trifluoromethyl)-2,3,6,7-tetramethylxanthene, consisting of several previously prepared batches was oxidized by the Marvel/Rassweiler method. The tetraacid was isolated by filtration and refluxed in acetic anhydride, and the solution was filtered and stripped at reduced pressure. The residue was crystallized from xylene, producing the dianhydride in a 71-g (83%) yield. It was sublimable at 240 °C (1 Torr). The mp (DSC's) of samples of 95.5 and 95.3% purity were 294 and 291 °C, respectively. The structure of this dianhydride was confirmed by the NMR of a bis(propylimide) derivative, mp 125–126 °C (from heptane), prepared in the usual fashion: 8.40 (br s), 7.74 (s), 3.71 (t), 1.75 (sextet), 1.00 (t) ppm in a 2:2:4:4:6 ratio.

9-Phenyl-9-(pentafluoroethyl)-2,3,6,7-xanthenetetracarboxylic Dianhydride (5FCDA). The precursor, 9-phenyl-9-(pentafluoroethyl)-2,3,6,7-tetramethylxanthene (TMPX2), was prepared in 1-mol batches by the reaction of DXE with pentafluoropropiophenone and 12 mol of HF at 125 °C for 8 h. The average yield of recrystallized material from four runs was 70%. Final purification of both, TMPX2 and TMPX3 (see below), consisted of distilling the materials [bp 200–210 °C (0.7 Torr)] and pouring the melt into stirred decane, which results in the separation of a fine granular product. The slurry was then diluted with hexane, and the product was isolated by filtration and dried overnight.

Oxidation of several batches of TMPX2 by the Marvel/Rassweiler method yielded 5FCDA in 70–80% yield. It was purified by recrystallization from acetic anhydride and characterized as the bis(propylimide) derivative.

a. 9-Phenyl-9-(pentafluoroethyl)-2,3,6,7-xanthenetetracarboxylic Bis(propylimide). The bis(propylimide) of 5FCDA was prepared in standard fashion and had a mp of 199–200 °C. NMR: 7.70 (s), 7.50 (split "s"), 7.38 (sharp m, almost s), 3.64 (t), 1.68 (sextet), 0.94 (t) ppm in a 2:2:5:4:4:6 ratio.

9-Phenyl-9-(heptafluoropropyl)-2,3,6,7-xanthenetetracarboxylic Dianhydride (7FCDA). The precursor, 9-phenyl-9-(heptafluoropropyl)-2,3,6,7-tetramethylxanthene (TMPX3), was prepared in 1-mol batches by the reaction of DXE with heptafluorobutyrophenone and 12 mol of HF at 130 °C for 8 h. The average yield of recrystallized material from four runs was 60%.

Oxidation of a 96.4-g (0.2-mol) batch of TMPX3 by the Marvel/Rassweiler method yielded 7FCDA, which was purified by recrystallization from acetic anhydride and melted at 269–272 °C. Yield of purified dianhydride was 45 g (40%). NMR: 7.92 (sharp s), 7.71 ("s", F split), 7.43 (m), and 7.35 (m) ppm in a 2:2:3:2 ratio. Anal. Calcd for $C_{26}H_9F_7O_7$: C, 55.1; H, 1.59; F, 23.5. Found: C, 55.1; H, 1.83; F, 23.5.

9-Phenyl-9-(heptafluoropropyl)-2,3,6,7-xanthenetetracarboxylic Bis(propylimide). The bis(propylimide) of 7FCDA was prepared in a standard fashion and melted at 192–194 °C. NMR: 7.72 (very sharp), 7.53 (m, sharp, shows F splitting), 7.38 (m), 3.64 (t), 1.69 (sextet), 0.94 (t) ppm in a 2:2:5:4:4:6 ratio.

9-[*m*-(Trifluoromethyl)phenyl]-9-(trifluoromethyl)-2,3,6,7-xanthenetetracarboxylic Dianhydride. The precursor, 9-[*m*-(trifluoromethyl)phenyl]-9-(trifluoromethyl)-2,3,6,7-tetramethylxanthene, was prepared from 0.82 mol of DXE and 0.82 mol of *m*-(trifluoromethyl)phenyl trifluoromethyl ketone in 11 mol of HF at 130 °C for 8 h. It was obtained as a crystalline solid, mp 169–171 °C, in 33% yield after recrystallization from isopropyl alcohol and from heptane. NMR: 7.75 (s, unique aromatic 2-H), 7.4–7.6 (m), 6.97 (s), 6.48 (s), 2.25 (s), 2.07 (s) ppm in the correct 1:3:2:2:6:6 ratio. Anal. Calcd for $C_{25}H_{20}F_6O$: C, 66.7; H, 4.44; F, 25.3. Found: C, 66.6; H, 4.23; F, 25.1.

Standard Marvel/Rassweiler oxidation of the above material produced the tetraacid, which was boiled in acetic anhydride, the solution was filtered through Celite, and the filtrate was stripped. The crude product was recrystallized from anisole and was obtained, after drying, in 99.7% purity (by DSC) with mp 270.5 °C. IR: 1850, 1785 (vs) cm^{-1}. NMR: 7.94 (s), 7.78 (d), 7.6–7.7 (m), 7.54 (s) ppm in a 2:1:3:2 ratio.

Dianhydrides Based on 9-aryl-9-X-xanthenes (X = halogen, OH, OAc). 1. 9-Phenyl-9-hydroxy-2,3,6,7-tetramethylxanthene. a. From Benzaldehyde. A mixture of 113 g (0.5 mol) of DXE, 53 g (0.5 mol) of benzaldehyde, and 160 g (8 mol) of HF was kept in an autoclave at 120 °C for 8 h. After venting off HF and transferring the reaction mixture to a 4-L polyethylene jar containing 500 mL of 50% NaOH and half-filled with ice water, the organic material was extracted with methylene chloride. The extracts were filtered through a layer of alumina and stripped, yielding 77.8 g (47%) of a cream-colored solid. It did not have a sharp melting point but instead turned orange from about 185 °C, started sintering around 192 °C, and decomposed amidst bubbling to a dark brown froth around 200–202 °C. IR: sharp peak at 3500 cm^{-1}. NMR: 7.41 (d), 7.27 (t), 7.17 (t), 7.03 (s), 6.97 (s), 2.54 (s, OH), 2.24 (s), 2.12 (s) ppm in a 2:2:1:2:2:1:6:6 ratio.

b. From Benzophenone. A mixture of 169 g (0.75 mol) of DXE, 137 g (0.75 mol) of benzophenone, and 220 g (11 mol) of HF was kept in an autoclave at 140 °C for 6 h. It was processed as in the experiment above. Some product was lost mechanically during transfers and filtration. A total of 120 g (48%) of product was obtained with an IR spectrum matching that of the authentic material.

2. 9-[*p*-(Trifluoromethyl)phenyl]-9-hydroxy-2,3,6,7-tetramethylxanthene. A mixture of 130 g (0.57 mol) of DXE, 100 g of *p*-(trifluoromethyl)benzaldehyde, and 230 g (11.5 mol) of HF was kept in an autoclave at 110 °C for 8 h. After the usual workup there was obtained 33 g (15%) of the title compound as a cream-colored solid, identified by NMR: 7.52 (s, compressed A_2B_2 pattern of C_6H_4), 6.97, and 6.94 (s, xanthene 1 and 4 protons), 2.63 (s, OH), 2.24, 2.14 (s, methyls) ppm in the correct 4:2:2:1:6:6 ratio.

3. 9-(*p*-Chlorophenyl)-9-hydroxy-2,3,6,7-tetramethylxanthene. A mixture of 90.4 g (0.4 mol) of DXE, 70.5 g (0.4 mol) of *p*-chlorobenzoyl chloride, and 160 g (8 mol) of HF was kept in an autoclave at 125 °C for 8 h. After processing as in the above experiments, there was obtained a total of 94 g (64%) of a cream-colored solid, which had no sharp melting point but started turning orange and melting around 193 °C and decomposed around 199 °C. IR: sharp peak at 3500 cm^{-1}. NMR: 7.04 (d), 6.93 (d), 6.66 (s), 6.62 (s), 2.26 (s, OH), 1.93 (s), 1.82 (s) ppm in a 2:2:2:2:1:6:6 ratio. Anal. Calcd for $C_{23}H_{21}ClO_2$: C, 75.7; H, 5.76. Found: C, 75.9; H, 5.84.

4. 9-Phenyl-9-hydroxy-2,3,6,7-xanthenetetracarboxylic Acid. 9-Phenyl-9-hydroxy-2,3,6,7-xanthenetetracarboxylic Dianhydride, and 9-Phenyl-9-acetoxy-2,3,6,7-xanthenetetracarboxylic Dianhydride. A 77-g batch of 9-phenyl-9-hydroxy-2,3,6,7-tetramethylxanthene was oxidized by the Marvel/Rassweiler method, and the dried tetraacid was obtained in a 86-g (90%) yield.

All of the above tetraacid was converted to the dianhydride, by refluxing it in 500 mL of acetic anhydride and then stripping the solution in vacuo. The residue was isolated by stirring it with chloroform, which removed reddish impurities, followed by filtration. The rather insoluble product was obtained in a 73-g (73%) yield. This yield calculation is based on the product being a roughly 1:1 mixture of the 9-hydroxy and 9-acetoxy dianhydrides with an "average molecular weight" of 435. IR: 1850, 1770 (vs), 1745 and 1600 cm^{-1}. The product was analyzed by mass spectrometry which showed it to be a roughly 1:1 mixture of 9-phenyl-9-hydroxyxanthene-2,3,6,7-tetracarboxylic dianhydride (*m/e* 414 = $C_{23}H_{10}O_8$) and 9-phenyl-9-acetoxyxanthene-2,3,6,7-tetracarboxylic dianhydride (*m/e* 456 = $C_{25}H_{12}O_9$).

5. 9-Phenyl-9-(propylamino)-2,3,6,7-xanthenetetracarboxylic Bis(propylimide). A sample of the dianhydride mixture from the above experiment was heated with excess propylamine in THF, ultimately at 230 °C to ensure complete imidization. The product was dissolved in methylene chloride and purified by chromatography on alumina. Stripping of the eluate and trituration of the residue with methanol gave 5.1 g of a white solid, which decomposed with bubbling at 255–257 °C. IR: sharp NH at 3520 cm^{-1}; also peaks at 1760, 1710, 1700, and 1620 cm^{-1}. On vacuum drying at 120 °C, the 3520-cm^{-1} band shifts to 3500 cm^{-1}. NMR: 7.82 (s), 7.66 (s), 7.18–7.38 (m), 3.64 (t), broad hump around 2.3 (NH), 2.10 (t), 1.67 (sextet), 1.50 (sextet), 0.94 (t), 0.86 (t) ppm in a 2:2:5:4:1:2:4:2:6:3 ratio. The underlined peaks belong to the imide propyl groups and the doubly underlined ones to the 9-propylamino group. Anal. Calcd for $C_{32}H_{31}N_3O_5$: C, 71.5; H, 5.77; N, 7.82. Found: C, 71.0; H, 5.76; N, 7.62.

6. 9-(*p*-Chlorophenyl)-9-hydroxy-2,3,6,7-xanthenetetracarboxylic Acid. 9-(*p*-Chlorophenyl)-9-hydroxy-2,3,6,7-xanthenetetracarboxylic Dianhydride, and 9-(*p*-Chlorophenyl)-9-acetoxy-2,3,6,7-xanthenetetracarboxylic Dianhydride. A 83-g (0.23-mol) batch of 9-(*p*-chlorophenyl)-9-hydroxy-2,3,6,7-tetramethylxanthene was oxidized by the Marvel/Rassweiler method, and the dried crude tetraacid was obtained in a 110-g (99%) yield. It was stirred and heated to reflux in 500 mL of acetic anhydride. After everything initially dissolved, a solid started appearing during the reflux. After 1 h the slurry was cooled and filtered, yielding a total of 74 g (72%, based on the tetramethyl precursor). The actual percent yield was lower, since partial acylation of the 9-OH group took place during anhydride formation. The product turned gradually orange from about 290 °C, with major decomposition taking place at 320 °C. It was analyzed by mass spectrometry, which shows the product to be a mixture of 9-(*p*-chlorophenyl)-9-hydroxyxanthene-2,3,6,7-tetracarboxylic anhydride (*m/e* 448 = $C_{23}H_9O_8Cl$) and 9-(*p*-chlorophenyl)-9-acetoxyxanthene-2,3,6,7-tetracarboxylic dianhydride (*m/e* 490 = $C_{25}H_{11}O_9Cl$).

9-(*p*-Chlorophenyl)-9-(propylamino)xanthene-2,3,6,7-tetracarboxylic Bis(propylimide). A 9.6-g sample of the above dianhydride mixture was treated with excess propylamine as before. The product, which was obtained in a 9.4-g yield, was recrystallized from a xylene/octane mixture. It melted at 245–247 °C, and on further heating, decomposition took place around 300 °C. IR: sharp spike at 3300 cm^{-1}, broad hump at 3100–3600 cm^{-1}, imide bands at 1760, 1710 (vs), 1625 cm^{-1}. NMR: 7.76 (s), 7.67 (s), 7.29 (A2B2 of C_6H_4), 3.63 (t), 2.08 (t), 1.70 (sextet), 1.29 (sextet), 0.95 (t), 0.83 (t) ppm in a 2:2:4:4:2:4:2:6:3 ratio. The underlined peaks belong to the imide propyl groups and the doubly underlined ones to the 9-propylamino group. The NH proton, of intensity = 1, was very broad but could be seen by integration around 2.2 ppm.

9-(*p*-Chlorophenyl)-9-(*p*-tolylamino)xanthene-2,3,6,7-tetracarboxylic Bis(*p*-tolylimide). A 5-g mixture of the above dianhydrides and 5 g of *p*-toluidine (large excess) was dissolved in 200 mL of THF. The solvent was boiled off, and the residue was gradually heated to 250 °C, then cooled, and dissolved in methylene chloride. The solution was filtered through alumina, stripped, and triturated with methanol, yielding 4.8 g of a pale yellowish solid. NMR: 8.14 (s), 7.80 (s), 7.22–7.32 (m), 7.12 (d), 6.77 (d), 6.25 (d), 5.1 (br NH), 2.40 (s), 2.13 (s) ppm in the correct 2:2:10:2:2:2:1:6:3 ratio.

Polymer Synthesis. Polyimides were prepared either by the standard room-temperature synthesis of the poly(amic acid) from diamine and dianhydride monomers with subsequent coating and thermal cure to polyimide or, in some cases, by a one-pot solution imidization method at elevated temperatures. Typical examples of both are given below.

Poly(amic acid) (PAA). A 100-mL reaction kettle fitted with a mechanical stirrer and nitrogen inlet and outlet was charged with 3.2239 g (10.0672 mmol) of TFMB and ~28 mL of anhydrous *N*-methyl-2-pyrrolidinone (NMP). Stirring was begun, and after dissolution of the diamine, 4.7761 g (10.0672 mmol) of PPXDA was added as a solid to the reaction mixture and rinsed in with ~4 mL of NMP (32 mL of total NMP). The reaction was allowed to proceed under nitrogen at room temperature overnight. The next day, a homogeneous, viscous, light amber solution resulted which was diluted to 15 wt % (w/v) with NMP. The diluted solution was allowed to stir overnight to allow for equilibration. The following day, the PAA solution was pressure-filtered through a 1-μm filter in preparation for spin coating.

Solution Polyimide (PI). A 100-mL reaction kettle fitted with a nitrogen inlet and outlet and a mechanical stirrer was charged with 3.6208 g (10.8324 mmol) of 6FDAm and 25 mL of a *N*-methyl-2-pyrrolidinone/*N*-cyclohexyl-2-pyrrolidinone (NMP/CHP 4/1, v/v) solvent mixture. Stirring was begun, and after dissolution of the diamine, 4.3791 g (10.8324 mmol) of MTXDA was added as a solid. As the MTXDA dissolved and reacted, the viscosity built noticeably and the reaction was allowed to proceed overnight at room temperature under nitrogen. The next day, the viscous, amber poly(amic acid) solution was diluted to ~15 wt % solids (w/v) with the NMP/CHP 4/1 solvent mixture. The reaction kettle was then fitted with a Dean–Stark trap and water condenser on the outlet side for thermal imidization. The reaction kettle was heated in a temperature-controlled oil bath to 180–190 °C and maintained in this temperature range overnight with good stirring under a nitrogen purge. The following day, the resulting homogeneous, viscous polyimide solution was allowed to cool to room temperature and then further diluted with NMP. The solution was then precipitated into methanol to isolate the polyimide as a solid. This solid was dissolved in chloroform and then reprecipitated into methanol. Finally, the polymer was dissolved at 15% w/v in TCE and filtered at 1 μm in preparation for spin coating.

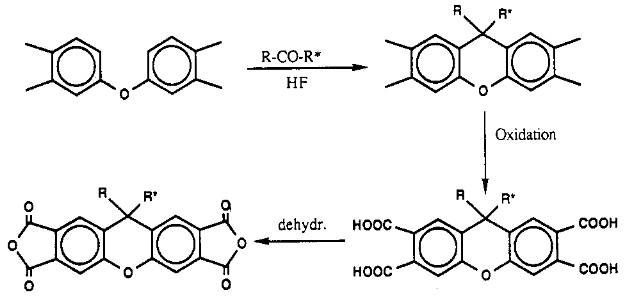
Film Preparation. Films were prepared by spin coating the filtered poly(amic acid) or polyimide solution onto 5-in. silicon wafers containing 1000 Å of thermally grown oxide on the surface, followed by drying at 135 °C for 30 min in air, and then heating under nitrogen to 200 °C (2 °C/min) and holding for 30 min, followed by heating to 350 °C (2 °C/min) and holding for 1 h. Free-standing films of about 10-μm thickness (goal) were obtained by etching the oxide layer of the silicon wafer in dilute aqueous HF to release the film.

Techniques. Gel permeation chromatography (GPC) on PAAs and some PIs was performed on a Waters GPC 2 at 35 °C with four linear Phenogel columns in the DMAC/LiBr/H_3PO_4/THF solvent system[7] or, where necessary for PIs, on a Waters instrument (150C) with a Zorbax TMS precolumn and two Shodex AD80M/S columns in DMAC at 135 °C. The flow rate was 1 mL/min, detection was by RI, and calibration was based on polystyrene standards in both cases. Mechanical properties of the films were measured in accordance with ASTM D-882-83 (method A) on an Instron Model 4501 tensile tester (crosshead speed = 0.2 in./min). The in-plane, linear coefficient of thermal expansion (CTE) was obtained from a P-E TMA-7 thermomechanical analyzer (5 °C/min, −10 to +225 °C, 30 mN tension). The value (0–200 °C) was recorded after an initial conditioning step (heat to 250 °C, hold 5 min, cool). The temperature of 5% weight loss in air was measured on a DuPont 951 TGA at 15 °C/min from 50 to 600 °C. The measurements were taken after an initial 150 °C/5 min drying step. The dielectric constant was measured by the parallel-plate capacitor method in the frequency range 10 kHz to 10 MHz on thin (10–20 μm) films. Gold electrodes were vacuum deposited on both surfaces of dried films, followed by thorough drying (minimum of 48 h) at 150 °C under vacuum/N_2 prior to measurement in a sealed humidity chamber at 0%

relative humidity. Moisture absorption measurements were made by the quartz crystal microbalance technique (QCM)[8] on thin (~3 μm) films spin coated and cured (as above) onto electroded quartz crystals. Measurements were taken at various humidity settings in a controlled humidity chamber and are reported at 85% relative humidity. DSC melting points (peak maximum) and purity analyses were performed on a DuPont 2100 DSC at 1 °C/min. Purity was calculated by standard instrument software which uses the van't Hoff relation to define purity by analyzing peak shape. The sample size was <2 mg. Other melting points were obtained by a standard capillary melting point apparatus.

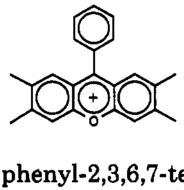
Results and Discussion

Preparation of New Dianhydrides. The various novel dianhydrides were prepared starting with dixylyl ether (DXE) which reacted in HF with a ketone, R–CO–R*, producing 9-R-9-R*-2,3,6,7-tetramethylxanthene. These tetramethyl precursors were oxidized with a permanganate ion to the tetracarboxylic acid and dehydrated by several methods (thermally, with acetic anhydride, or with thionyl chloride), yielding the corresponding dianhydrides, as shown in the following:

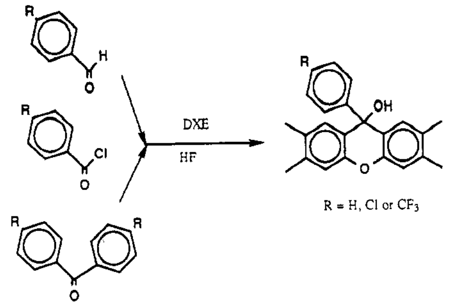


PPXDA (R = R* = phenyl)
MPXDA (R = Me, R* = phenyl)
MMXDA (R = R* = Me)
EMXDA (R = Me, R* = Et)
EEXDA (R = R* = Et)
C4XDA (R,R* = $-(CH_2)_4-$)
C5XDA (R,R* = $-(CH_2)_5-$)
MTXDA (R = Me, R* = CF_3)
8FCDA (R = CF_3, R* = C_2F_5)
7FCDA (R = C_3F_7, R* = phenyl)
5FCDA (R = C_2F_5, R* = phenyl)

When R or R* were methyl groups, they were not oxidized during oxidation of the 2,3,6,7 methyl groups. Yields ranged from poor to good, depending on the structure of the ketone. For instance, while with cyclopentanone the dianhydride C4XDA was obtained in 60% yield, with cyclohexanone the yield of C5XDA was poor; nonetheless the desired product was isolated and characterized. The desired condensation of DXE with the ketones proceeded in some instances in only a fairly narrow temperature range, as with benzophenone, which gave at higher temperatures monophenyl products derived from the 9-phenylxanthenium ion[9]



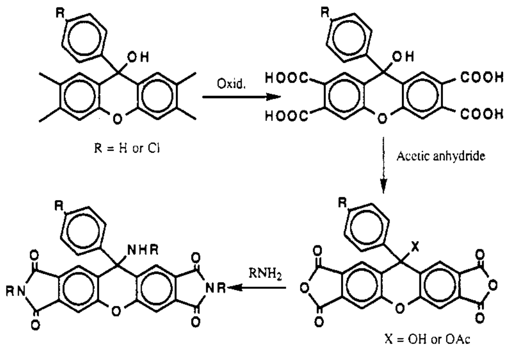
such as hydroxy-9-phenyl-2,3,6,7-tetramethylxanthene. Similar products were also obtained from the reaction of DXE with either benzaldehyde or with *p*-chlorobenzoyl chloride:



Oxidation of the above precursors with permanganate ion yielded tetraacids (the tertiary hydroxyl group remaining unaffected), and refluxing these in acetic anhydride yielded readily the corresponding dianhydrides, exhibiting typical anhydride bands at 1840 and 1775 cm^{-1}. These materials were very insoluble and were characterized by mass spectrometry. The mass spectrum of the 9-phenyl derivative showed the presence of a rougly 1:1 mixture of species with *m/e* 414 and 456, corresponding to the dianhydrides with 9-OH and 9-acetoxy substituents, respectively, indicating partial acetylation of the 9-hydroxy group during anhydride formation.

Treatment of these dianhydrides with propylamine under conditions where bis(imides) are formed, in order to prepare the bis(propylimide) derivative, yielded cleanly a single product which contained not only the two expected propylimide functions but also a third propylamino group in the 9-position, as was established unequivocally by NMR. It is also noteworthy that both the 9-acetoxy and 9-hydroxy groups are replaced by RNH– with seemingly equal ease, which is probably due to the facile nature of the xanthenium ion intermediate.

In order to determine whether these dianhydride mixtures will also react in the 9-position with an aromatic amine, the 4-chlorophenyl dianhydride was treated with *p*-toluidine. The product was a bis(imide), which also contained a *p*-tolylamino substituent in the 9-position.



These results point to a fundamentally new class of dianhydrides, novel functionally as well as structurally. They not only form normal polyimide chains but also can react with aromatic diamines at the 9-position, leading to cross-linking of the polyimide backbone. A schematic example of such cross-linked polyimide structures is as follows:

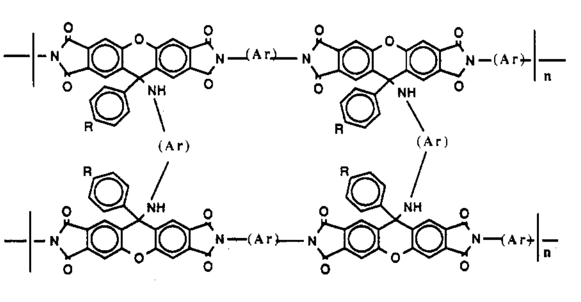
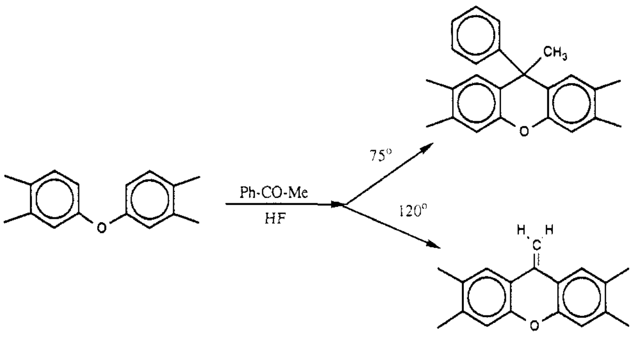


Table 1. GPC Molecular Weights of Poly(amic acid)s and Soluble Polyimides Based on PPXDA or MTXDA

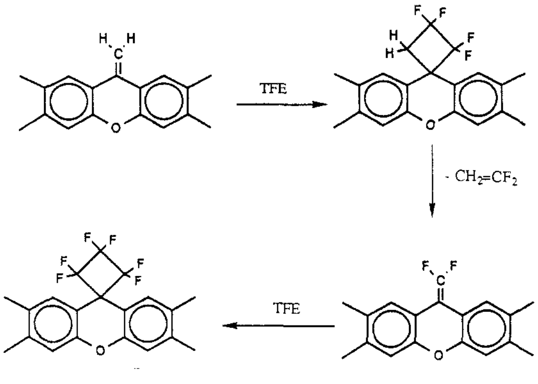
sample	PAA or PI	M_n[a]	M_w[a]	M_w/M_n	coating solvent/% solids
PPXDA/TFMB	PAA	100 000	224 000	2.2	NMP/15
PPXDA/DMB	PAA	115 000	304 000	2.6	NMP/10
PPXDA/TMB[b]	PI	79 600	166 000	2.1	TCE/16
PPXDA/DAD	PI	110 000	330 000	3.0	TCE/8
		72 300[c]	187 000[c]	2.6	
PPXDA/PPD	PAA	181 000	328 000	1.8	NMP/11
PPXDA/PPD/ODA (100/40/60)	PI	43 000	101 000	2.4	TCE/7
PPXDA/PPD/ODA (100/20/80)	PI	75 100	243 000	3.2	TCE/10
PPXDA/ODA	PAA	171 000	392 000	2.3	NMP/11
PPXDA/ODA	PI	50 200	175 000	3.5	NMP/CHP/10 or TCE/6
		54 400[d]	218 000[d]	4.0	
MTXDA/TFMB	PAA	105 000	249 000	2.4	NMP/12
MTXDA/6FDAm	PI	121 000	335 000	2.8	TCE/10
		83 600[d]	310 000[d]	3.7	
MTXDA/DMB	PAA	76 000	186 000	2.5	NMP/12
MTXDA/PPD	PAA	113 000	280 000	2.5	NMP/10

[a] GPC of PAA at RT in the DMAC solvent system unless otherwise indicated. [b] Solution in TCE gelled upon standing, not coated. [c] GPC of PI in DMAC at 135 °C. [d] GPC of PI at RT in the DMAC solvent system.

Another example of the thermal dependence of the reaction course was the reaction of DXE with acetophenone. At the usual conditions of condensation in HF (120 °C), the major product was 9,9-methylene-2,3,6,7-tetramethylxanthene, but at 75 °C the normal condensation product was obtained.



Oxidation and dehydration of this compound should yield the already known xanthone-2,3,6,7-tetracarboxylic dianhydride.[10] The 9,9-methylene-2,3,6,7-tetramethylxanthene reacted with tetrafluoroethylene, yielding the spirotetrafluorocyclobutyl bridgehead structure. Mass spectrometry indicated a dual mode of cleavage of the cyclobutyl ring: reversal of the original TFE addition, as well as a loss of 1,1-difluoroethylene, which should generate 6,6-difluoromethylene-2,3,6,7-tetramethylxanthene. This could add TFE again, yielding the perfluorocyclotrimethylene bridge, leading to novel fluorinated dianhydrides. This latter reaction was not investigated.



It should be noted that the geometry of the various xanthene rings was not the same and depended on the nature of the 9,9-substituents. While all the xanthene-derived molecules, planar and nonplanar, were crescent-shaped, i.e., with the benzo rings pulled (bent) toward the oxygen atom due to the difference in the C–C versus C–O bond lengths (1.54 and 1.36 Å, respectively), some were planar and some had a butterfly-like fold along the O—C9 axis. The structure of the bis(butylimide) of PPXDA showed a fold (deviation from planarity) of about 31°, with one phenyl group fitting flatly into the fold and the other phenyl being orthogonal to it and protruding away from the fold.[11] We assume that xanthenes with symmetrical substituents at the 9,9-positions (such as 9,9-dimethyl or 9,9-cyclotetramethylene) would be planar, while the less symmetrical ones would exhibit varying degrees of nonplanarity. These features will obviously affect the chain structure of the derived polyimides. A schematic representation of the crescent-shape and folded nature of some of these xanthene dianhydrides is shown for 3FCDA in ref 2.

Discussion of New Polyimides. Many of the new dianhydride structures where reacted with various diamines to yield poly(amic acid)s and polyimides. These structures are given in Figure 1. The standard reaction procedure was employed for poly(amic acid) synthesis, namely, room temperature reaction of dianhydride and diamine in anhydrous NMP under nitrogen. In most cases, high molecular weights were obtained as indicated by GPC (Tables 1 and 2). Although these values are only relative (based on polystyrene), they compare very favorably with values for standard commercial materials like Pyralin PI-2540 (PMDA/ODA), e.g., M_n = 51 000, M_w = 125 000, and PI-2611 (BPDA/PPD), e.g., M_n = 58 000, M_w = 157 000. There were a few cases, however, in which the molecular weights were noticeably lower, namely, for 8FCDA, EMXDA, EEXDA, and C4XDA. These dianhydrides were prepared in a small quantity, so rigorous purification was not attempted. In any case, all PAAs, with the exception of PPXDA/PPD, gave good quality, creaseable films when spin-coated and thermally cured to polyimide. For PPXDA/PPD a brittle film was obtained, although the molecular weight of the PAA was high. This was likely due to the very stiff nature of the backbone and the thermal conversion process. Processing conditions were not optimized.

In addition to the poly(amic acid) synthesis, several compositions were prepared directly as the polyimide in solution at elevated temperature using the NMP/CHP solvent system described by Summers et al.[12] This could be done when the backbone was such that it allowed solubility in the solvent system at the reaction temperature (ca. 180 °C). In many cases, the polyimide remained soluble in the NMP/CHP when cooled to room temper-

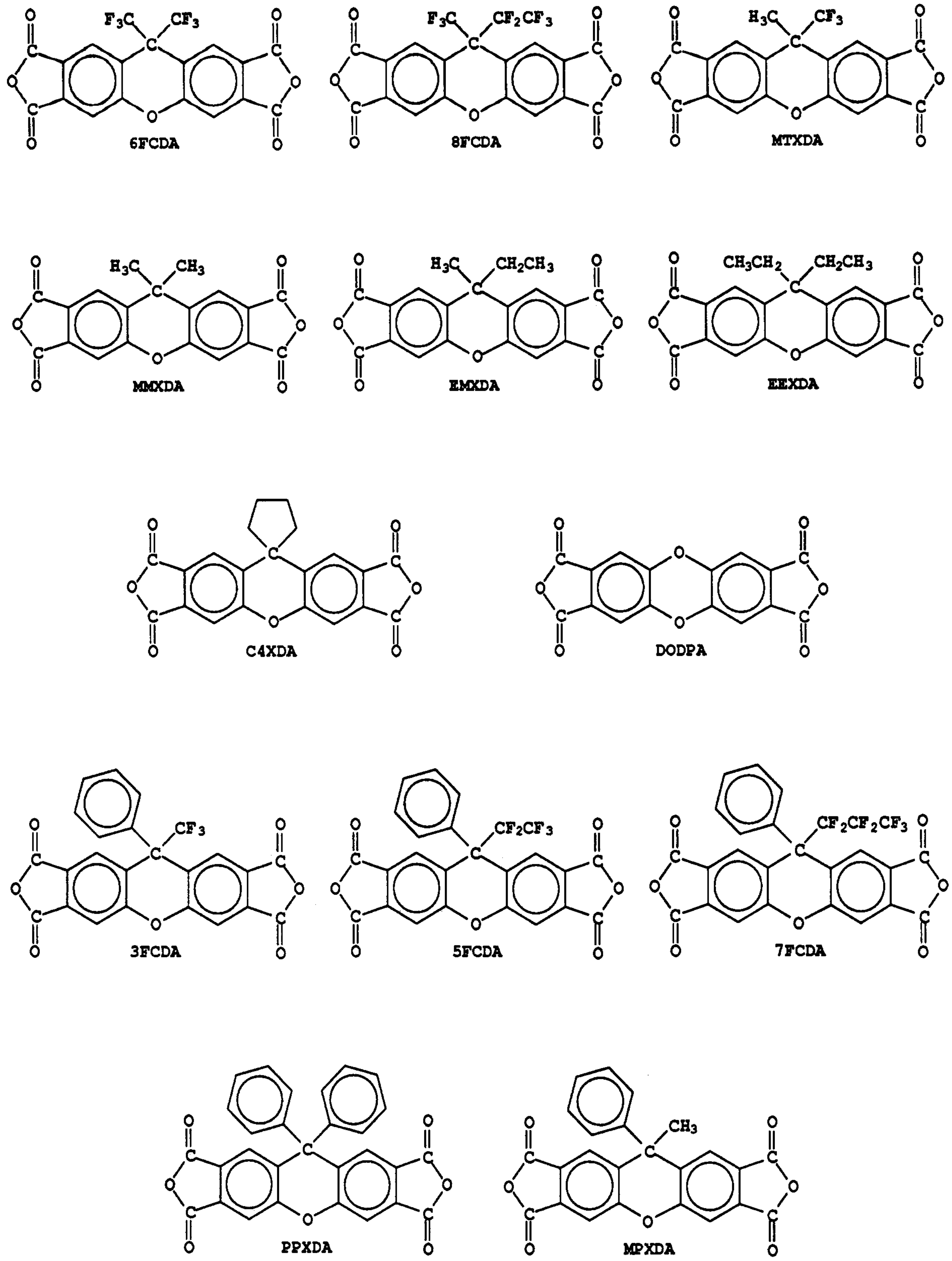


Figure 1. Xanthene dianhydrides used in polyimide synthesis.

ature, but in some cases, gelation was experienced. This gelation was thermally reversible, but for purposes of coating, the polyimides were normally precipitated into methanol and redissolved in TCE for spin coating. This was often necessary even for the room-temperature soluble PIs because the hygroscopic nature of NMP usually resulted in precipitation of the polyimide during spin coating. Most of the soluble PIs were coated from TCE solution, except as noted in Tables 1 and 2. PPXDA/TMB produced a soluble PI at high temperature in NMP/CHP but gelled from NMP/CHP when cooled to room temperature. It gave a hazy solution in TCE at room temperature which gelled upon standing and was not further explored. For 7FCDA/TFMB PI a suitable solvent at room temperature for spin coating was not found. The rest of the soluble polyimides were spin-coated and dried (same thermal conditions as for the PAAs) to give good quality, creasable films.

Table 3 summarizes various properties of polyimide films based on PPXDA and various diamines. The mechanical properties of the polyimides were generally good, although elongation tended to be somewhat lower than standard polyimides. For the polyimides from PPXDA and rodlike diamines (TFMB, DMB, DAD) both the modulus was notably lower and the CTE noticeably higher than for similar polyimides based on 6FCDA and 3FCDA inves-

Table 2. GPC Molecular Weights of Various Poly(amic acid)s and Soluble Polyimides

sample	PAA or PI	M_n[a]	M_w[a]	M_w/M_n	coating solvent/% solids
8FCDA/TFMB	PAA	25 300	47 300	1.9	NMP/20
6FCDA/TFMB	PAA	126 000	215 000	1.7	NMP/16
7FCDA/TFMB	PI	129 000[b]	329 000[b]	2.6	
5FCDA/TFMB	PAA	87 300	182 000	2.1	NMP/16
5FCDA/TFMB	PI	154 000[b]	387 000[b]	2.5	DMAC/10
3FCDA/TFMB	PAA	208 000	396 000	1.9	NMP/10
DODPA/TFMB	PAA	48 800	95 000	1.9	NMP/20
6FCDA/ODA	PAA	134 000	250 000	1.9	NMP/~16
7FCDA/ODA	PAA	63 900	167 000	2.6	NMP/16
7FCDA/ODA	PI	68 500 130 000[b]	133 000 265 000[b]	1.9 2.0	NMP/10
5FCDA/ODA	PAA	156 000	285 000	1.8	NMP/16
5FCDA/ODA	PI	123 000[b]	300 000[b]	2.5	NMP/12.5
3FCDA/ODA	PAA	148 000	325 000	2.2	NMP/16
3FCDA/ODA	PI	138 000[b]	327 000[b]	2.4	TCE/8
MMXDA/ODA	PAA	44 700	110 000	2.5	NMP/15
MPXDA/ODA	PI	59 000	138 000	2.3	TCE/10
EMXDA/ODA	PAA	41 400	86 400	2.1	NMP/20
EEXDA/ODA	PAA	37 700	85 400	2.3	NMP/20
C4XDA/ODA	PAA	26 600	56 800	2.1	NMP/20

[a] GPC of PAA at RT in the DMAC solvent system unless otherwise indicated. [b] GPC of PI at RT in the DMAC solvent system.

Table 3. Comparison of Polyimide Films Based on PPXDA and Selected Diamines

sample[a]	PAA or PI[a]	% fluor	film thickness (μm)	tensile strength (MPa)	% elongation	modulus (GPa)	CTE ppm/°C	% H_2O absorption @ 85% RH	dielectric const @ 1 MHz, dry	TGA temp 5% wt loss in air
PPXDA/TFMB	PAA	15.0	7.7	172	10	3.2	35	2.5	2.6	526
PPXDA/DMB	PAA	0	11.5	187	8	4.5	28	3.8	2.8	496
PPXDA/DAD	PI	0	8.0	161	9	3.0	15	2.1	2.8	462
PPXDA/PPD	PAA	0	too	brittle	to	test				
PPXDA/PPD/ODA (100/40/60)	PI	0	solution	gelled	upon	standing			2.8	
PPXDA/PPD/ODA (100/20/80)	PI	0	12.2	216	47	2.3	25	2.8	2.7	542
PPXDA/ODA	PAA	0	6.5	117	9	2.3	36	3.4		537
PPXDA/ODA	PI[b]	0	13.2	141	20	2.3	25	9.0	2.7	541
PPXDA/ODA	PI	0						4.5		

[a] Films prepared either from poly(amic acid) (PAA) and thermally imidized or from soluble polyimide (PI) solution with thermal solvent removal. Thermal conditions equivalent. [b] NMP/CHP coating solvent; other PIs, TCE coating solvent.

Table 4. Comparison of Polyimide Films Based on MTXDA and Selected Diamines

sample[a]	PAA or PI[a]	% fluor	film thickness (μm)	tensile strength (MPa)	% elongation	modulus (GPa)	CTE ppm/°C	% H_2O absorption @ 85% RH	dielectric const @ 1 MHz, dry	TGA temp 5% wt loss in air
MTXDA/TFMB	PAA	24.8	9.3	212	13	4.9	10	2.3	2.7	512
MTXDA/6FDAm	PI	24.3	7.0	136	52	1.9	35	1.5	2.5	510
MTXDA/DMB	PAA	9.8	8.9	286	18	5.7	8	na	2.6	494
MTXDA/PPD	PAA	12.0	8.8	189	4	5.8	2	4.1	2.9	498

[a] Films prepared from either poly(amic acid) (PAA) and thermally imidized or from soluble polyimide (PI) solution with thermal solvent removal. Thermal conditions equivalent. na = not available

tigated previously[1] (see also Table 5), despite the quasi rodlike nature of the backbone. This is likely the result of the shape of the PPXDA unit, which deviates substantially from linearity due to the bend and fold in the molecule as noted earlier. This and likely the steric bulk of the two phenyl groups combine to disturb the orientation process which occurs during film formation, resulting in higher CTE and lower modulus. For most polyimides studied based on PPXDA, the CTE values were typical of a standard, moderate CTE polyimide like PMDA/ODA (Table 6) and substantially higher than a low CTE, highly oriented polyimide like BPDA/PPD (Table 5).

The dielectric constants of polyimides based on PPXDA were all noticeably lower than the 3.0–3.2 value for standard polyimides, with the lowest value obtained for the polyimide containing the fluorinated TFMB. One could speculate that this is due to the "dilution" effect of the polar imide groups by the phenyl groups (on a weight basis based on polymer).[13] The moisture absorptions of the polyimides were variable, likely the result of the contribution of free volume differences in the polymers. The fluorine-containing material again tended to be on the low side. Interestingly, when PPXDA/ODA film was prepared from soluble PI in a NMP/CHP solution, the moisture value was very high (average of three similar values), quite in contrast to the same backbone prepared from a PAA solution. The reason for this is not clear and appears to be related to the solvent, as the same PI when precipitated and redissolved in TCE gave a polyimide film which showed a moisture value more comparable to the PAA-prepared film.

Thermal stabilities of the polyimides based on PPXDA by dynamic TGA measurement were all generally very good. While the aliphatic containing polymers (PPXDA/DMB, PPXDA/DAD) were somewhat lower in thermal stability, the fully aromatic materials had values similar to PMDA/ODA (see Table 6) and appears somewhat better than similar polyimides based on 6FCDA and 3FCDA reported earlier[1] (see also Tables 5 and 6).

Table 4 details the properties of polyimide films based on MTXDA and several diamines. The mechanical properties of these films were generally very good. The quasi rodlike structures (TFMB, DMB, PPD) tended to give the higher modulus and lower elongation typical of

Table 5. Comparison of Polyimide Films Based on Xanthene Dianhydrides and TFMB

sample[a]	PAA or PI[a]	% fluor	film thickness (μm)	tensile strength (MPa)	% elongation	modulus (GPa)	CTE ppm/°C	% H_2O absorption @ 85% RH	dielectric const @ 1 MHz, dry	TGA temp 5% wt loss in air
8FCDA/TFMB	PAA	33.6	6.4	185	12	3.9	18	1.7	2.5	416
6FCDA/TFMB	PAA	30.7	10.3	200	6	6.1	6	1.3	2.5	473
5FCDA/TFMB	PAA	26.1	8.6	163	11	3.6	34	1.1	2.7	415
5FCDA/TFMB[b]	PI	26.1	3.6	238	4	7.4	6	0.8		414
3FCDA/TFMB	PAA	22.8	8.1	197	8	5.0	13	1.9	2.7	484
MTXDA/TFMB	PAA	24.8	9.3	212	13	4.9	10	2.3	2.7	512
PPXDA/TFMB	PAA	15.0	7.7	172	10	3.2	35	2.5	2.6	526
DODPA/TFMB	PAA	18.7	10.2	267	13	8.1	−3		2.75	521
BPDA/PPD	PAA	0	10.0	424	52	5.7	4	1.4	3.1	606

[a] Films prepared from either poly(amic acid) (PAA) and thermally imidized or from soluble polyimide (PI) solution with thermal solvent removal. Thermal conditions equivalent. [b] DMAC coating solvent.

Table 6. Comparison of Polyimide Films Based on Xanthene Dianhydrides and ODA

sample[a]	PAA or PI[a]	% fluor	film thickness (μm)	tensile strength (MPa)	% elongation	modulus (GPa)	CTE ppm/°C	% H_2O absorption @ 85% RH	dielectric const @ 1 MHz, dry	TGA temp 5% wt loss in air
6FCDA/ODA	PAA	18.3	9.7	226	55	1.9	30	2.7	2.7	490
7FCDA/ODA	PAA	18.2	10.9	75	5	2.0	45	3.1		399
7FCDA/ODA	PI	18.2	11.3	130	10	2.3	32	3.9	2.8	400
5FCDA/ODA	PAA	13.6	9.6	117	13	2.2	48	2.4, 2.9	2.8	422
5FCDA/ODA	PI	13.6	16.6	157	23	2.3	31	1.9	2.8	422
3FCDA/ODA	PAA	9.0	14.8	78	4	2.0	39	3.4		448
3FCDA/ODA	PI	9.0	10.6	186	34	2.4	51	3.5	2.8	496
MMXDA/ODA[c]	PAA	0	10.7	241	67	2.1	29		2.9	511
MPXDA/ODA	PI	0	6.7	177	36	2.4	22	2.8	3.1	501
PPXDA/ODA	PAA	0	6.5	117	9	2.3	36	3.4		537
PPXDA/ODA	PI[b]	0	13.2	141	20	2.3	25	9.0 (4.5)[d]	2.7	541
EMXDA/ODA	PAA	0	10.8	173	38	2.0	34	4.9	3.0	474
EEXDA/ODA	PAA	0	10.4	170	35	2.2	36	4.2	3.0	466
C4XDA/ODA	PAA	0	10.6	178	47	1.9	41	4.2	3.2	494
PMDA/ODA	PAA	0	12.2	168	82	1.3	31	3.5	3.2	565
6FDA/ODA	PAA	18.7	8.1	131	10	2.8	52	2.0	2.9	537

[a] Films prepared from either poly(amic acid) (PAA) and thermally imidized or from soluble polyimide (PI) solution with thermal solvent removal. Thermal conditions equivalent. [b] NMP/CHP coating solvent; other PIs, TCE coating solvent. [c] Hazy film. [d] Value in parentheses is the same polymer prepared as a film from TCE coating solvent.

very stiff, rodlike backbones, while the polyimide from "flexible" 6FDAm had a reduced modulus and high elongation. The same trend was evident in CTE, as the rodlike backbones had very low CTE, while that based on 6FDAm was moderate. In this respect, the results are similar to those obtained for 6FCDA reported earlier[1] and in Tables 5 and 6 and different from those of PPXDA with rodlike diamines. This is again likely related to the size of the R and R* groups and their impact on the conformation of the molecule. Also note that, unlike PPXDA, MTXDA gave a good, albeit low elongation film with PPD.

Dielectric constants of the MTXDA-derived polyimides were usually notably lower than those of standard polyimides. Moisture results again indicated a beneficial effect of fluorine incorporation, while the thermal stability was generally high and apparently not substantially impacted by the presence of the methyl group in the xanthene unit, at least by dynamic TGA measurement.

Table 5 compares the properties of various polyimides based on a variety of xanthene dianhydrides with the rodlike fluorinated diamine, TFMB. In principle, all these polyimides have a nearly rodlike structure and would therefore be expected to have low in-plane CTE in films. As noted earlier, however, the size and shape of the R and R* groups and the molecular composition can have a profound impact on the ability of the polymer to orient in the plane of the film and thus on the CTE. In general, as the size/bulk of the R and R* increase, so does the CTE of PAA prepared polyimide films. For DODPA, where there are no R or R* groups, the CTE is very low and actually slightly negative. For large bulky group containing dianhydrides, i.e., 5FCDA and PPXDA, the CTE is higher and typical of more flexible polyimide backbones, like PMDA/ODA. A very similar trend is also seen for the modulus, the larger R and R* groups yielding the lower modulus.

Interestingly, when one of the materials in Table 5, 5FCDA/TFMB, was also prepared as a soluble polyimide, quite different properties could be obtained than from the PAA. Note the difference in mechanical and CTE results for 5FCDA/TFMB PAA and PI. The film prepared from soluble PI solution gives a much higher modulus and much lower CTE versus the PAA-prepared film. This is likely due to the much higher rigidity of the PI vs PAA during the film-forming process, leading to a much higher orientation for the PI-prepared sample. Although no blanket statement can be made because of differences in solvent, molecular weight, and film thickness, this appears to be a real trend and is supported by three of four similar comparative samples listed in Table 6 (7FCDA/ODA, 5FCDA/ODA, PPXDA/ODA). Even with a flexible diamine like ODA, the films prepared from soluble PIs appear to have lower CTEs than their corresponding PAA-prepared films. This is further indicated by comparison of results from Harris[14] on BPDA/TFMB-soluble PI in *m*-cresol which gave a CTE of ~7 ppm/°C, while a PAA with the same composition prepared by us in NMP yielded a CTE of 20 ppm/°C. Again although the results are not directly comparable, the indication is that producing a polyimide film from polyimide solution will generally give lower CTE than from the corresponding PAA, which intuitively makes sense based on relative rigidity and its impact on the orientation process.

Regarding the other properties listed in Table 5, the mechanical properties were generally very good, but the elongations were on the low side as is often seen with rodlike backbones. Moisture absorptions and dielectric constants were both low for most of the polymers listed, with some advantage found for the more highly fluorinated materials.

In terms of thermal stability, the materials with longer Rf chains in the bridge positions (8FCDA, 5FCDA) were notably inferior to the other polymers. This was noted not only in the TGA numbers for both samples but also in the case of 5FCDA, in the darkening of the film upon thermal imidization. Of the other polymers, PPXDA/TFMB and DODPA/TFMB exhibited the highest stability in dynamic TGA.

Table 6 lists the characterization of polyimide films based on a variety of xanthene dianhydrides paired with ODA. The mechanical properties of these films were on the whole very good, with a few exceptions. Many of the films gave fairly high elongations, especially when compared to the polyimides based on TFMB. The more flexible nature of the backbone due to the presence of the flexible ODA is the likely reason for these higher elongations. Interestingly, in some cases in which low elongations were obtained from PAA-prepared films (7FCDA/ODA, 5FCDA/ODA, 3FCDA/ODA, PPXDA/ODA), the same backbones gave significantly better elongation when prepared from a soluble polyimide solution. In these cases, the tensile strength was also significantly higher. This indicates the fact that the conversion process of poly(amic acid) to polyimide which is accompanied by solvent loss and an initial drop and then a recovery of molecular weight can have a significant impact on film properties. Preparing the polymer directly as a polyimide (if soluble) appears, in general, to give films with improved properties.

The CTEs of the ODA-based xanthene polyimides are also listed in Table 6. Because ODA is a flexible diamine and does not give rise to a rodlike polyimide structure, the CTE values are moderate. The rigid xanthene structure, however, maintains a fairly stiff structure so that the values are still comparable with a semirigid polyimide like PMDA/ODA and usually lower than typical flexible polyimides like 6FDA/ODA.

Moisture absorptions of these ODA-based polyimides were on par with standard polyimides like PMDA/ODA, with some benefit noted for some of the fluorinated polymers. Dielectric constants showed some improvement for the fluorinated materials and PPXDA over PMDA/ODA, while little advantage was noted for the samples containing the alkyl groups in the xanthene unit.

The thermal stabilities of these ODA-based materials showed significant variations depending on the xanthene structure. The polyimide based on PPXDA was the most stable, while the polyimides based on 7FCDA and 5FCDA exhibited lower stability as indicated both by TGA numbers and also in the darkening of the film upon thermal cure (for both PAA- and PI-prepared films). Interestingly, the 6FCDA sample (two CF3 groups) did not show any significant advantage in thermal stability by dynamic TGA over many of the alkyl-containing samples (e.g., MMXDA, MPXDA) as might be expected. It can be speculated that the perfluoroalkyl groups in the 9,9-positions have a destabilizing effect on the xanthene unit and thus show lower thermal stability than normally expected versus alkyl groups. This was especially evident in the 5FCDA and 7FCDA samples which contain longer perfluoroalkyl chains in the 9-position. This same effect was evident in the TFMB samples shown in Table 5 (8FCDA/TFMB and 5FCDA/TFMB) in which the dianhydride units contain longer perfluoroalkyl chains and exhibited lower thermal stability.

For most of the polyimides prepared T_g was not measured; however, based on previous DMA data for 6FCDA- and 3FCDA-based polyimides,[1,2] the T_gs are expected to be in the 350–400 °C range for the diamines studied. These high T_gs result from the very high stiffness of the xanthene unit. More flexible diamines would be expected to give somewhat lower T_gs.

Conclusions

A variety of xanthene dianhydrides (and their precursors) has been prepared and evaluated in polyimides. The method used for dianhydride preparation appears to be very versatile and can lead to a wide range of structures. Polyimides from these dianhydrides, in general, produced good quality films with good mechanical properties. Pairing of these rigid dianhydrides with a rigid diamine yielded polyimides with a substantially rodlike structure which usually gave low CTE films. The CTE was found to be influenced by the size of the groups in the 9,9-positions of the xanthene unit, with the larger groups giving higher CTE. The other properties studied were generally typical of standard polyimides, with some advantages realized for the fluorinated materials in both dielectric constant and moisture absorption. These materials have potential uses in electronics (e.g., as interlayer dielectrics), as well as, in other film, fiber, and part applications. These new dianhydrides may also find uses as curing agents for epoxies.

References and Notes

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