Macromolecules **1993,** *26,* 2779–2784

Synthesis and Properties of Fluorinated Polyimides from Novel 2,2′-Bis(fluoroalkoxy)benzidines

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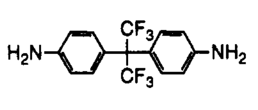
Received October 5, 1992; Revised Manuscript Received March 2, 1993

ABSTRACT: New polyimides have been prepared from 2,2′-bis(fluoroalkoxy)benzidines and several dianhydrides. The new diamines, with fluoroalkoxy groups OCF_3, OCF_2CF_2H, and $OCF_2CFHOC_3F_7$, were obtained from the corresponding 3-(fluoroalkoxy)nitrobenzenes by reduction to hydrazo derivatives, followed by benzidine rearrangements. High-quality polyimide films from these diamines have been prepared by standard procedures and their thermal, mechanical, and electrical properties compared to known polyimides, including those derived from 2,2′-bis(trifluoromethyl)benzidine. Polymers from the diamine with OCF_3 substituents show an especially favorable combination of low dielectric constant, moisture absorption, and coefficient of thermal expansion (CTE) and high thermal stability, suggesting promise as a next-generation material for electronics applications. Polymers from diamines with the largest fluoroalkoxy substitutents have very low moisture absorption, but surprisingly high CTE.

Polyimides have found wide usage as films, coatings, adhesives, and matrix resins due to their excellent electrical and mechanical properties, high thermal and chemical stability, good solvent resistance, and dimensional stability.[1] They have diverse applications in the electronics industry as flexible circuitry substrates, stress buffers, interlayer dielectrics, and passivation layers. With the ever increasing sophistication in electronics devices (smaller and faster), new demands are being placed on the materials comprising these devices. Improvements in polyimide properties have been sought by incorporating trifluoromethyl or other perfluoroalkyl groups leading to lower moisture pickup, lower dielectric constant, and better solubility.[2] Perhaps, the most common fluorinated monomers for engineering resins are those derived from hexafluoroacetone,[3] illustrated by diamine 1.[4] More recently, it has been recognized that an even better combination of mechnical and electrical properties might be achieved by incorporating fluorinated groups into more rigid, nonplanar monomers (for low coefficient of thermal expansion (CTE)).[5-7] Some of the most promising new materials combine rigid 9,9-bis(trifluoromethyl)xanthene-2,3,6,7-tetracarboxylic dianhydride (6FCDA) with rigid 2,2′-bis(trifluoromethyl)benzidine (TFMB). The TFMB monomer has been previously employed in polyamides[8] and polyimides.[9]



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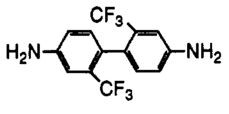
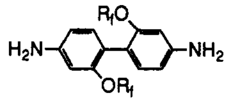
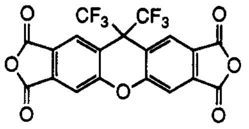


TFMB

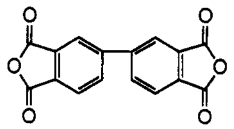
We considered that a further improvement in polyimide properties might be achieved by replacing the trifluoromethyl groups in TFMB with trifluoromethoxy substituents. The trifluoromethoxy group is very chemically and thermally stable[10] and is significantly less electron withdrawing than trifluoromethyl,[11] so the diamine should be more reactive in condensation polymerization. We have prepared bis(trifluoromethoxy)benzidine (TFMOB), as well as analogs TFEOB and DFPOB having larger fluoroalkyl substituents. These novel diamines have been used with the stiff dianhydrides 6FCDA, 3FCDA, BPDA, and PMDA to make several new polyimides whose properties can be compared to those of polyimides from TFMB.



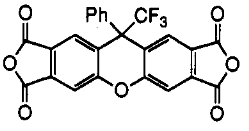
TFMOB, $R_f = CF_3$
TFEOB, $R_f = CF_2CF_2H$
DFPOB, $R_f = CF_2CFHOCF_2CF_2CF_3$



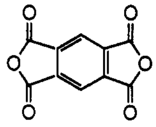
6FCDA



BPDA



3FCDA



PMDA

Experimental Section

Materials. Pyromellitic dianhydride (PMDA) was obtained in high-purity from DuPont. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) was obtained from Chriskev. 9,9-Bis(trifluoromethyl)xanthene-2,3,6,7-tetracarboxylic dianhydride (6FCDA) and 9-phenyl-9-(trifluoromethyl)xanthene-2,3,6,7-tetracarboxylic dianhydride (3FCDA) were prepared in high purity by Dr. S. Trofimenko at DuPont. All dianhydrides were thoroughly dried under vacuum/N_2 bleed at 150–180 °C prior to use. 2,2′-Bis(trifluoromethyl)benzidine (Marshallton) was sublimed and recrystallized from toluene prior to use. Anhydrous *N*-methylpyrrolidinone (99+%, Aldrich) was used as received. *N*-Cyclohexylpyrrolidinone (CHP) was distilled from CaH_2. All other solvents were reagent grade materials and were used as received.

3-(Trifluoromethoxy)nitrobenzene (2a). A 1.4-L Hastelloy pressure vessel was charged with 150 g (1.08 mol) of 3-nitrophenol and 380 g (2.47 mol) of carbon tetrachloride. The vessel was closed, cooled in dry ice, evacuated, and charged with 400 g of anhydrous HF and 15 g of anhydrous boron trifluoride. The contents were heated to 130 °C for 12 h with vigorous agitation.

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The vessel was cooled to room temperature and vented to atmospheric pressure. The contents of the vessel were transferred to a polyethylene bottle, diluted with methylene chloride, treated with powdered anhydrous potassium fluoride to absorb the excess HF, and filtered. The combined filtrates from two runs were concentrated on a rotary evaporator to a dark oil. Kugelrohr distillation at a bath temperature of about 75 °C and 1-mm pressure gave 425 g (97%) of the product[13] as a light yellow oil.

4,4'-Diamino-2,2'-bis(trifluoromethoxy)biphenyl (TFMOB). A flame-dried 5-L flask with a mechanical stirrer, addition funnel, and thermometer was charged under N_2 with 1.2 L of dimethyl sulfoxide (DMSO). The flask was cooled in an ice water bath, and 58.6 g (1.55 mol) of sodium borohydride was slowly added so that the temperature was maintained at 18–20 °C. To this stirred mixture was added 161.5 g (0.78 mol) of 3-(trifluoromethoxy)nitrobenzene over 0.25 h. The cooling bath was removed, allowing the mixture to warm exothermally in stages to about 55 °C, after which it began to cool spontaneously. The mixture was then heated to 105 °C, maintained for 5 min, and then allowed to cool to room temperature. The mixture was diluted with 1 L of methylene chloride and 1.5 L of water and cooled in an ice bath to about 10 °C. Concentrated hydrochloric acid (200 mL) was added slowly. (*Caution*! Foaming.) The methylene chloride layer was separated, washed with 1 L of water, dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator to 134.8 g of an orange oil whose structure is assigned as 3,3-bis(trifluoromethoxy)hydrazobenzene: ^{1}H NMR (δ, $CDCl_3$) 5.7 (s, 2 H), 6.7 (m, 6 H), 7.2 (t, 2 H); ^{19}F NMR (δ, $CDCl_3$) −58.14; IR (neat) 3359 cm^{-1}.

A 40.4-g portion of the above product in 50 mL of ether was added to a stirred mixture of 400 mL of 6 N hydrochloric acid, 10 g of hydrated stannous chloride, and 100 mL of ether at 0 °C. The mixture was stirred for 0.5 h at 0 °C, and 850 mL of concentrated hydrochloric acid was added over 2.5 h. The mixture was stirred overnight at room temperature. The resulting mixture was cooled to 10 °C and filtered. The solid was treated with 500 mL of 6 N sodium hydroxide and 1 L of ether. The ether solution was dried over magnesium sulfate and concentrated on a rotary evaporator to 29.8 g of oil. The oil was distilled in a Kugelrohr apparatus, giving a 3.5-g forerun (mostly 3-(trifluoromethoxy)aniline) at a pot temperature of 70–140 °C and 0.3 mm, followed by 25.5 g of oil at 140–155 °C and 0.1 mm. The product was recrystallized as its hydrochloride salt by treating the oil with 200 mL of 6 N HCl and heating to boiling. Water (ca. 1.5 L) was added until precipitation just started. Darco was added, and the hot solution was filtered and cooled to room temperature. The white solid was collected and washed with 6 N HCl. The salt was converted to the free diamine by treatment with aqueous sodium hydroxide and extraction into ether to give 23.5 g (57%) of the title product as an oil which crystallized on scratching and standing: mp 67.5–68 °C; ^{1}H NMR (δ, $CDCl_3$) 3.82 (s, 4 H), 6.59 (d, 2 H), 6.63 (d, 2 H), 7.08 (d, 2 H); ^{19}F NMR (δ, $CDCl_3$) −57.5.

Anal. Calcd for $C_{14}H_{10}F_6N_2O_2$: C, 47.74; H, 2.86; N, 7.95. Found: C, 47.75; H, 2.96; N, 8.01.

4,4'-Diamino-2,2'-bis(1,1,2,2-tetrafluoroethoxy)biphenyl (TFEOB). 1-Nitro-3-(1,1,2,2-tetrafluoroethoxy)benzene (200 g, 0.84 mol) (Aldrich) was reacted with sodium borohydride (100 g, 2.64 mol) in 1.2 L of DMSO as described above to give 171.8 g of the intermediate hydrazo compound: ^{1}H NMR (δ, $CDCl_3$) 5.79 (s, 2 H), 5.86 (tt, 2 H), 6.70 (m, 6 H), 7.20 (t, 2 H). The crude product in 250 mL of ether was added dropwise to 500 mL of concentrated hydrochloric acid, 125 g of stannous chloride, 250 mL of ether, and 250 mL of methylene chloride which was cooled in an ice water bath. An additional 500 mL of concentrated hydrochloric acid was added, and the mixture was allowed to warm to room temperature and stirred overnight. The mixture was distilled to remove the organic solvents. A white solid was removed by filtration and stirred with 300 mL of methylene chloride and 300 mL of 10% aqueous sodium hydroxide solution. The organic solution was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator to a dark oil. Kugelrohr distillation at 180–185 °C and 0.5-mm pressure gave 151.4 g of oil, determined to be a mixture of about 67% of the desired 4,4'-diamine and 33% of isomeric product(s) by proton NMR. The isomer mixture was indicated by the presence of a second triplet of triplets (H–C–*F*) centered at δ 5.89 in addition to the absorption at δ 5.58 for the desired product plus a complex aromatic pattern. The desired isomer was obtained in pure form by dissolving the mixture in about 1 L of methylene chloride, which was then saturated with gaseous hydrogen chloride. The precipitate was collected and converted to the free diamine by stirring with ether and 10% aqueous sodium hydroxide solution. The ether solution was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. This fraction was precipitated a second time from methylene chloride saturated with HCl and Kugelrohr distilled at 150 °C and 0.2 mm to give 95.8 g (55%) of the title product: ^{1}H NMR (δ, $CDCl_3$) 3.77 (s, 4 H), 5.58 (tt, 2 H), 6.55 (d, 2 H), 6.64 (s, 2 H), 7.05 (d, 2 H); ^{19}F NMR (δ, $CDCl_3$) −88.63 (s, 4 F), −137.32 (dt, 4 F).

Anal. Calcd for $C_{16}H_{12}F_8N_2O_2$: C, 46.16; H, 2.90; N, 6.73. Found: C, 45.46; H, 3.35; N, 6.34.

3-[2-(Heptafluoropropoxy)-1,1,2-trifluoroethoxy]nitrobenzene (2c). Potassium *tert*-butoxide (5 g, 0.045 mol) was added to a solution of 106 g (0.76 mol) of 3-nitrophenol in 700 mL of DMF at 15 °C. The solution was stirred 10 min at room temperature. Perfluoropropyl vinyl ether (242 g, 0.91 mol) (DuPont) was added dropwise over 2 h with an exotherm to about 30 °C. The solution was stirred overnight and then poured into 3 L of ice water containing 10 mL of concentrated hydrochloric acid. A lower layer was separated and the aqueous solution was extracted with methylene chloride. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. Kugelrohr distillation of the residue at 0.5 mm and a pot temperature of 83–91 °C gave 285 g (93%) of oily product: ^{1}H NMR (δ, $CDCl_3$) 6.15 (dt, 1 H), 7.60 (m, 2 H), 8.09 (s, 1 H), 8.20 (m, 1 H).

4,4'-Diamino-2,2'-bis[2-(heptafluoropropoxy)-1,1,2-trifluoroethoxy]biphenyl (DFPOB). 3-[2-(Heptafluoropropoxy)-1,1,2-trifluoroethoxy]nitrobenzene (225.7 g, 0.557 mol) was reacted with sodium borohydride (66.20 g, 1.75 mol) in DMSO as described above to give 191.1 g of the intermediate hydrazo compound. A 65.1-g portion of this product in 75 mL of methylene chloride and 50 mL of ether was added dropwise to a solution of 400 mL of concentrated hydrochloric acid and 40 g of stannous chloride at −4 °C. An additional 50 mL of methylene chloride was added, and the solution was allowed to warm to room temperature and stirred overnight. The mixture was concentrated on a rotary evaporator at 35 °C to remove the organic solvents, and the aqueous solution was decanted from a gum. The gum was rinsed with water and stirred with 1 L of ether and 500 mL of 10% aqueous potassium hydroxide solution. The aqueous phase was saturated with sodium chloride and separated from the ether solution. The ether solution was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator to 63.15 g of dark oil. A Kugelrohr distillation of the oil gave 6.0 g of 3-[2-(heptafluoropropoxy)-1,1,2-trifluoroethoxy]aniline at a pot temperature up to 140 °C and 0.3-mm pressure, followed by 53.9 g of oil at a pot temperature of 149–163 °C and 0.3-mm pressure. The latter material was determined to be a mixture of benzidine isomers by NMR spectroscopy. The product was chromatographed on a 6 × 34 cm column of silica gel, eluting with 5% ethyl acetate in hexane (5.7 L), followed by 10% ethyl acetate in hexane (2.6 L). From the 5% ethyl acetate fractions was isolated 19.8 g of oil whose structure was assigned as 2,2'-diamino-4,4'-bis[2-(heptafluoropropoxy)-1,1,2-trifluoroethoxy]biphenyl from its NMR spectrum: ^{1}H NMR (δ, $CDCl_3$) 3.81 (s, 4 H), 6.03 (dt, 2 H), 6.60 (s, 2 H), 6.66 (d, 2 H), 7.08 (d, 2 H). The desired product (15.9 g) was isolated from the 10% ethyl acetate fractions and Kugelrohr distilled at 150–160 °C and 0.3-mm pressure: ^{1}H NMR (δ, $CDCl_3$) 3.78 (s, 4 H), 5.70 (dt, 2 H), 6.57 (d, 2 H), 6.65 (s, 2 H), 7.03 (d, 2 H); ^{19}F NMR (δ, $CDCl_3$) −81.95 (t, 6 F), −85.82 (tt, 4 F), −87.20 (t, 4 F), −130.34 (s, 4 F), −144.77 (dm, 2 F).

Anal. Calcd for $C_{22}H_{12}F_{20}N_2O_4$: C, 35.31; H, 1.62; N, 3.74. Found: C, 34.86; H, 1.72; N, 3.61.

The title product could also be isolated from the isomeric mixture by recrystallization of the hydrochloride salt from methylene chloride. In one example, a 182.4-g portion of mixed isomers was dissolved in 500 mL of methylene chloride, and anhydrous hydrogen chloride gas was passed into the solution.

The solid which formed was filtered, converted to free amine, and Kugelrohr distilled to give 33.8 g of pure product.

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 a few 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 4.5231 g (9.8708 mmol) of 6FCDA and 3.4769 g (9.8708 mmol) of TFMOB. Shortly thereafter, 32 mL of NMP was added and stirring was begun. 6FCDA dissolved slowly into the reaction mixture, and the reaction was allowed to stir under nitrogen at room temperature overnight (ca. 18 h). The next day, a homogeneous, viscous, pale yellow solution resulted which was diluted to 16 wt % (from the original 20 wt %) with NMP. The solution was allowed to stir overnight (ca. 18 h) to allow for further equilibration. The following day, the solution was pressure filtered through a 1-μm filter in preparation for spin-coating.

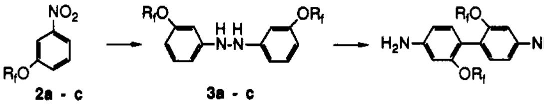
Solution Polyimide (PI). A 100-mL reaction kettle fitted with a nitrogen inlet and outlet and a mechanical stirrer was charged with 3.4181 g (7.330 mmol) of 3FCDA and 2.5819 g (7.330 mmol) of 2,2′-bis(trifluoromethoxy)benzidine (TFMOB). Shortly thereafter, 24 mL of NMP/CHP (4/1 v/v) was added and stirring was begun. The solution was initially heterogeneous but homogenized slowly as the monomers dissolved. The viscosity increased noticeably within ~10 min of stirring at room temperature. Stirring under nitrogen at room temperature was continued overnight (ca. 18 h). The next day, the extremely viscous, very pale yellow poly(amic acid) solution was diluted to ~10 wt % solids (from the original 20 wt % solids) with the 4/1 NMP/CHP solvent mixture. The reaction kettle was then fitted with a Dean–Stark trap and a water condenser on the outlet side for thermal imidization. The reaction kettle was heated in a temperature-controlled oil bath to 180–190 °C. This temperature range was maintained overnight (ca. 18 h) with good stirring under a nitrogen purge. The following day, the pale yellow solution was allowed to cool to room temperature. The solution upon cooling became a white waxlike gel. The solution was again heated, via the oil bath, to redissolve the solid and diluted to 6 wt % solids with NMP. Cooling to room temperature again caused the formation of the gellike solid. The heterogeneous solution was poured into an excess amount (~1 L) of methanol to precipitate the polyimide as a solid, filtered, and dried under vacuum. The polymer was poorly soluble at room temperature in common solvents ($CHCl_3$, NMP, DMAC), but was found to be soluble in hot DMAC when dilute. No coating of this hot solution was attempted.

Film Preparation. Films were prepared by spin coating the filtered poly(amic acid) 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.

Polymer Characterization. Gel permeation chromatography (GPC) on PAAs 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, or for PIs on a Waters instrument (150C) with a Zorbax TMS precolumn and two Shodex AD80M/S columns in DMAC at 135 °C. 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 Perkin-Elmer 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. Glass transition temperatures (T_g) were obtained from a Rheometrics RSA-II dynamic mechanical analyzer in tension (frequency = 10 rad). T_g was taken as the peak maximums of the loss modulus and tan δ curves. 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)[12] 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.

Results and Discussion

Monomer Synthesis. Bis(fluoroalkoxy)benzidines were prepared by reduction of 3-(fluoroalkoxy)nitrobenzenes (**2a–c**) to the corresponding hydrazo derivatives, followed by benzidine rearrangement (eq 1). The 3-(fluoroalkoxy)nitrobenzenes (**2**) were prepared from 3-nitrophenol—**2a** by boron trifluoride catalyzed reaction with carbon tetrachloride in anhydrous hydrogen fluoride[13] (eq 2), and **2b** and **2c** by base-catalyzed addition to tetrafluoroethylene[14] and perfluoropropyl vinyl ether,[15] respectively, in excellent yield. Compound **2b** was also obtained from a commercial source.



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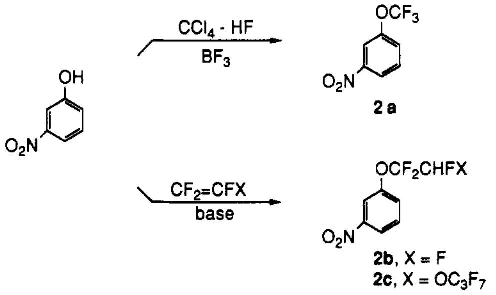


(2)

(3)

The nitroaromatics (**2**) were reduced to the corresponding hydrazo compounds (**3**) using sodium borohydride in dimethyl sulfoxide. Although this reaction is reported[16] to give azoxy and azo compounds, we found that the desired hydrazo derivatives were formed when the reaction mixture was heated to higher temperatures. Crude products **3** were subjected to acid-catalyzed benzidine rearrangement in the presence of stannous chloride. Although the reducing agent should not be required in these reactions, we obtained better yields of the desired benzidines in its presence. Perhaps, it serves to reduce small amounts of azo or azoxy compounds present in crude **3** or formed in situ by air oxidation.

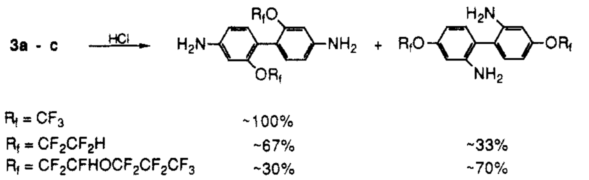
Proton and fluorine NMR spectra of crude TFMOB, after removal of smaller amounts of 3-(trifluoromethoxy)aniline by distillation, suggested formation of a single benzidine isomer. Its structure was confirmed as the desired 4,4′-diamino isomer (TFMOB) by X-ray crystallographic examination of its bis-acetamide derivative. The diamine was isolated as an oil which was eventually induced to crystallize by stirring and scratching.

In contrast, complexity of the NMR spectra of the crude benzidines from rearrangement of **3b** and **3c** (after removal of the corresponding anilines by distillation) suggested the presence of isomers. From **3b**, the desired 4,4′-diamine (TFEOB) could be isolated in pure form by crystallization

Table I. GPC Molecular Weight Characterization and Film Appearance of Fluoroalkyl- and Fluoroalkoxy-Substituted Benzidine-Based Poly(amic acid)s

monomers	M_n	M_w	M_w/M_n	% solids	film appearance
6FCDA/TFMB	126000	215000	1.71	16	clear
6FCDA/TFMOB	107000	217000	2.02	16	clear
6FCDA/TFEOB	88800	205000	2.31	16	clear
6FCDA/DFPOB	52900	106000	2.01	20	clear
3FCDA/TFMB	208000	396000	1.90	10	clear
3FCDA/TFMOB	149000	354000	2.36	14	clear
3FCDA/TFEOB	98200	203000	2.07	16	clear
BPDA/TFMB	315000	520000	1.65	11.5	clear
BPDA/TFMOB	165000	342000	2.07	14	hazy
BPDA/TFEOB	113000	318000	2.81	14	hazy
BPDA/DFPOB	65900	140000	2.13	20	hazy
PMDA/TFMB	107000	207000	1.94	12	clear
PMDA/TFMOB	87400	203000	2.33	13	clear
PMDA/TFEOB	121000	256000	2.11	14	clear
PMDA/DFPOB	61300	122000	2.00	20	clear
BPDA/PPD	58100	157000	2.66	13.5	clear
PMDA/ODA	63600	181000	2.85	14	clear

of its hydrochloride salt as detailed in the Experimental Section. The structure of this isomer was assigned as TFEOB, because the aromatic pattern is its proton NMR spectrum was identical to that of the previously identified TFMOB. By integration of appropriate peaks in the proton NMR of the crude material, the initial product ratio was about 67% TFEOB and 33% of material whose structure was assigned as the corresponding 2,2′-diamino isomer (eq 4). From **3c**, the desired isomer DFPOB was



(4)

the minor product (ca. 30%). It and the 2,2′-diamino isomer were initially separated by column chromatography. Pure DFPOB could also be obtained by fractional precipitation of its hydrochloride salt. The NMR spectra suggested that small amounts of the 2,4′-diamino isomers were also formed during rearrangements of **3b** and **3c**, but these compounds were not isolated in pure form. Presumably, steric effects, the increasing size of the fluoroalkoxy substituents, $OCF_3 < OCF_2CF_2H < OCF_2CFHOC_3F_7$, are responsible for formation of varying amounts of the isomeric products.

Polyimide Synthesis and Properties. To produce polyimide structures with low CTE, the substituted benzidines of this work were paired with "rodlike" dianhydrides to yield polyimide backbones of high stiffness and thereby films with high in-plane orientation. The polymerization of the substituted benzidines by the standard poly(amic acid) route typically proceeded well to highly viscous solutions. Viscosity buildup, however, was noticeably slower than for standard diamines like 4,4′-oxydianiline. The electron-withdrawing character of the OR_f groups is likely strong enough to lower somewhat the basicity and thereby the reactivity of the diamine. According to GPC data, very high molecular weights were usually attainable (Table I). Although these GPC numbers are relative (based on polystyrene), comparison to commercial BPDA/PPD and PMDA/ODA indicates high molecular weight. Only the DFPOB gave somewhat lower values, but in any case, all poly(amic acid) samples gave good, creasable films when spin coated and thermally converted to polyimides. Polydispersity values were also close to the most probable distribution, indicating that substantial equilibration of the poly(amic acid)s had taken place. In fact, all M_w/M_n's were lower than those of the commercial materials, which may be a benefit of the somewhat lower reactivity (reduced initial buildup in M_w due to interfacial effects,[17] faster equilibration).

Table II. GPC Characterization of Fluoroalkoxy-Substituted Benzidine-Based Solution-Imidized Polyimides[a]

	poly(amic acid)s			polyimides		
monomers	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
3FCDA/TFMB				72400	171000	2.36
3FCDA/TFMB[b]				234000	628000	2.68
3FCDA/TFMOB	100000	223000	2.21			
3FCDA/TFEOB	146000	303000	2.07	154000	379000	2.46
3FCDA/DFPOB	64000	133000	2.09	21700	54700	2.53

[a] Polyimides in DMAC at 135 °C, poly(amic acid)s in DMAC mixture at 35 °C. [b] Prepared in *m*-cresol (2% isoquinoline) at ~200 °C.

The direct synthesis of polyimides in a one-pot/two-stage solution polymerization[18] also proceeded smoothly in the NMP/CHP reaction mixture. Based on previous experience,[5,7] 3FCDA was chosen as dianhydride for initial studies due to its ability to yield *soluble* quasi-rodlike polyimides. Upon heating the poly(amic acid) solution formed in the initial step, the reaction solution viscosity dropped quite sharply and then increased gradually as imidization proceeded. A high-viscosity homogeneous solution resulted at high temperature after overnight imidization, but upon cooling to room temperature, the reaction solution became a waxlike gel (reversible upon reheating). GPC of these polyimides at 135 °C in DMAC (Table II) indicated (with the exception of 3FCDA/DFPOB) high molecular weights comparable to those of their precursor PPAs. Because of the solubility typically found only at elevated temperatures, film formation was not attempted as part of this work. Certainly formation of film and fibers from hot solution is feasible, but was left for later work. The quasi-rodlike nature of these soluble polyimides is especially interesting for the preparation of high-modulus/high-strength fibers and low-CTE/low-"cure" temperature films.

In addition to the NMP/CHP route, direct imidization was also possible via one-pot synthesis using *m*-cresol as solvent. As shown in Table II for 3FCDA/FTMB, this also could give very high molecular weight. Besides CHP, other azeotroping solvents (xylene, *o*-dichlorobenzene) are also feasible.

Physical property characterization of the films prepared from the poly(amic acid) solution is given in Table III. The results here are compared to those for TFMB. In general, the mechanical properties of films from TFMB, TFMOB, and TFEOB were largely similar. DFPOB-based films (long pendant fluoroalkoxy group) tended to have higher elongation, lower modulus, and generally lower strength. The modulus values observed in many cases were typical of very stiff backbones like BPDA/PPD. Because of this high stiffness and thereby ability to provide films with high in-plane orientation, CTEs were usually low and in the region desired to match most substrates encountered in electronics (metals like copper or aluminum, ceramics like silica or alumina). Very notably, DFPOB did not give low CTE in films, at least as prepared from poly(amic acid) solution. In fact, the CTEs of DFPOB-based films were quite high, despite the very stiff nature of the backbones. The long fluoroalkoxy pendant

Table III. Characterization of Fluorinated Polyimides Based on Benzidine Derivatives

sample	% fluorine	tens str (MPa)	% elong	mod (GPa)	CTE (ppm)	% H_2O abs at 85% RH	dielec const (dry, 1 mHz)	T_g DMA at 10 rad/s E'', tan δ	TGA 5% wt loss in air
6FCDA/TFMB	30.7	200	6	6.1	6	1.2, 1.4	2.4, 2.7	420, 427	473
6FCDA/TFMOB	29.4	411	18	5.1	10	0.8	2.8	375, 375	491
6FCDA/TFEOB	31.7	294	15	5.3	10	0.7	3.0	363, 386	477
6FCDA/DFPOB	42.2	221	27	2.6	109	0.1	2.5	350, 355	470
3FCDA/TFMB	22.8	197	8	5.0	6, 20	1.9	2.7	>400, 426	484
3FCDA/TFMOB	21.8	143	7	3.4	36	NA	2.6, 2.6	400, 406	487
3FCDA/TFEOB	24.7	249	19	4.0	40	0.8	3.1		480
BPDA/TFMB	19.7	286	31	4.1	20	1.3	2.9, 3.0	~330, 373	580
BPDA/TFMOB	18.7	316	39	4.4	37	0.6	2.7	335, 384	606
BPDA/TFEOB	22.5	239	30	3.8	48	1.4	3.3		558
BPDA/DFPOB	37.8	145	45	1.8	133	0.2	2.7		516
PMDA/TFMB	22.7	374	28	7.4	−3	1.9	2.6, 2.6	379, 379	592
PMDA/TFMOB	21.3	378	18	7.2	−3	0.7	2.6	363, 394	591
PMDA/TFEOB	25.4	333	14	6.9	−7	1.6	3.3		549
PMDA/DFPOB	40.8	226	24	3.1	81	<0.05	2.5		496
BPDA/PPD	0.0	424	52	5.7	4	1.4	3.1		606
PMDA/ODA	0.0	168	82	1.3	31	3.5	3.2		565

chains were likely responsible either because of their high content (fluoropolymers tend to have very high CTEs) and/or because they disturbed the orientation processes that normally occur when poly(amic acid)s are converted to polyimides (with accompanying solvent loss and film collapse). In any case, there was an indication that the CTE tended to increase with pendant chain length on the benzidine (BPDA samples). The dianhydride chosen also had an effect on the CTE observed, the more "rodlike" dianhydrides yielding lower CTEs in the order PMDA < 6FCDA < 3FCDA ~ BPDA.

Moisture absorptions of these fluorinated polyimides were noticeably low. This was most noteworthy for the TFMOB material as compared to TFMB. For the same dianhydride, the TFMOB exhibited ca. 40–50% lower moisture absorption than for TFMB. The very highly fluorinated DFPOB materials exhibited extremely low moisture absorptions, more typical of fluoropolymers than polyimides. All samples yielded moisture values much lower than standard PMDA/ODA and usually lower or comparable to one of the lowest nonfluorinated materials, BPDA/PPD.

Dielectric constants were also notably lower than the nonfluorinated materials with the exception of TFEOB. In this case, the presence of the lone hydrogens on the fluoroalkoxy pendant groups likely creates a strong dipole which increases the dielectric constant significantly, despite the presence of the fluorine in the polymer. The same effect may be operative in the DFPOB cases, but this effect may be much diluted by the high level of fluorine and length of the pendant fluoroalkoxy chains. The dielectric constants of the TFMB and TFMOB appear largely equivalent within the error of the parallel-plate measurement.

The glass transition temperatures by both E'' and tan δ (peak maximum, DMA) of the polyimide films were all high owing to the very stiff natures of the backbones. Quantification of the exact value was often difficult due to the fact that the samples exhibited a stiffening phenomenon after passing through T_g (initial drop in E' followed by an increase at a temperature of ca. 400 °C). Likely, at these high temperatures other processes may be involved (e.g., cross-linking, densification, crystallization) which affects the data. For the 6FCDA case, increasing the length of the pendant group on the benzidine decreased the T_g. As the dianhydride was varied for a given diamine, the T_g roughly followed the order 3FCDA > 6FCDA > PMDA > BPDA. A typical dynamic mechanical trace is given in Figure 1. This trace also shows a very prominent subglass transition in the 100–200 °C range which may be related to the rotation about the central C–C bond in the benzidine. This subglass transition was present in all samples containing the benzidines, although the temperatures varied considerably. A more detailed report on dynamic mechanical properties of these polyimides will be published later.[19]

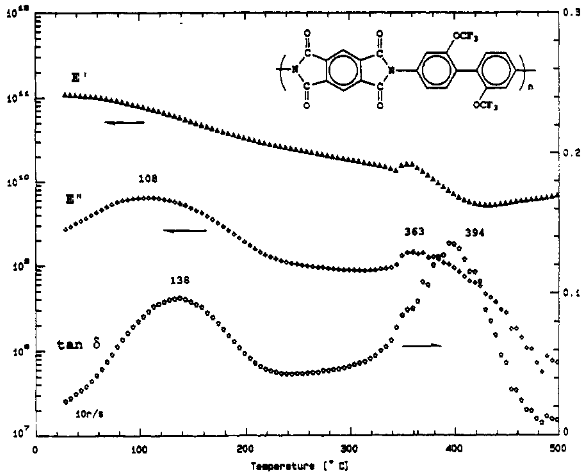


Figure 1. Dynamic mechanical analysis (DMA) of PMDA/TFMOB polyimide film.

Thermal stabilities as measured by dynamic TGA showed that the thermal stabilities of TFMOB-containing polymers were about equivalent to those of TFMB. Polyimides based on TFEOB or DFPOB which contained aliphatic hydrogen were somewhat lower in stability than the fully aromatic materials. As noted before,[5] the stabilities of 6FCDA- and 3FCDA-based materials were somewhat lower than those based on the standard PMDA and BPDA dianhydrides. In any case, all the polymers exhibited 5% weight loss values in air in excess of 450 °C.

In general, the TFMOB-based polyimides show great promise as next-generation polyimides for electronics. In addition to low dielectric constant, low thermal expansion coefficient, and excellent thermal stability, these materials have good mechanical properties and low moisture absorption. Compared to TFMB materials, TFMOB polyimides have equivalent properties and similar optical clarity (important for display applications), but significantly reduced moisture absorption. The other monomers, namely, TFEOB and DFPOB, while possessing valuable properties, suffer somewhat from higher dielectric constant or high CTE, respectively, and somewhat lower thermal stability. Although not studied as part of this work, these polyimides may have high permeabilities/selectivity due to the presence of the pendant fluoroalkoxy groups and therefore may prove useful in membrane applications. The rodlike nature of these monomers when paired with the proper dianhydride or diacid may lead to high-strength/high-modulus fibers.[20]

Conclusions

A series of three new 2,2′-fluoroalkoxy-substituted-4,4′-benzidines were prepared. Polyimides based on these materials were shown to have valuable properties for electronics applications such as low moisture absorption, low dielectric constant, and low thermal expansion coefficient. Trifluoromethoxy substitution was shown to give similar properties to trifluoromethyl, but with significantly reduced moisture absorption. In addition to applications in electronics, polyimides and polyamides from these new materials may find use in plastics, fiber, and membrane applications.

Acknowledgment. The authors would like to thank Michael Grovola for his assistance in polyimide preparation and Dr. S. Trofimenko for providing 6FCDA and 3FCDA monomers. The authors would also like to thank DuPont Central Research, Polymers, and Electronics analytical personnel for help with various characterization techniques.

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