BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 3, pp. 651–656, 1995

0032-3861/95/$10.00+0.00

Synthesis of a new fluoroalkylated diamine, 5-[1*H*,1*H*-2-bis(trifluoromethyl)-heptafluoropentyl]-1,3-phenylenediamine, and polyimides prepared therefrom

Brian C. Auman*, David P. Higley, Kirby V. Scherer Jr, Elizabeth F. McCord and William H. Shaw Jr

E. I. du Pont de Nemours & Co. Inc., Experimental Station, Wilmington, DE 19880, USA

(Received 30 August 1993; revised 16 June 1994)

The preparation of a new perfluoroalkylated diamine, 5-[1*H*,1*H*-2-bis(trifluoromethyl)heptafluoropentyl]-1,3-phenylenediamine, is described. Poly(amic acid)s and polyimides were prepared from this new diamine and polyimides were evaluated as films for electronics applications. The polyimides evaluated were found to yield low dielectric constant and low moisture absorption, but were found to have exceptionally high thermal expansion coefficient. The materials are envisioned to have applications in electronics, where a low and humidity-stable dielectric constant is required.

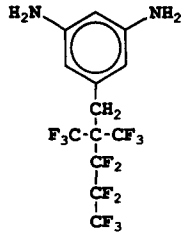
(Keywords: fluoroalkylated diamine; fluorinated polyimides; synthesis)

INTRODUCTION

Fluorinated polyimides have been receiving much attention lately, especially in the electronics industry, owing to their potential for lower dielectric constant and lower moisture absorption[1–3]. Addition of fluoroalkyl groups pendent from the polymer backbone is an interesting way of introducing a high level of fluorine into the polymer without greatly affecting the backbone stiffness and thus the high T_g typical of aromatic polyimides. Previously, perfluoroalkyl (Rf) groups, in these cases trifluoromethyl, have been introduced directly onto the aromatic ring of a simple diamine like *m*-phenylenediamine (MPD)[4,5]. Direct attachment of such groups, however, has the drawback that the highly electron-withdrawing Rf group, especially longer chains[6], lowers the reactivity of the diamine such that it is sometimes difficult to obtain high-molecular-weight poly(amic acid)s, the precursors to polyimides. Further, if the pendent group is directly adjacent (e.g. 4 position) to one of the amino groups (1 and 3 positions in MPD), then the reactivity is further reduced owing to steric hindrance.

Various researchers[7–9] have prepared MPD derivatives incorporate a spacing group between the aromatic ring and the perfluoroalkyl segment. This spacing group, usually $-OCH_2-$, $-OCH_2CH_2-$ or $-CH_2O-$ can indeed result in improved reactivity (especially when in the 5 position) but suffers from the reduced thermal stability of the aliphatic groups. Other researchers[10] have employed OC=C as a spacing group.

Our approach provides a novel fluoroalkylated monomer that attempts to circumvent both the reactivity and stability issues. This new monomer, 5-[1*H*,1*H*-2-bis (trifluoromethyl)heptafluoropentyl]-1,3-phenylenediamine (RfbMPD), has a unique branched structure, which allows for high fluorine content, but shows good reactivity and thermal stability. The fluoroalkyl group (Rf) is separated from the aromatic ring by a CH_2 group and the first carbon of this Rf group is quaternary. This arrangement not only allows for good reactivity of the amino groups, but because of the inability to eliminate HF directly from the structure, the thermal stability is also largely preserved. The methylene unit is also somewhat shielded from oxidation, both electronically and sterically, by the vicinal trifluoromethyl groups. This paper details the synthesis of this new fluorinated diamine, summarizes the synthesis and basic characterization of several polyimides from this novel monomer (see also ref. 11), and describes the n.m.r. characterization of some of these new polyimides.



RfbMPD

* To whom correspondence should be addressed

EXPERIMENTAL

Materials

The 3,5-dinitrobenzyl alcohol (Aldrich) was used as received. Perfluoro-2-methyl-2-pentene and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were obtained in high purity from sources within DuPont. The 9,9-bis (trifluoromethyl)- and 9-phenyl-trifluoromethyl-xanthene-2,3,6,7-tetracarboxylic dianhydrides (6FCDA and 3FCDA) were prepared by Trofimenko[12]. Other dianhydrides were obtained in high purity through Chriskev. All dianhydrides were dried at 150–180°C under vacuum/N_2 bleed for several hours prior to use and stored in a dry box. *N*-Methylpyrrolidinone (NMP; Aldrich anhydrous 99 + %), acetic anhydride and pyridine (both Fisher) were used as received. *N,N*-Dimethyl-acetamide (DMAc) was dried over 4 Å molecular sieves prior to use. Other reagents and solvents were reagent grade and were used as received.

Synthesis of 3,5-dinitrobenzyl bromide

In a two-litre three-necked flask, equipped with a reflux condenser with gas inlet, a mechanical stirrer and a 250 ml addition funnel, were combined under nitrogen 100.0 g (0.505 mol) of 3,5-dinitrobenzyl alcohol and one litre of chloroform. The addition funnel was charged with a solution of 136.7 g (48.0 ml, 0.505 mol) of phosphorus tribromide in 150 ml of chloroform. This solution was added to the rapidly stirred contents of the reaction flask during a period of 3 h. Upon completion of this addition, the reaction mixture was heated at reflux for 2 h, and then was left at room temperature overnight. The organic solution was then decanted from a residue of phosphorus compounds, into 1000 g of ice. The resulting mixture was transferred to a separatory funnel, and the organic layer was drawn off and saved. The aqueous layer was extracted with a small portion of chloroform. The combined organic solutions were washed with water, then with dilute aqueous sodium bicarbonate, and dried over anhydrous magnesium sulfate. Solvent was removed by rotary evaporation at reduced pressure to leave a solid product, m.p. 91–94°C, which was identified by n.m.r. spectroscopy as the desired product, 3,5-dinitrobenzyl bromide. The yield was 126.6 g (mol. wt 261.0; 0.485 mol; 96.0% of theory). A small portion of the product was recrystallized from a mixture of hexane and ethyl acetate, to obtain a purified sample with m.p. 93–94°C.

Synthesis of 5-[1H,1H-2-bis(trifluoromethyl)heptafluoro-pentyl]-1,3-dinitrobenzene

A two-litre three-necked round-bottomed flask with a magnetic stirring bar was charged in a dry atmosphere (nitrogen glove box) with 45 g (0.78 mol) of spray-dried potassium fluoride and 122.3 g (0.469 mol) of 3,5-dinitrobenzyl bromide. The flask was capped with rubber septum stoppers and taken into the hood. A needle was inserted into one septum and under gentle nitrogen pressure, another septum was removed and 727 g of dried dimethylacetamide and 160.3 g of perfluoro-2-methyl-2-pentene (0.534 mol) were added. The septum was replaced and the mixture was stirred magnetically at room temperature for 11 days. The mixture was then worked up by slowly adding water until the flask was nearly full. [CAUTION: The mixture warms slightly and some of the excess perfluoromethylpentene may boil out.] The mixture was allowed to stand for two days, then filtered and the filter cake was washed well with water. The crude product was a heavy granular solid, about the colour and consistency of light brown sugar. After air drying, the crude product weighed 223.5 g (95.4% yield). Proton and fluorine n.m.r. spectra were consistent with complete conversion of the starting benzyl bromide to the desired product. The crude product was then recrystallized from methanol to give purified product, m.p. 81–82.3°C. ^{1}H n.m.r. ($CDCl_3$): δ9.06 (t, $J = 1.9$ Hz, 1H), 8.53 (bs, 2H), 3.78 (bs, 2H), ^{19}F n.m.r. ($CDCl_3$): −62.5 (m, 6F), −80.3 (t, $J = 13.7$ Hz, 3F), −106.2 (m, 2F), −123.3 (m, 2F).

Synthesis of 5-[1H,1H-2-bis(trifluoromethyl)heptafluoro-pentyl]-1,3-phenylenediamine (RfbMPD)

A 27.0 g portion of the purified dinitro compound was combined in a glass pressure bottle with 200 ml of absolute ethanol and 2.7 g of 5% palladium on carbon, then shaken at room temperature under a hydrogen pressure of 60 psig (~415 kPa) for 4 h. The product mixture was filtered, solvent was removed from the filtrate at reduced pressure, and the residue was recrystallized from hexane to obtain 12.3 g of purified product, m.p. 66–67°C. In the same manner, a 25.6 g portion of the dinitro compound was hydrogenated for about 3 h over 2.6 g of 5% palladium on carbon. Isolation and recrystallization of the product as above gave 12.3 g of the diamine, m.p. 66–66.5°C. The combined mother liquors from the recrystallizations of the two hydrogenation products yielded, upon concentration and cooling, an additional 13.2 g crop of purified product, m.p. 65–66.5°C. From 52.6 g of the dinitro compound (mol. wt 500.2; 0.105 mol), there was thus obtained a total of 37.8 g of RfbMPD (mol. wt 440.2; 0.086 mol; 82% of theory). ^{1}H n.m.r. ($CDCl_3$): δ6.04 (bs, 2H), 5.98 (t, $J = 1.9$ Hz, 1H), 3.56 (bs, 4H), 3.34 (bs, 2H). ^{19}F n.m.r. ($CDCl_3$): −62.6 (m, 6F), −80.5 (t, $J = 13.4$ Hz, 3F), −106.4 (m, 2F), −123.3 (m, 2F). High-resolution mass spectrometry: calculated ($C_{13}H_9N_2F_{13}$, $M+$) 440.0558, observed 440.0558.

Synthesis of poly(amic acid) from 6FDA and RfbMPD

Into a 100 ml reaction kettle equipped with a mechanical stirrer and nitrogen inlet and outlet were charged: 3.9818 g (9.0452 mmol) of RfbMPD and 30 ml of NMP. After dissolution of the diamine, 4.0182 g (9.0452 mmol) of 6FDA were added as a solid (2 ml NMP used to rinse in). The dianhydride dissolved quickly upon addition and the reaction mixture warmed slightly. The reaction was allowed to proceed overnight to form a moderately viscous poly(amic acid) solution. This solution was pressure-filtered through a 10 μm filter in preparation for spin coating onto silicon waters. Other poly(amic acid)s were formed in a similar manner.

Synthesis of polyimide from 6FDA and RfbMPD

Into a 100 ml reaction kettle equipped with a mechanical stirrer and nitrogen inlet and outlet were charged: 5.9727 g (13.567 mmol) of RfbMPD and 6.0273 g (13.567 mmol) of 6FDA along with 36 ml of NMP. The reaction was allowed to proceed overnight at room temperature. The following day the poly(amic acid) solution was diluted with 12 ml NMP, and after thorough mixing, 10.2 ml of acetic anhydride followed by 7.7 ml pyridine were added. The reaction was allowed to proceed

for several additional hours at room temperature and the resulting polyimide was precipitated into methanol, filtered and dried. The white, fibrous polymer, which was readily soluble in chloroform, was further purified by reprecipitation into methanol. After thorough drying under vacuum/N_2, the polyimide was dissolved at about 25% solids in butyl acetate and filtered to 1 μm for spin coating onto silicon wafers.

Synthesis of polyimides from 6FCDA, 3FCDA and RfbMPD

A similar procedure as for 6FDA above was used for the preparation of 6FCDA- and 3FCDA-based polyimides with RfbMPD, except that 1,1,2,2-tetrachloroethane (TCE) was used as spin coating solvent. The polyimide based on 6FCDA produced a highly swollen precipitate upon imidization in NMP, but was found to be readily soluble in chloroform or TCE after isolation.

Techniques

Gel permeation chromatography (g.p.c.) of the poly (amic acid) solutions was performed on a Waters GPC 2 at 35°C with four linear Phenogel columns at a flow rate of 1 ml min^{-1}. The solvent was the DMAc/LiBr/H_3PO_4/THF solvent system described in the literature[13], detection was by refractive index (*RI*) and calibration was based on polystyrene standards. G.p.c. of soluble polyimides was performed as above if the polyimide was soluble in DMAc at room temperature; if not, the analysis was performed on a separate Waters instrument (150C) with a Zorbax TMS precolumn and two Shodex AD80M/S columns in DMAc (with a trace (0.25 g l^{-1}) of toluenesulfonic acid) at 135°C (1 ml min^{-1}, *RI* detector, polystyrene standards).

Films were prepared by spin coating the filtered poly(amic acid) or polyimide solution onto 5 inch (~127 mm) silicon wafers with 1000 Å of thermally grown surface oxide, followed by drying at 135°C for 30 min in air, and then heating under nitrogen to 200°C (2°C min^{-1}) and holding for 30 min followed by heating to 300–350°C (2°C min^{-1}) 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.

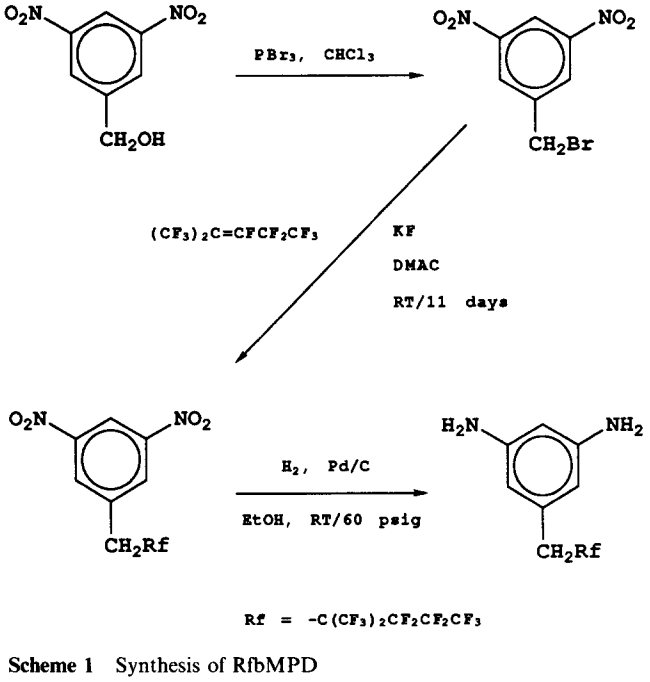
Fourier-transform infra-red (*FT*i.r.) spectra of the polyimide films were taken with a Nicolet 60 SXB spectrometer in attenuated total reflectance (a.t.r.) mode. Mechanical properties of the films were measured in accordance with ASTM D-882-83 (method A) on an Instron model 4501 tensile tester. Crosshead speed was 0.2 inch/min (~5 mm min^{-1}). Linear coefficient of thermal expansion (*CTE*) was obtained from a Perkin–Elmer TMA-7 thermomechanical analyser (5 or 10°C min^{-1}, −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 thermogravimetric analyser (t.g.a.) at 15°C min^{-1} from 50 to 600°C. The measurements were taken after the sample was initially heated to 150°C for 5 min in order to substantially remove absorbed moisture. Glass transition temperatures (T_g) were obtained either from a DuPont 1090 DSC (25°C heating rate, second heat) or from a Rheometrics RSA-II dynamic mechanical analyser (d.m.a.) in tension at a frequency of 10 rad (5° increments). The d.m.a. values were taken from the peak maximum in the loss modulus (E'') curve. Dielectric constant was measured by the parallel-plate capacitor method in the frequency range 10 kHz–10 MHz on thin (10–20 μm) films. Gold electrodes were vacuum deposited on both surfaces of dried films, followed by thorough drying (at least 48 h) at 150°C under vacuum/N_2 prior to measurement. Measurements were performed in a sealed humidity chamber at 0% r.h. Moisture absorption measurements were made by the quartz crystal microbalance technique (q.c.m.)[14,15] on thin (~3 μm) films spin coated and thermally cured, as above, onto electroded quartz crystals. Measurements were taken at various humidity settings in a controlled humidity chamber. Values are reported at 85% r.h.

Proton n.m.r. spectra were obtained with a Bruker AM 300 MHz instrument on 2% (wt/vol) solutions in chloroform-d at 40°C using a spectral width of 3600 Hz, a 90° pulse, an acquisition time of 4.6 s and a relaxation delay of 30 s. Spectra were referenced to $CHCl_3$ at 7.24 ppm. The carbon n.m.r. spectrum was obtained on a Varian VXR 400 MHz instrument on a 10% (wt/vol) solution in 1,1,2,2-tetrachloroethane-d_2 (TCE) at 100°C using a spectral width of 30 kHZ, a 90° pulse, continuous Waltz decoupling, an acquisition time of 0.64 s and a relaxation delay of 5 s. The spectrum was referenced to TCE at 74.2 ppm.

RESULTS AND DISCUSSION

Synthesis of monomer

The reaction scheme to produce RfbMPD is outlined in *Scheme 1*. The first step, namely the conversion of the benzyl alcohol to the benzyl bromide, proceeded in straightforward fashion to high yield. The reaction of the benzyl bromide with perfluoro-2-methyl-2-pentene to yield the fluoroalkylated dinitro precursor proceeded likewise to high yield. The long reaction times were a matter of convenience and probably can be substantially shortened. This reaction proceeds, in general, by an addition of the KF to the double bond to give a tertiary



Scheme 1 Synthesis of RfbMPD

carbanion stabilized by the attached perfluoropropyl and trifluoromethyl groups. This carbanion can then displace the bromine from the benzylic carbon to yield the dinitro product and KBr. Catalytic hydrogenation of this dinitro precursor led to the desired diamine in good yield. In addition to the purification discussed in the 'Experimental' section, the diamine can also be sublimed.

Polymer synthesis and properties

The RfbMPD was reacted in the conventional way with several fluorinated and non-fluorinated dianhydrides to form poly(amic acid)s. The g.p.c. molecular weights of these poly(amic acid)s are given in *Table 1* and compared to a commercial PMDA/ODA sample (PI-2540). As one can see from the table, the relative molecular weights (based on polystyrene) obtained are at least equivalent to the commercial sample indicating high molecular weight. Initial attempts at film preparation with these various poly(amic acid) (PAA) samples were only partially successful as in several cases the film would crack and peel away from the silicon wafer during processing. At least two good, albeit very thin ($\leqslant 5\,\mu m$), films, however, could be obtained from two of these samples, namely from 6FDA and BTDA. Mechanical properties were measured on the 6FDA-based film and are included in *Table 2*.

Because of the initial difficulties encountered with the poly(amic acid)s (process optimization was not performed), it was decided to attempt the preparation of soluble polyimides by chemical conversion of the poly(amic acid) in solution. With the 6FDA, 6FCDA and 3FCDA dianhydrides, this procedure did indeed give soluble polyimides, which could be easily coated and dried into good-quality, coherent, creasable films. The g.p.c. molecular weights of these soluble polyimides are also included in *Table 1* and again indicate moderate to very high molecular weight. The physical properties of the polyimide films are given in *Table 2*.

The mechanical properties of the 6FDA material were interestingly similar whether prepared from poly(amic acid) or soluble polyimide solution; however, these were markedly reduced *versus* those for PMDA/ODA. It should also be noted that the *CTE* of this polyimide was very high, substantially higher than PMDA/ODA (ca. 30 ppm) and other more flexible polyimides (ca. 40–50 ppm). This is probably the result of the bulky pendent fluoroalkyl group, which probably hinders and also interferes with chain orientation during the film forming process, known to have a profound impact on *CTE*. It is also interesting to note that the *CTE* of this highly fluorinated polyimide is similar to that of Teflon® AF (ca. 80–100 ppm). Similar results were seen in another highly fluorinated polyimide

Table 1 Characterization of poly(amic acid)s and polyimides based on RfbMPD

Dianhydride[a]	Fluorine in PI (%)	M_n	M_w	M_w/M_n	PI T_g (°C)	Coating solvent	PI film quality
PMDA	39.7	92 100	304 000	3.3	n.a.	NMP	Cracked
BPDA	35.4	56 000	210 000	3.7	n.a.	NMP	Cracked
BTDA	34.0	31 500	79 000	2.5	243[c]	NMP	Fair
6FDA	42.5	82 700	147 000	1.8	257[c]	NMP	Fair
6FCDA	41.9	76 600	181 000	2.4	n.a.	NMP	Cracked
6FDA[b]	42.5	47 500	89 600	1.9	257	BuAc	Good
6FCDA[b]	41.9	53 200[d]	114 000[d]	2.1	347	TCE	Good
3FCDA[b]	34.9	122 000	315 000	2.6	394	TCE	Good
PMDA/ODA (PI-2450)	0.0	50 800	125 000	2.5	~425	NMP	Good

[a] PMDA, pyromellitic dianhydride; BPDA, biphenyltetracarboxylic dianhydride; BTDA, benzophenonetetracarboxylic dianhydride
[b] Converted to polyimide in solution by chemical imidization
[c] From d.s.c. (second heat), all others from d.m.a. (E'' peak max.); n.a. = not available
[d] G.p.c. of PI in DMAc at 135 C, all others of PAA in DMAc solvent mixture at 35 C

Table 2 Characterization of polyimide films from RfbMPD

Dianhydride	Film thickness (μm)	Tensile strength (MPa)	Elongation (%)	Modulus (GPa)	*CTE* (ppm/°C)	H_2O absorbed at 85% r.h. (%)	Dielectric constant at 1 MHz, dry	T.g.a. 5% weight loss in air (°C)
6FDA	5.2	65	5	1.6	98	n.a.	n.a.	n.a.
6FDA[a]	14.6	72	6	1.7	86	0.5	2.7	472
6FCDA[a]	10.5	116	28	2.0	70	0.6	2.3	458
3FCDA[a]	13.6	115	25	1.9	67	1.1	2.5	465
PMDA/ODA	12.2	168	82	1.3	31	3.5	3.2	565

[a] Film prepared from polyimide solution rather than poly(amic acid); n.a. = not available

system investigated in our laboratory[16]. The *CTE* of the soluble PI prepared film was also found to be somewhat lower than that from the PAA.

For the 6FCDA- and 3FCDA-based polymers, the mechanical properties were found to be much improved vs. 6FDA and more typical of standard polyimides. Here again, however, the *CTE* was high, but owing to the increased chain rigidity imparted by the very stiff 6FCDA and 3FCDA, the *CTE* was significantly lower than for the 6FDA material.

In terms of moisture absorption, all three soluble PI films gave very low moisture absorption compared to conventional PMDA/ODA. Values as low as 0.5 wt% at 85% r.h. were observed, attributed to the high fluorine level, *versus* 3.5% for PMDA/ODA. Dielectric constants, although some scatter was evidenced, were also found to be significantly reduced *versus* standard polyimides, again ascribed to the very high fluorine content in these polyimides. This low dielectric constant combined with the low moisture absorption indicates that the dielectric constant would be low and fairly constant over the entire humidity range unlike PMDA/ODA, which can vary from about 3 to 4 at the humidity extremes. This fact allows circuit designers more latitude in that they must design with the highest dielectric constant in mind that will be seen under typical use conditions.

In terms of thermal stability, t.g.a. results in air showed the 5% weight loss for all the RfbMPD-based polyimides to be above 450°C. Although these values are not as high as for standard polyimides such as PMDA/ODA, they are nonetheless representative of high thermal stability especially considering the presence of the $-CH_2-$ linkage. Isothermal t.g.a. of the 6FDA/RfbMPD PI at 300°C in air for 14 h showed a total weight loss, after initial loss (H_2O, solvent), of only 0.6% (rate = 0.04%/h). The T_g values of these polyimides ranged from about 250°C to near 400°C depending on dianhydride used. This is quite high especially considering the high content of fluoroalkyl segment in the polymer.

In addition to the backbones discussed above, soluble polyimide preparation was also attempted with RfbMPD and a few other dianhydrides, e.g. BPDA, PMDA, BTDA, but these materials precipitated from solution upon chemical imidization.

N.m.r. characterization

In order to verify and elucidate the structure of these new polyimides, an n.m.r. study was undertaken. *Figures 1, 2* and *3* depict the proton n.m.r. spectra of the RfbMPD polyimides from 6FDA, 6FCDA and 3FCDA, respectively. Interesting to note are the differences in the proton chemical shifts for the different anhydride residues. For 6FDA, the A protons (nearest to 6F group) appeared at 7.95 ppm while in the closed ring 6FCDA they appeared much farther downfield at 8.54 ppm. In 3FCDA, in which one of the CF3 groups of the closed ring is replaced by a phenyl group, these A protons were shifted significantly upfield to 7.54 ppm due to the shielding effect of the phenyl group. The B protons showed only a very minor change in going from 6FCDA to 3FCDA (7.89 to 7.85 ppm); this B signal was a doublet (8.03 ppm) in the 6FDA polyimide. It was coupled to the adjacent C protons (doublet) at 7.86 ppm. In the diamine segment, the protons D between the amino groups appeared at 7.70, 7.77 and 7.64 ppm for 6FDA, 6FCDA and 3FCDA,

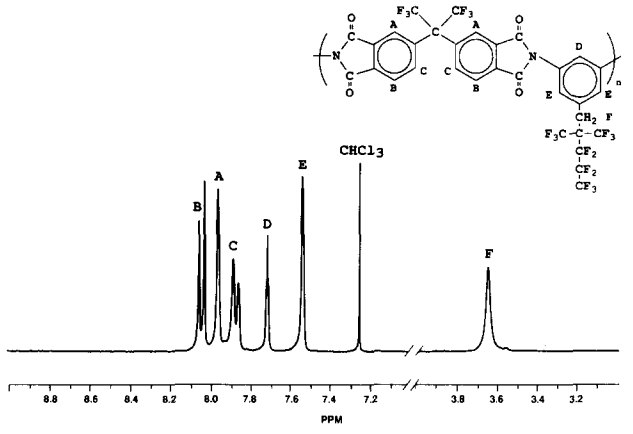


Figure 1 ^{1}H n.m.r. spectrum of 6FDA/RfbMPD polyimide

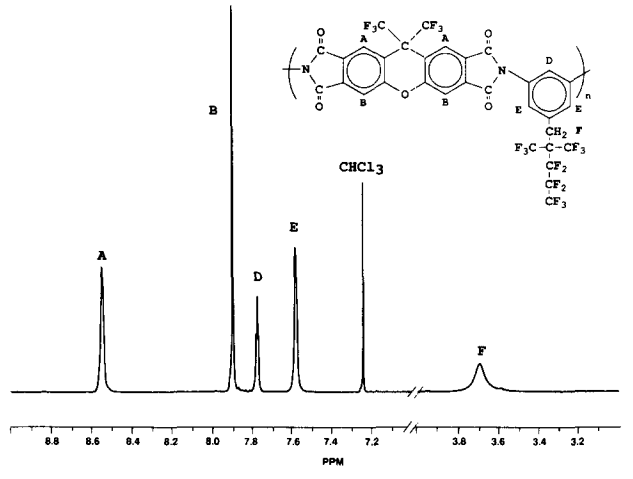


Figure 2 ^{1}H n.m.r. spectrum of 6FCDA/RfbMPD polyimide

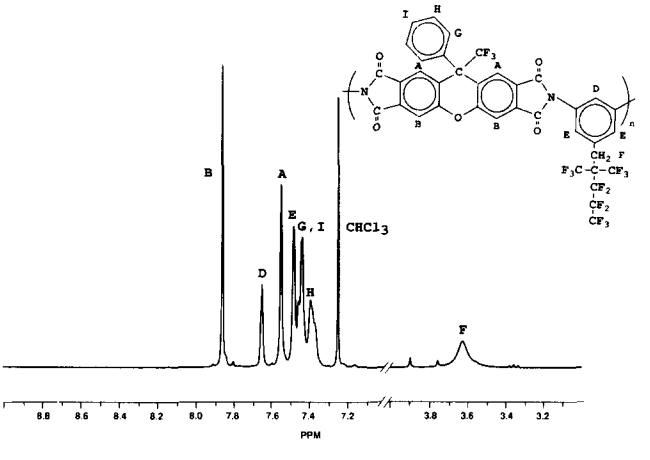


Figure 3 ^{1}H n.m.r. spectrum of 3FCDA/RfbMPD polyimide

respectively. The E protons (between amino and pendent fluoroalkyl group) appeared at 7.53, 7.58 and 7.47 ppm for the same materials. The CH_2 protons of the pendent group appeared at 3.65, 3.70 and 3.62 ppm for the 6FDA, 6FCDA and 3FCDA, respectively. The other aromatic protons of the bridging phenyl group for the 3FCDA-based polyimide (signals F, G, H) appeared as a multiplet at about 7.4 ppm. In 6FDA, the B and C assignments were made assuming the proton *ortho* to the C=O ('B')

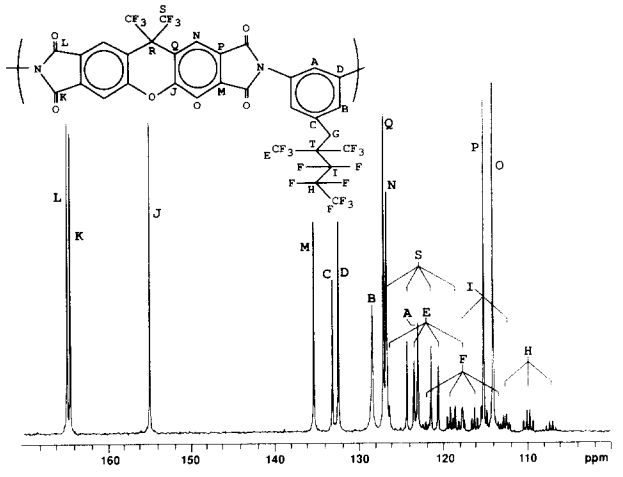


Figure 4 ^{13}C n.m.r. spectrum of 6FCDA/RfbMPD polyimide

was shifted farthest downfield. Also, the C proton signal was broadened through interaction with the nearby CF_3 groups, and possibly by unresolved *meta* coupling with the A proton. The spectrum of 6FCDA was assigned by inspection. The spectrum of 3FCDA was assigned using a combination of COSY (correlation spectroscopy), 2D *J*-resolved spectroscopy and inspection of molecular models. From the molecular model, it was seen that the A proton lay under the phenyl ring, and thus should be shifted substantially upfield. In agreement with the 6FDA assignment, the A protons were broadened relative to the B protons through interaction with the CF_3 groups in both 6FCDA and 3FCDA. In *Figure 3*, the small triplet at 3.35 ppm is from residual NMP; the assignment of the small singlets at 3.75 and 3.9 ppm is not known at this time.

The ^{13}C n.m.r. spectrum of 6FCDA is shown in *Figure 4*. This spectrum was assigned using a combination of DEPT (distortionless enhancement by polarization transfer), HETCOR (2D heteronuclear shift-correlated spectroscopy) and model compounds. The details of the assignment of the ^{13}C n.m.r. spectra of this and of other fluorinated polyimides will be discussed elsewhere[17]. Carbons T, R and G (not in the figure) were assigned to 62.1, 54.0 and 33.0 ppm, respectively.

CONCLUSIONS

Several new polyimides have been prepared from a new fluoroalkylated diamine, RfbMPD. This monomer exhibits good reactivity in poly(amic acid) synthesis, while the thermal stability of the polyimides was not substantially affected by the presence of the isolated $-CH_2-$ group. Polyimide films were shown to have very low moisture absorption and low dielectric constant. The in-plane thermal expansion coefficients, however, were very high for polyimides, probably a result of the bulky, pendent fluorocarbon chain, and its effect on the orientation process during film formation. The low dielectric constant and moisture absorption make these materials attractive for applications in electronics in which a low and stable dielectric constant is desired. The new monomer may also prove useful in other applications, for example, as an agent to alter surface properties. In addition to polyimides, use in other polymer systems including polyamides and epoxies may provide useful and interesting properties.

ACKNOWLEDGEMENTS

The authors would like to thank Michael J. Grovola and Mark A. Guidry for excellent technical support. They would also like to thank Dr. S. Trofimenko for supplying the 6FCDA and 3FCDA dianhydrides, and the Du Pont Electronics (M. Pottiger, R. Subramanian, R. Pryor) and Central Research analytical groups for the polymer characterization measurements.

REFERENCES

1 Goff, D. L., Yuan, E. L., Long, H. and Neuhaus, H. J. in 'Polymers for Electronic Packaging and Interconnection' (Eds. Lumpinski and Moore), ACS Symp. Ser. 407, American Chemical Society, Washington, DC, 1989, p. 93
2 St Clair, A. K., St Clair, T. L. and Winfree, W. P. *Polym. Mater. Sci. Eng. Proc.* 1988, **59**, 28
3 Stoakley, D. M., St Clair, A. K. and Baucom, R. M. *Sampe Q.* 1989, October, p. 3
4 Chiang, W. L., Fjare, D. E. and Nowicki, N. R., US Patent 4876329, 1989
5 Gerber, M. K., Pratt, J. R., St Clair, A. K. and St Clair, T. L. *Polym. Prepr.* 1990, **31**(1), 340
6 Auman, B. C., unpublished results
7 Nagase, Y., Takamura, Y. and Akiyama, E. *Polym. Prepr., Japan (Engl. Edn.)* 1990, **39**, 5–11
8 Inchino, T., Sasaki, S., Matsuura, T. and Nishi, S. *J. Polym. Sci., Polym. Chem.* 1990, **28**, 323; JP Kokai 2-281037, 2-281038, 1990
9 Misra, A. C., Tesoro, G., Hougham, G. and Pendharkar, S. M. *Polymer* 1992, **33**, 1078
10 Yusa, M., Takeda, S. and Miyadera, Y. *Polym. Prepr., Japan (Engl. Edn.)* 1990, **39**, 5; *Polym. Prepr., Japan* 1991, **40**(3), 817
11 Auman, B. C., Higley, D. P. and Scherer, K. V. *Polym. Prepr.* 1993, **34**(1), 389; US Patent 5145999, 1992
12 Trofimenko, S. in 'Advances in Polyimide Science and Technology' (Eds. Feger, Khojasteh, and Htoo), Technomic, Lancaster, PA, 1993, p. 3; US Patent 5051520, 1990
13 Walker, C. C. *J. Polym. Sci., Polym. Chem. Edn.* 1998, **26**, 1649
14 Subramanian, R., Pottiger, M. T. and Ward, M. D. Proc. Symp. on Recent Advances in Polyimides and Other High Performance Polymers, Am. Chem. Soc., Div. Polym. Chem., San Diego, CA, 1990
15 Moylan, C. R., Best, M. E. and Ree, M. *J. Polym. Sci., Polym. Phys. Edn.* 1991, **29**, 87
16 Feiring, A. E., Auman, B. C. and Wonchoba, E. R. *Macromolecules* 1993, **26**, 2779
17 McCord, E. F. and Auman, B. C. *J. Appl. Polym. Sci.* in preparation