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Synthesis and characterization of polyimides from novel 1-(3′,5′-bis(trifluoromethyl)benzene) pyromelliticdianhydride (6FPPMDA)

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Abstract

Mono-substituted dianhydride monomer, 1-(3′,5′-bis(trifluoromethyl)phenyl) pyromellitic dianhydride (6FPPMDA), was prepared via the Suzuki cross coupling reaction followed by oxidation and cyclodehydration. The monomer was characterized by FT-IR, NMR, elemental analyzer (EA) and melting point apparatus. For comparison, 1-(4′-trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA) and 1-phenyl pyromellitic dianhydride (PPMDA) were also utilized. The dianhydrides were used to prepare polyimides with aromatic diamines such as bis(3-aminophenyl) 3,4-bis(trifluoromethyl)phenyl phosphine oxide (*m*DA6FPPO), bis(3-aminophenyl) 4-(trifluoromethyl)phenyl phosphine oxide (*m*DA3FPPO), bis(3-aminophenyl) phenyl phosphine oxide (*m*DAPPO) and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (*p*3FDAm). The polyimides were synthesized via a two-step process; preparation of poly(amic-acid) in *p*-chlorophenol with isoquinoline, followed by solution imidization at the reflux temperature for 12 h. Polymer characterization was carried out by FT-IR, NMR, GPC, DSC and TGA, and their solubility, solution viscosity, water absorption, CTE, dielectric constant and refractive index were also evaluated.

Keywords: Polyimides; Fluorinated; Dielectric constant

1. Introduction

Aromatic polyimides are known to have excellent thermal, mechanical, dielectric and optical properties, along with good chemical resistance and high dimensional stability. They are, therefore, excellent candidates for microelectronics applications such as interlayer dielectrics and flexible circuitry carriers [1,2]. As the electronic devices have become smaller and lighter, so has the demand increased for a new class of polyimides with low dielectric constants and excellent solubility that retain their good thermal properties [3–5]. This has led to considerable research being carried out to improve the dielectric properties of polyimides through methods such as fluorination [3–5], incorporation of adamantane groups [6–8], polyimide nanofoam [9–11] and organic–inorganic hybrid nanocomposites [12–16].

Polyimide nanofoams looked promising when they provided a dielectric constant of 2.3, contrary to much lower values anticipated. Unfortunately, there is s critical problem of foam collapsing during high temperature processing (375 °C) [10]. Meanwhile, nanoporus materials from organic–inorganic hybrid nanocomposites exhibited a dielectric constant of 2.1 or lower [15,16], but further studies are needed on the synthesis and mechanical properties of inorganic materials. Compared to these methods, polyimides containing cage molecules such as adamantane and diamantane groups exhibited a dielectric constant of 2.5–2.7 along with excellent solubility [7].

Fluorination of polyimides, which Critchley pioneered [17], has received much attention since this method can improve dielectric and optical properties and enhance solubility, while reducing moisture absorption due to their low polarity. Consequently, a number of diamines and dianhydrides containing fluorine moieties have been introduced and utilized for preparing polyimides [3–5]. A dielectric constant as low as 2.3 has been reported via fluorination [3], but at the expense of deteriorated thermal, mechanical and adhesion properties [4]. Thus, it was recently attempted to prepare monomers containing fluorine and phosphine oxide moieties [18,19] since the latter is

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known to be very effective in improving adhesion as well as fire-resistance [20,21]. In fact, polyimides containing these diamines provided excellent adhesion and solubility, as well as good thermal properties.

It was also attempted to improve the thermal and mechanical properties of fluorinated polyimides by utilizing rigid-rod type aromatic monomers as the backbone structure. Among the number of diamines and dianhydrides containing fluorine or fluoro-phenyl moieties that were introduced [22–28], PMDA-based monomers have received great attention due to its rigid structure. This has led to the introduction of a number of dianhydrides with fluorine or fluoro-phenyl moieties, which provided good thermal properties and solubility, but relatively high dielectric constants [26–28]. Recently, a dielectric constant of 2.49 was reported with disubstituted PMDA-based fluoro-phenyl containing dianhydride, 3,6-di(3′,5′-bis(trifluoromethyl)-phenyl)pyromellitic dianhydride (12FPMDA) [29], but this was still higher than the values reported earlier.

In this study, therefore, it was attempted to prepare mono-substituted asymmetric dianhydride monomer containing fluoro-phenyl moiety, 1-(3′,5′-bis(trifluoromethyl)-phenyl) pyromellitic dianhydride (6FPPMDA), via the Suzuki cross coupling reaction followed by oxidation and cyclodehydration, in an effort to prepare polyimides with high T_g, good solubility, and good dielectric and optical properties. In addition, 1-(4′-trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA) and 1-phenyl pyromellitic dianhydride (PPMDA) were also prepared for comparison. These monomers were then utilized to prepare polyimides with a controlled molecular weight of 20,000 g/mol. The polyimides were characterized by FT-IR, NMR, GPC, DSC and TGA, and their solubility, solution viscosity, moisture absorption, dielectric constant and refractive index were also evaluated.

2. Experimental

2.1. Materials

3,5-Bis(trifluoromethyl)bromobenzene (6FB, 99%), 4-trifluoromethyl bromobenzene (3FB, 99%), bromobenzene (99%) trimethylborate (99.5%), Mg turnings (98%), 1-bromo-2,3,4,5-tetramethyl-benzene (98%), tetrakis(triphenylphosphine)palladium (($Pd(PPh_3)_4$, 99.9%), sodium carbonate (Na_2CO_3, 99.99%), isoquinoline (97%) and calcium hydride (95%) were obtained from Aldrich, and used as-received. Tetrahydrofurane (THF, 99.9%, Fisher), toluene (99.9%, Fisher) and *p*-chlorophenol (99.9%, Aldrich) were vacuum distilled after drying over calcium hydride, while ethylacetate (99.8%, Aldrich) was used without further purification. Bis(3-aminophenyl) 3,4-bis-(trifluoromethyl)phenyl phosphine oxide (*m*DA6FPPO) [18], bis(3-aminophenyl) 4-(trifluoromethyl)phenyl phosphine oxide (*m*DA3FPPO) [19], bis(3-aminophenyl) phenyl phosphine oxide (*m*DAPPO) [30], and 1-bis(4-aminophenyl)-2,2,2-trifluoroethane (*p*-3FDAm) [31], as well as PPMDA [32], were synthesized as described in the literature. Phthallic anhydride (PA, 99 + %) was purchased from Aldrich and sublimed prior to use.

2.2. Characterization of monomers and their intermediate compounds

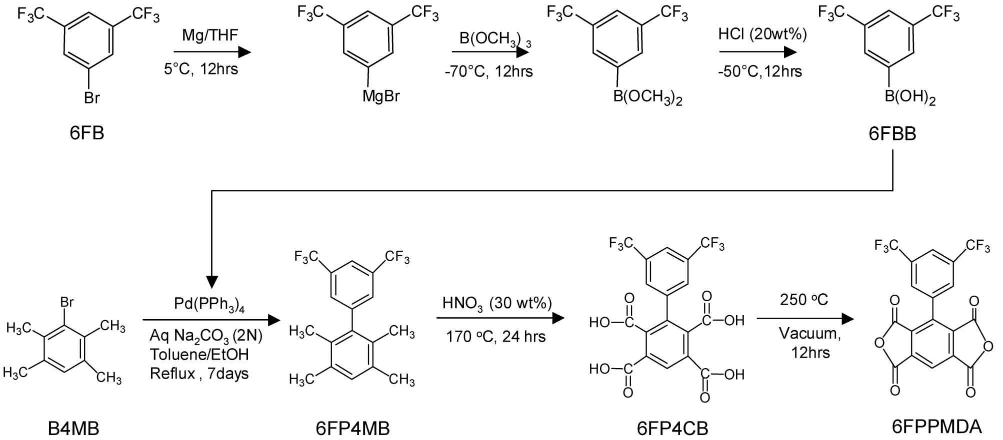
The monomers were characterized by FT-IR (IR 2000, Perkin–Elmer) and NMR (JEOL, JNM-LA300WB, 300 MHz) using $CDCl_3$ or deuterated dimethyl sulfoxide (DMSO-d_6). The chemical shifts in NMR were calibrated with tetramethylsilane (^1H) or fluorotrichloromethane (^{19}F) as the internal standard. Elemental analysis (EA) was also carried out with CE Instruments' EA110 Analyzer, while melting temperatures were measured with a melting point apparatus (Fisher 1A9100).

2.3. Synthesis of 1-(3′,5′-bis(trifluoromethyl)phenyl)pyromellitic dianhydride (6FPPMDA)

The monomer, 1-(3′,5′-bis(trifluoromethyl)phenyl)pyromellitic dianhydride (6FPPMDA), was synthesized via a 3-step process: (1) preparation of 3,5-bis(trifluoromethyl) benzene boronic acid (6FBB); (2) Suzuki cross coupling reaction of 6FBB with 1-bromo-2,3,5,6-tetramethylbenzene (B4MB), resulting in 1-(3′,5′-bis(trifluoromethyl)phenyl) tetramethylbenzene (6FP4MB); and (3) oxidation and cyclodehydration of 6FP4MB to afford 1-(3′,5′-bis(trifluoromethyl)phenyl)pyromellitic dianhydride (6FPPMDA) (Scheme 1).

2.3.1. 1-(3′,5′-Bis(trifluoromethyl)phenyl)-2,3,5,6-tetramethylbenzene (6FP4MB)

1-(3′,5′-Bis(trifluoromethyl)phenyl)-2,3,5,6-tetramethylbenzene (6FP4MB) was synthesized from 3,5-bis(trifluoromethyl)benzene boronic acid (6FBB) and 1-bromo-2,3,5,6-tetramethylbenzene (B4MB) via the Suzuki cross coupling reaction in the presence of Pd-catalyst, while 6FBB was prepared from 3,5-bis(trifluoromethyl)bromobenzene and trimethylborate via the Grignard reaction (Scheme 1) as previously reported [29]. First, 27.54 g (129.234 mmol) of B4MB were charged into a 1000 ml 3-neck round bottom flask equipped with a mechanical stirrer, condenser and nitrogen inlet. Next, 330 ml of toluene was added to the flask. After complete dissolution of B4MB, 40.00 g (155.08 mmol) of 6FBB, 1.4934 g (1.2923 mmol) of tetrakis(triphenylphosphine)palladium, 164 ml of aqueous Na_2CO_3 solution (2 N) and 67 ml of ethanol were charged into the flask, and the reaction mixture was refluxed for 7 days. Upon cooling, the solution mixture formed two layers; an organic and aqueous layer. The organic layer was isolated and dried with a rotary evaporator. The resulting



Scheme 1. Synthesis of 1-(3′,5′-bis(trifluoromethyl)phenyl)-pyromellitic dianhydride (6FPPMDA).

residue was recrystallized in ethyl acetate to provide the white crystals of 6FP4MB.

Yield: 89%; mp: 117.5–118.4 °C. FT-IR (KBr): 2940 and 2854 cm^{-1} (C–H s), 1421 and 1383 cm^{-1} (C–H b), 1363, 1291, 1177 and 1112 cm^{-1} (C–F s, b). ^{1}H NMR ($CDCl_3$): 7.862 ppm (s; 1H), 7.601 ppm (s; 2H), 7.043 (s; 1H), 2.258 ppm (s; 6H), 1.843 ppm (s; 6H). ^{19}F NMR ($CDCl_3$): -41.055 ppm. EA: calcd for $C_{18}H_{16}F_6$: C, 62.43%; H, 4.66%. Found: C, 62.51%; H, 4.70%.

2.3.2. *1-(3′,5′-Bis(trifluoromethyl)phenyl)pyromellitic dianhydride (6FPPMDA)*

Synthesized 6FP4MB was subjected to oxidation and cyclodehydration to afford 1-(3′,5′-bis(trifluoromethyl)phenyl)pyromellitic dianhydride (6FPPMDA) (Scheme 1). Oxidation was carried out by charging 44.73 g (0.129 mmol) of 6FP4MB and 230 ml of nitric acid (30 wt%) into a stainless steel autoclave (Reaction Engineering, Inc., Korea) and allowing the mixture to react at 170 °C for 24 h. The hot solution was filtered and the resulting pale yellow solution was placed at RT for 12 h, followed by an additional 12 h in a freezer. Off white crystals of 1-(3′,5′-bis(trifluoromethyl)phenyl)pyromelliticacid (6FP4CB) were collected by vacuum filtration and subjected to cyclodehydration in a vacuum oven at 250 °C for 12 h. Finally, the monomer was purified via sublimation and white crystals were obtained.

Yield: 56%; mp: 209.3–210.1 °C. FT-IR (KBr): 1857 cm^{-1} (C=O as), 1794 cm^{-1} (C=O s), 1358, 1285, 1172 and 1134 cm^{-1} (C–F s). ^{1}H NMR (DMSO-d_6): 8.456 ppm (s; 1H, H^{3}), 8.165 ppm (s; 1H, H^{1}), 7.789 ppm (s; 2H, H^{2}). ^{19}F NMR (DMSO-d_6): -39.935 ppm. EA: calcd for $C_{18}H_4F_6O_2$: C, 50.25%, H, 0.94%, O, 22.31%. Found: C, 50.50%, H, 0.96%, O, 22.38%.

2.4. *Synthesis of 1-(4′-trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA)*

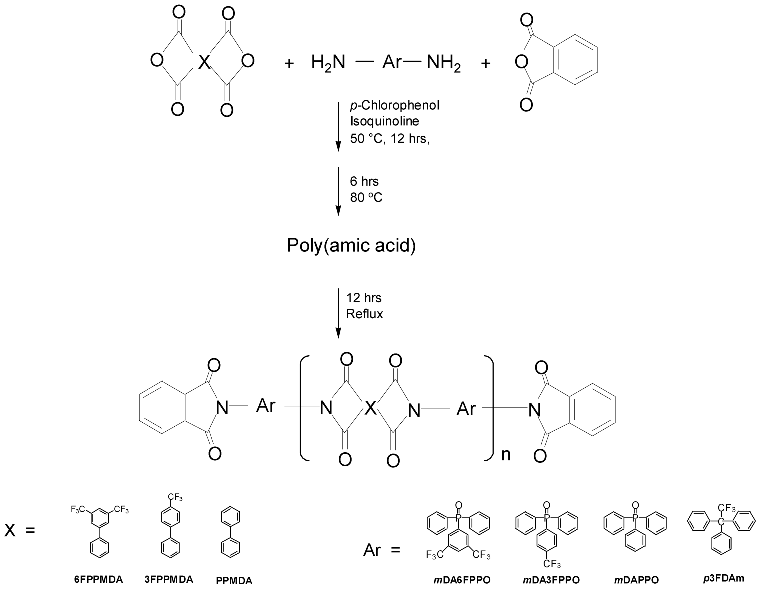
Another novel fluorinated mono-substituted dianhydride, 1-(4′-trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA), was prepared by the same synthetic route used for 6FPPMDA, except that 4-(trifluoromethyl)benzene boronic acid (3FBB) was utilized instead of 3,5-bis(trifluoromethyl)benzene boronic acid (6FBB).

Yield: 49%; mp: 211.0–211.8 °C. 1864 cm^{-1} (C=O as), 1780 cm^{-1} (C=O s), 1323, 1249, 1161 and 1121 cm^{-1} (C–F s). ^{1}H NMR (DMSO-d_6): 8.410 ppm (s; 1H), 7.831 ppm (d; 2H), 7.591 ppm (d; 2H). ^{19}F NMR (DMSO-d_6): -39.087 ppm. EA: calcd for $C_{17}H_5F_3O_6$: C, 56.37%; H, 1.39%; O, 26.50%. Found: C, 56.41%, H, 1.41%, O, 26.48%.

2.5. *Synthesis and characterization of polyimides with 6FPPMDA and 3FPPMDA*

Novel mono-substituted pyromellitic dianhydrides, 6FPPMDA and 3FPPMDA, were utilized to prepare polyimides in combination with diamines such as bis(3-aminophenyl) 3,4-bis(trifluoromethyl)phenyl phosphine oxide (*m*DA6FPPO) [18], bis(3-aminophenyl) 4-(trifluoromethyl)phenyl phosphine oxide (*m*DA3FPPO) [19], bis(3-aminophenyl) phenyl phosphine oxide (*m*DAPPO) [30], and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (*p*3FDAm) [31]. In addition, 1-phenyl pyromellitic dianhydride (PPMDA) [32] was also utilized for comparison purposes. All polyimides were prepared by a two-step process; synthesis of poly (amic-acid), followed by solution imidization (Scheme 2). The number-average molecular weight was controlled to 20,000 g/mol via off-stoichiometry and all polymers were designed to have non-reactive end groups by adding phthalic anhydride (PA), as previously suggested [33].

Polymerization was carried out in a three-neck round-bottom flask equipped with a mechanical stirrer, drying tube and a nitrogen inlet with thermometer. A detailed synthesis of 6FPPMDA-*m*DA6FPPO polyimide is described here. After flame drying the reaction apparatus under N_2 flow, 3.892 g (8.76 mmol) of *m*DA6FPPO was charged into a 250 ml three-neck round-bottom flask, followed by *p*-chlorophenol (70 ml) and isoquinoline (1 ml), which were



Scheme 2. Synthesis of polyimides with mono-substituted pyromellitic dianhydride via a two-step process.

selected as solvent and catalyst, respectively, to provide the proper environment for high molecular weight poly(amic acid) [34]. Upon complete dissolution of the diamine monomer, 3.557 g (8.27 mmol) of 6FPPMDA and 0.144 g (0.98 mmol) of PA were added to afford a molecular weight of 20,000 g/mole, while the solid concentration was controlled to 10 wt%.

The reaction temperature was maintained at 50 °C in order to keep *p*-chlorophenol in liquid form and to increase the solubility of 6FPPMDA. The mixture was allowed to react overnight, and then allowed to react for an additional 6 h at 80 °C, which resulted in yellow viscous poly(amic-acid) solution. Imidization was carried out at the reflux temperature of *p*-chlorophenol for 12 h under strong nitrogen flow, which necessitated the continuous addition of *p*-chlorophenol to maintain its level. Finally, after allowing the reaction mixture to reach RT, it was diluted with chloroform, precipitated into water–methanol (1:1) mixture, filtered and dried. The resulting polymer was again dissolved in chloroform, precipitated, filtered and dried in a vacuum oven at 200 °C for 24 h, and then subjected to characterization.

2.6. Characterization and property measurement of polyimides

All polyimides were characterized by FT-IR (IR 2000, Perkin–Elmer) and NMR (JEOL, JNM-LA300WB) using DMSO-d_6. Thermal properties were analyzed by DSC (TA-2910) and TGA (TA-2950) at 10 °C/min, with the latter being carried out in air. The solubility of polyimides was evaluated by immersing a polymer film (5 mm × 5 mm) into solvents such as NMP, DMAc, THF, $CHCl_3$, TCE, acetone and toluene at 10 wt% concentration at RT for 24 h. Cannon-Ubbelohde viscometer was used to measure solution viscosity at 25 °C in NMP, and molecular weights were evaluated by GPC (Waters, M77251, M510) in THF with polystyrene standard.

The polyimides were also subjected to CTE, water absorption, refractive index and dielectric constant measurements. CTE values were measured by TMA (TA-2000) in the 50–250 °C range in the 2nd scan at 5 °C/min, after heating to 300 °C followed by slow cooling. For water absorption measurements, polyimide films (5 mm × 5 mm) were immersed in deionized water at 25 °C for 7 days and their weight difference before and after immersion was determined. The dielectric constant (ε) of polyimides was evaluated by parallel-plate capacitor method at 1 MHz using a Capacitance Meter (HP 4155). Refractive indices were also measured by prism coupler (Metricon-2010) via a 1.55 μm laser diode with thin polymer films. Both in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices were measured and birefringence ($\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$) was calculated. The samples for dielectric constant and refractive index measurements were prepared via spin casting, as described previously [18].

3. Results and discussion

3.1. Synthesis and characterization of 6FPPMDA

The FT-IR analysis of 6FP4MB, which is an intermediate compound for 6FPPMDA, showed CF_3 multiple stretching (1363–1112 cm^{-1}) and aliphatic CH_3 asymmetric and symmetric stretching absorptions (940, 2854, 1421 and 1383 cm^{-1}), but did not show either the O–H stretching absorption (3158 cm^{-1}) or the C–Br stretching absorption (1172 cm^{-1}), indicating successful Suzuki cross coupling reaction. The oxidation of 6FP4MB was evidenced by the appearance of O–H stretching absorption at 2973 cm^{-1} and C=O stretching at 1710 cm^{-1}, confirming the formation of 6FP4CB with carboxylic acid groups. After cyclodehydration, the 6FPPMDA structure was confirmed by the split C=O absorption peaks at 1857 and 1794 cm^{-1}, which can be attributed to the asymmetric and symmetric stretching of anhydride moieties, and by the disappearance of the O–H stretching absorption peak at 2973 cm^{-1}, due to the loss of hydrogen bonding upon cyclodehydration (Fig. 1).

In the ^1H NMR (300 MHz, $CDCl_3$) analysis, 6FP4MB exhibited 5 proton peaks; ones at 7.862 (1H) and 7.601 ppm (2H) from substituted 3′,5′-bis(trifluoromethyl)phenyl moiety, one at 7.043 ppm (1H) from *p*-positioned aromatic proton between CH_3 groups, and ones at 2.258 (6H) and 1.843 ppm (6H) from CH_3 groups. The oxidation of 6FP4MB to 6FP4CB was demonstrated by the new proton peak at 13.782 ppm (4H) resulting from the carboxylic acid group and by the movement of aromatic proton (1H) peak downfield (7.842 ppm), due to the electron withdrawing effect of the carboxylic acid group. In addition, the protons from 3′,5′-bis(trifluoromethyl)phenyl moiety appeared at 7.769 (1H) and 7.617 ppm (2H).

Upon cyclodehydration, the peak from carbonyl O–H moiety (at 13.784 ppm) disappeared, but one from aromatic proton (1H, H^3) appeared at 8.456 ppm. In addition, peaks from substituted 3′,5′-bis(trifluoromethyl)phenyl moiety moved downfield to 8.165 (1H, H^1) and 7.789 ppm (2H, H^2) because of the deshielding effect of the electron-withdrawing anhydride group (Fig. 2). In ^{19}F NMR analyses, a sharp single peak was observed at −41.056 ppm (6FP4MB), −39.933 (6FP4CB) and −39.935 ppm (6FPPMDA), providing evidence for the successful synthesis of 6FPPMDA. The EA of 6FPPMDA exhibited 50.25 (C), 0.94 (H) and 22.31 wt% (O), which were in good agreement with the calculated values of 50.50 (C), 0.96 (H) and 22.38 wt% (O).

3.2. Synthesis and characterization of 3FPPMDA

1-(4′-Trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA) containing one CF_3 moiety was also prepared via a 3-step process: (1) preparation of 4-(trifluoromethyl)-benzeneboronic acid (3FBB), (2) Suzuki cross coupling reaction of 3FBB with 1-bromo-2,3,5,6-tetramethylbenzene (B4MB), resulting in 1-(4′-trifluoromethylphenyl)-2,3,5,6-tetramethylbenzene (3FP4MB), and (3) oxidation and cyclodehydration to afford 1-(4′-trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA). The characterization of 3FPPMDA and its intermediate compounds by FT-IR, ^1H NMR, ^{19}F NMR, EA and melting point apparatus demonstrated the successful preparation of 3FPPMDA. The overall yield of 3FPPMDA was 49%.

3.3. Characterization of polyimides

All polyimides were characterized by FT-IR, ^1H NMR, ^{19}F NMR, DSC and TGA, and their solubility and intrinsic viscosity were also measured. As noted in the FT-IR of polyimide from 6FPPMDA-*m*DA6FPPO, the amide-carbonyl peak at 1650 cm^{-1} disappeared, while imide C=O stretching absorptions at 1776 and 1733 cm^{-1} (asymmetric and symmetric), and C–N stretching absorption at 1359 cm^{-1} were observed, suggesting complete imidization (Fig. 3). As expected, C–F multiple stretching absorptions were also found at 1376, 1282, 1176 and 1139 cm^{-1}.

In the ^1H NMR (300 MHz, $CDCl_3$) spectrum, 6FPPMDA-*m*DA6FPPO polyimide exhibited 4 proton peaks as shown in Fig. 4, two of which are from the polymer and the other two from water and DMSO. The reason for the peak's appearance far downfield (at 8.478 ppm) is attributed to the proton between the two imide carbonyl groups in the dianhydride unit being affected by the strong electron-withdrawing nature of imide carbonyl groups. The next deshieled protons (at 8.368 and 8.336) are those at the *ortho*-position to the trifluoromethyl moieties in the diamine (2H, H^8) and dianhydride unit (2H, H^2), followed by protons between the two trifluoromethyl moieties (2H, H^1, H^9), which appear at 8.302 ppm. The peaks at 8.022 (4H, H^4), 7.977 (2H, H^7), 7.864 (2H, H^6) and 7.831 ppm (2H, H^5) are assigned to protons from the phenyl moiety in diamines, considering the position and distance from the imide, phopshine oxide and trifluoromethyl moieties.

Polyimides with 6FPPMDA exhibited high T_gs (280–

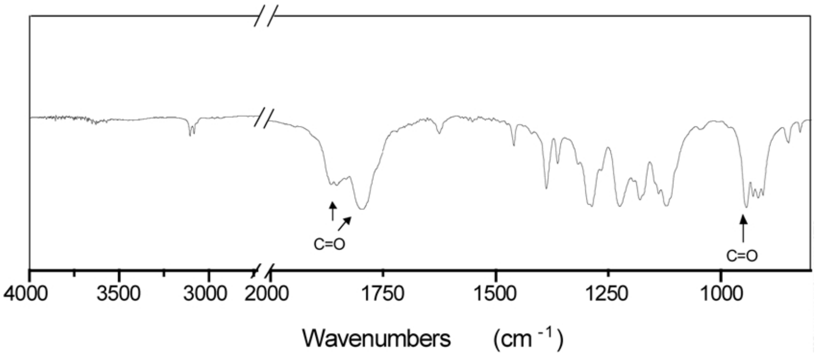


Fig. 1. FT-IR of 6FPPMDA.

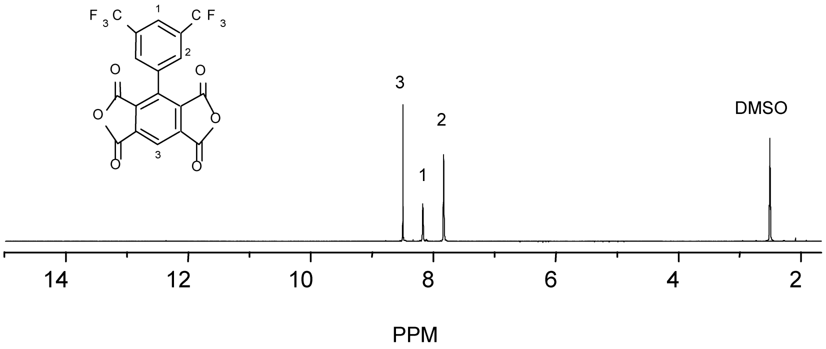


Fig. 2. ^{1}H NMR of 6FPPMDA.

316 °C), while those with 3FPPMDA (292–331 °C) and PPMDA (300–342 °C) exhibited even higher T_gs, demonstrating the positive effect of the stiff backbone structure of PMDA with its bulky phenyl groups and the negative effect of CF_3 moiety (Table 1). Among the 6FPPMDA-based polyimides, 6FPPMDA-*m*DA6FPPO polyimide provided a T_g of 280 °C, compared to 290 °C obtained from 6FPPMDA-*m*DA3FPPO polymide, 299 °C from 6FPPMDA-*m*DAPPO polyamide and 316 °C from 6FPPMDA-*p*3FDAm polyamide, once again demonstrating the effect of CF_3 moiety on T_g. A similar trend was also observed from the 3FPPMDA- and PPMDA-based polyimides.

In the TGA analyses, all polyimides showed excellent thermal stability in air, showing 5 wt% loss at 520 °C or higher temperatures, with 6FPPMDA-based polyimides exhibiting slightly better thermal stability, followed by 3PPMDA and PPMDA-based polyimides, possibly due to their higher fluorine content (Table 1). In addition, *m*DA6FPPO-based polyimides exhibited slightly better thermal stability than *m*DA3FPPO and *m*DAPPO-based polyimides, with 6FPPMDA-*m*DA6FPPO polyimides exhibiting the best thermal stability, which is attributed to the highest fluorine content. However, the highest char yield at 800 °C was obtained from PPMDA-*m*DAPPO (32%) polyimide despite the fact that it showed the worst thermal stability among the polyimides prepared in this study. Therefore, the high char yield can be attributed to the phosphine oxide moiety.

The polyimides prepared in this study exhibited good solubility in a number of solvents, which is strongly dependent on the dianhydride as well as diamines used. As shown in Table 2, in general, the 6FPPMDA-based polyimides exhibited better solubility than the 3FPPMDA and PPMDA-based polyimides, demonstrating the effect of CF_3 moiety. As expected, *m*DA6FPPO-6FPPMDA polyimide showed the best solubility among the 6FPPMDA-based polyimides, being soluble in NMP, DMAc, TCE, THF, $CHCl_3$, acetone and toluene. This was followed by the *m*DA3FPPO, *m*DAPPO and p3FDAm-based polyimides in the order of decreasing solubility, demonstrating the effect of fluorine as well as phosphine oxide. A similar trend was observed from the 3FPPMDA- and PPMDA-based polyimides. Since all polyimides were soluble in NMP, intrinsic viscosities were evaluated in NMP at 25 °C with a Cannon-Ubbelohde viscometer and the results fell within the 0.26–

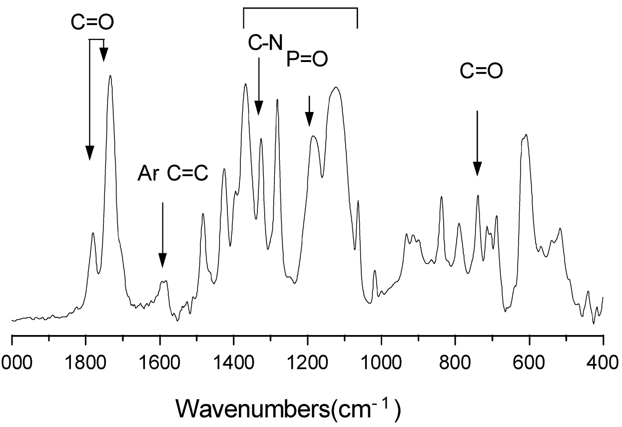


Fig. 3. FT-IR spectrum of 6FPPMDA-*m*DA6FPPO polyimide.

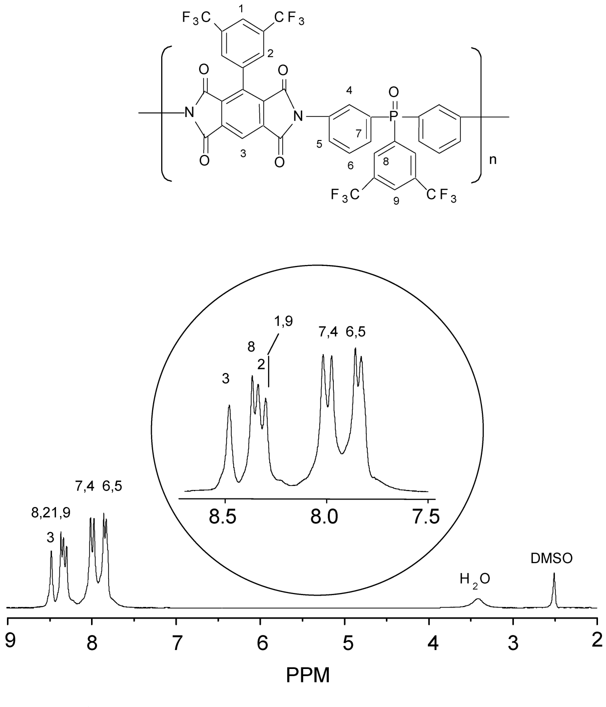


Fig. 4. ^{1}H NMR spectrum of 6FPPMDA-*m*DA6FPPO polyimide.

Table 1
Characteristics of polyimides with mono-substituted pyromellitic dianhydride

Anhydride	Diamine	$[\eta]$[a] (dl/g)	$\langle M_n \rangle$[b]	T_g (°C)[c]	T_d (°C)[d]	Residue (wt%)[e]
6FPPMDA	*m*DA6FPPO	0.27	18,600	280	543	5
	*m*DA3FPPO	0.27	18,300	290	539	11
	*m*DAPPO	0.26	19,000	299	537	16
	*p*3FDAm	0.27	19,600	316	530	0
3FPPMDA	*m*DA6FPPO	0.27	19,100	292	539	10
	*m*DA3FPPO	0.26	19,000	303	531	15
	*m*DAPPO	0.25	19,200	318	528	17
	*p*3FDAm	0.27	19,600	331	530	0
PPMDA	*m*DA6FPPO	0.27	18,200	300	532	14
	*m*DA3FPPO	0.26	–	317	528	19
	*m*DAPPO	0.26	–	322	522	32
	*p*3FDAm	0.27	–	342	524	0

[a] At 25 °C in NMP.

[b] By GPC.

[c] By DSC, 2nd heat, 10 °C/min in N_2.

[d] By TGA, 5 wt% loss, 10 °C/min in air.

[e] By TGA at 800 °C, 10 °C/min in air.

0.27 dl/g range. The number average molecular weights of the polyimides determined from GPC fell in the 18,200–20,000 g/mol range, indicating successful synthesis of polyimides with controlled molecular weight. However, as can be seen from Table 2, some PPMDA-based polyimides were insoluble and thus GPC could not be carried out.

3.4. Property measurement of polyimides

As anticipated, a low dielectric constant of 2.73 was obtained from 6FPPMDA-*m*DA6FPPO polyimide, followed by 2.88 from 6FPPMDA-*m*DA3FPPO polyimide, 2.91 from 6FPPMDA-p3FDAm polymide and 3.10 from 6FPPMDA-*m*DAPPO polyimide, (Table 3) demonstrating the effect of CF_3 moiety. Compared to these values, the 3FPPMDA-based polyimides exhibited slightly higher dielectric constants; 2.89 (*m*DA6FPPO), 3.01 (*m*DA3FPPO), 3.05 (p3FDAm) and 3.15 (*m*DAPPO), while the PPMDA-based polyimides showed even higher values (3.06–3.20). The relatively higher dielectric constant, compared to 2.45 with 12FPMDA-*m*DA6FPPO (32% F) [35] and 2.3 with 6FDCA-6FDAm (30.1 wt% F) [3], can be attributed to the lower fluorine content (26%) and possibly the phosphine oxide moiety in the *m*DA6FPPO unit. However, such a low dielectric constant obtained from 6FPPMDA-*m*DA6FPPO polyimide can be attributed to not only the CF_3 moieties but also to the non-coplaner structure of 6FPPMDA.

Refractive indices evaluated with a 1.55 μm laser diode showed 1.5104–1.5821 (n_{TE}) and 1.5052–1.5742 (n_{TM}) for the 6FPPMDA-based polyimides, compared to 1.5485–1.5887 (n_{TE}) and 1.5423–1.5777 (n_{TM}) for the 3FPPMDA-based polyimides, and 1.6046–1.6278 (n_{TE}) and 1.5857–1.6120 (n_{TM}) for the PPMDA-based polyimides. As expected, refractive index increased in the ascending order of 6FPPMDA, 3FPPMDA and PPMDA, demonstrating the effect of fluorine moiety. The same trend was also observed from *m*DA6FPPO, *m*DA3FPPO/p3FDAm and *m*DAPPO. The resulting birefringences were small, as low as 0.0052 with 6FPPMDA-*m*DA6FPPO polyimide, which was attributed to the bulky structure of 6FPPMDA and *m*DA6FPPO, as well as the asymmetrical structure of 6FPPMDA, providing a non-coplanar structure. As noted, birefringence increased as the fluorine content decreased; 6FPPMDA $<$ 3 FPPMDA $<$ PPMDA and *m*DA6FPPO $<$ *m*DA3FPPO $<$ *m*DAPPO $<$ p3FDAm. High birefringence with p3FDAm can be explained by the *para*-linkage, which resulted in very stiff polymer chains.

The polyimides provided fairly low CTE values: 40–28 ppm/°C (6FPPMDA-based); 37–26 ppm/°C (3FPPMDA-based); 33–24 ppm/°C (PPMDA-based) (Table 4), demonstrating the effect of bulky CF_3 moiety on CTE. The same trend was also observed from the 6FPPMDA-based polyimides; 40 ppm/°C (*m*DA6FPPO),

Table 2
Solubility of polyimides with mono-substituted pyromellitic dianhydride

Dianhydride	Diamine	NMP	DMAc	$CHCl_3$	TCE	THF	Acetone	Toluene
6FPPMDA	*m*DA6FPPO	S	S	S	S	S	S	S
	*m*DA3FPPO	S	S	S	S	S	S	S
	*m*DAPPO	S	S	S	S	S	S	P
	3FDAm	S	S	S	S	S	P	P
3FPPMDA	*m*DA6FPPO	S	S	S	S	S	S	S
	*m*DA3FPPO	S	S	S	S	S	P	P
	*m*DAPPO	S	S	S	S	S	P	P
	3FDAm	S	S	S	S	S	P	P
PPMDA	*m*DA6FPPO	S	S	S	S	S	P	I
	*m*DA3FPPO	S	S	S	P	P	P	I
	*m*DAPPO	S	S	P	P	P	P	I
	3FDAm	S	S	P	P	P	P	I

S, soluble; P, partially soluble, I in soluble.

Table 3
Dielectric and optical properties of polyimides with mono-substituted pyromellitic dianhydride

Anhydride	Diamine	F (wt%)	ε[a]	n_{TE}[b]	n_{TM}[c]	$\Delta n = n_{TE} - n_{TM}$
6FPPMDA	*m*DA6FPPO	26	2.73	1.15104	1.5052	0.0052
	*m*DA3FPPO	21	2.88	1.5468	1.5407	0.0061
	*m*DAPPO	16	3.10	1.5821	1.5742	0.0079
	*p*3FDAm	22	2.91	1.5426	1.5328	0.0098
3FPPMDA	*m*DA6FPPO	21	2.89	1.5485	1.5423	0.0062
	*m*DA3FPPO	16	3.05	1.5794	1.5713	0.0081
	*m*DAPPO	9	3.15	1.5887	1.5777	0.0110
	*p*3FDAm	16	3.01	1.5624	1.5498	0.0126
PPMDA	*m*DA6FPPO	16	3.06	1.6046	1.5961	0.0085
	*m*DA3FPPO	9	3.13	1.6164	1.6057	0.0107
	*m*DAPPO	0	3.20	1.6278	1.6120	0.0158
	*p*3FDAm	9	3.12	1.6148	1.5857	0.0291

[a] At 1 MHz.
[b] n_{TE} : in plane refractive index.
[c] n_{TM} out-of-plane refractive index.

36 ppm/°C (*m*DA3FPPO), 32 ppm/°C (*m*DAPPO) and 28 ppm/°C (*p*3FDAm). However, the lowest CTE with *p*3FDAm can be attributed to the *para*-linkage despite the presence of fluorine moiety. The CTE of 6FPPMDA-*m*DA6FPPO (40 ppm/°C) was slightly higher than the 31 ppm/°C reported for PMDA-*p* ODA polyimides [3], but slightly lower than the 49 ppm/°C from 12FPMDA-*m*DA6FPPO polyimide [35], again demonstrating the effect of bulky side groups on CTE values.

As expected, the 6FPPMDA-based polyimides showed very low water absorption; 1.46–2.16 wt%, compared to 1.76–2.32 wt% with the 3FPPMDA-based polyimides and 2.09–3.26 wt% with the PPMDA-based polyimides (Table 4). The low water absorption with the 6FPPMDA-based polyimides can be said to result from the hydrophobic nature of the CF$_3$ moiety. Among the 6FPPMDA-based polyimides, *m*DAPPO polyimide exhibited the highest water absorption (2.16 wt%), followed by 1.68 wt% with *m*DA3FPPO, 1.62 wt% with p3FDAm, and 1.46 wt% with *m*DA6FPPO, again demonstrating the effect of the hydrophobic nature of the CF$_3$ moiety on water absorption.

Table 4
CTE and water absorption of polyimides with mono-substituted pyromellitic dianhydride

Anhydride	Diamine	*F* (wt%)	CTE	Water absorption
6FPPMDA	*m*DA6FPPO	26	40	1.46
	*m*DA3FPPO	21	36	1.68
	*m*DAPPO	16	32	2.16
	*p*3FDAm	22	28	1.62
3FPPMDA	*m*DA6FPPO	21	37	1.76
	*m*DA3FPPO	16	34	1.91
	*m*DAPPO	9	30	2.32
	*p*3FDAm	16	26	1.82
PPMDA	*m*DA6FPPO	16	33	2.09
	*m*DA3FPPO	9	31	2.39
	*m*DAPPO	0	26	3.26
	*p*3FDAm	9	24	2.52

4. Conclusions

1. Novel dianhydrides, 1-(3′,5′-bis(trifluoromethyl)phenyl) pyromellitic dianhydride (6FPPMDA) and 1-(4′-trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA), were successfully prepared via the Suzuki cross coupling reaction followed by oxidation and cyclodehydration.
2. These novel dianhydrides were utilized to prepare polyimides, which provided intrinsic viscosity of 0.26–0.27 dl/g and number average molecular weights of 18,200–20,000 g/mol by GPC analysis, indicating successful synthesis of polyimides with controlled molecular weights.
3. The 6FPPMDA-based polyimides exhibited high T_g (280–316 °C), good thermal stability (> 520 °C in air), low CTE (41–28 ppm/°C), low water absorption (1.46–2.16 wt%) and excellent solubility, being soluble even in acetone.
4. The 6FPPMDA-based polyimides also showed low dielectric constants (2.73–3.10), low refractive indices and very low birefringence (0.0052–0.0098), compared to the 3FPPMDA and PPMDA-based polyimides, demonstrating the effect of the CF$_3$ moiety.

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