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Synthesis and characterization of polyimides from bis (3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethylphenyl phosphine oxide (*m*DA7FPPO)

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Abstract

A novel diamine, bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethylphenyl phosphine oxide (*m*DA7FPPO), was synthesized via Grignard reaction, followed by nitration and reduction. The monomer was characterized by FT-IR, NMR and melting point apparatus, and utilized to prepare polyimides with 6FDA, BTDA or ODPA via a conventional two-step synthesis; preparation of poly(amic acid), followed by solution imidization. The molecular weight of polyimides was controlled to 20,000 g/mol by off-stoichiometry and the polyimides were characterized by FT-IR, NMR, GPC, TGA and DSC. Solubility, intrinsic viscosity, dielectric constant and refractive index were also evaluated. The novel polyimides exhibited high T_g (229–252 °C), excellent thermal stability (>500 °C), low dielectric constant (2.65–2.81) and low birefringence (0.0019–0.0049).

Keywords: Polyimide; Fluorine; Phosphine oxide

1. Introduction

Aromatic polyimides have been widely utilized in electronic devices such as dielectric interlayer and flexible circuit boards due to their excellent thermal, mechanical and electrical properties, good chemical resistance, and high dimensional stability [1,2]. As electronic devices are miniaturized during the past decades, dielectric constant become one of the most important factors in decreasing electrical power loss and signal transmission delay [3,4]. Therefore, great amount of research effort has been focused on lowering dielectric constant of polyimides via fluorination [5–14], nanofoam technology [15,16] including adamantane/diamantane moieties [17–19], and organic–inorganic hybrid composites [20,21]. As expected, these approaches have advantages as well as drawbacks.

Fluorination may be the most widely adapted method in the synthesis of polyimides to lower their dielectric constant [5–14] because this method has a number of advantages aside from lowering dielectric constant, such as lowering moisture absorption and electrical conductivity, while improving optical properties and solubility. However, fluorinations have also several drawbacks such as poor adhesion, low glass transition temperature, high coefficient of thermal expansion and low mechanical strength [7]. Consequently, there has been an increasing demand for new techniques, which do not involve fluorine, and thus nanofoam technology, utilization of adamantane/diamantane moieties and organic–inorganic hybrid composites have been investigated.

In our laboratory, however, we have paid attention to phosphine oxide moiety since it is known to be very good in enhancing adhesive properties as well as thermal and mechanical properties and fire retardency [22,23]. In addition, the triphenyl phosphine oxide moiety in the polyimide backbone is known to give non-coplanar structure, providing low birefringence [13]. Therefore, we have attempted to synthesize diamine monomers containing fluorine and phosphine oxide moiety simultaneously in order to take benefits of fluorine and phosphine oxide moieties. We successfully prepared bis(3-aminophenyl)-3,5-bis(trifluoromethyl)phenyl phosphine oxide (*m*DA6FPPO) [13] and bis(3-aminophenyl)-4-trifluoromethylphenyl phosphine oxide (*m*DA3FPPO) [14]. The polyimides with these monomers exhibited low dielectric constants (2.8–2.9 at 1 MHz) as well as excellent thermal/mechanical properties and good solubility together with very high peel strengths with Cu foils. Unfortunately, however, dielectric constant with from these polyimides seems to be high compared to 2.3 with highly fluorinated polyimides [6].

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Therefore, in this study, it was attempted to prepare diamine monomer containing phosphine oxide and fluorine moiety, but higher fluorine content. The monomer designed was bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethylphenyl phosphine oxide (*m*DA7FPPO). This monomer was synthesized from diphenylphosphinic chloride and 2,3,5,6-tetrafluoro-4-(trifluoromethyl)bromobenzene, resulting in an intermediate compound, 2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl diphenyl phosphine oxide (7FPPO), which was subsequently nitrated and hydrogenated. After full characterization, *m*DA7FPPO was utilized for the synthesis of polyimides by a conventional two-step method. The polyimides were characterized by FT-IR, NMR, TGA, DSC, GPC and intrinsic viscosity measurement, and dielectric constant and refractive indices were also evaluated.

2. Experimental

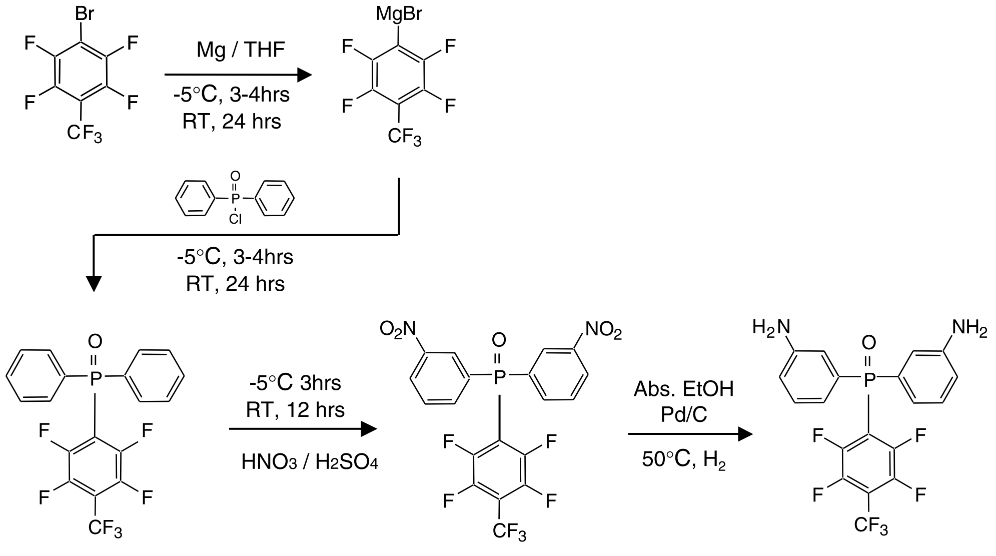
2.1. Materials

Diphenylphosphinic chloride (98%), 2,3,5,6-tetrafluoro-4-trifluoromethylbromobenzene (99%), triphenylphosphine oxide (98%), Mg powder, sulfuric acid, nitric acid and 10% palladium on an activated carbon (Pd/C) were purchased from Aldrich and used as received. Absolute ethanol and chloroform from Fisher were used as received, while tetrahydrofuran (THF, Aldrich), *N*-methylpyrrolidinone (NMP, Fisher) and 1,2-dichlorobenzene (*o*-DCB, Aldrich) were distilled after stirring over calcium hydride (CaH_2). Bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethyl phenyl phosphine oxide (*m*DA7FPPO), containing perfluorinated phenyl pendent with trifluoromethyl moiety (–CF_3) and phosphine oxide, was synthesized and used to prepare polyimides. Phthalic anhydride (PA, Aldrich), 4,4′-oxydiphthalic dianhydride (ODPA, Chriskev), 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA, Chriskev), and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, Allco) were purified by vacuum sublimation prior to use.

2.2. Preparation of 2,3,5,6-tetrafluoro-4-trifluoromethyl phenyl diphenyl phosphine oxide (7FPPO)

2,3,5,6-Tetrafluoro-4-trifluoromethyl phenyl diphenyl phosphine oxide (7FPPO) was synthesized from diphenylphosphinic chloride and 2,3,5,6-tetrafluoro-4-trifluoromethylbromobenzene via Grignard reaction (Scheme 1). 1.47 g (0.060 mol) of Mg powder and 150 ml of dried THF were added into a flame dried three-neck round bottom flask equipped with magnetic stirrer, addition funnel, drying tube and nitrogen gas inlet with thermometer. After cooling the solution mixture below −5 °C using an ice/salt bath, 15 g (0.0505 mol) of 2,3,5,6-tetrafluoro-4-trifluoromethylbromobenzene (99%) was added dropwise over a period of 3–4 h under vigorous stirring, while keeping the temperature below −5 °C. The mixture was then allowed to reach to RT as the ice/salt bath melted and react for 24 h under vigorous stirring. Next, an ice/salt bath was again placed around the flask and 11.4 g (0.0482 mol) of diphenylphosphinic chloride (98%) was added dropwise over a period of 3–4 h, while maintaining below −5 °C. The solution was reacted for 24 h without adding ice, resulting in a brown solution. Finally, 10% aqueous sulfuric acid was added until the solution reached pH 1, followed by adding about 500 ml water and 300 ml chloroform to separate into aqueous and organic layer. The organic layer was isolated and washed successively with 10% aqueous sodium bicarbonate and water, and then dried over magnesium sulfate. The chloroform was removed via evaporation to collect brown solid. The solid was recrystallized from hexane to afford light-brown crystal.

Yield: 81%, mp 115.4–116.1 °C. FTIR (KBr): 1195 cm^{-1} (P=O s), 1490 cm^{-1} (C–F v). ^1H NMR (300 MHz, $CDCl_3$): 7.76 (7.79–7.72) ppm (m, 4H), 7.62 (7.65–7.60) ppm (m, 2H), 7.52 (7.56–7.49) ppm (m, 4H). ^{19}F NMR (282.65 MHz,



Scheme 1. Synthesis of bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethyl phenylphosphineoxide (*m*DA7FPPO).

$CDCl_3$): −58.03 ppm (tri, 3F), −127.02 ppm (m, 2F), −139.04 ppm (m, 2F). ^{31}P NMR (304 MHz, $CDCl_3$): 19.27 ppm.

2.3. Preparation of bis(3-nitrophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethyl phenyl phosphine oxide (mDN7FPPO)

Bis(3-nitrophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethyl phenyl phosphine oxide (mDN7FPPO) was prepared via nitration of 7FPPO using sulfuric acid and nitric acid (Scheme 1). 7 g (0.0167 mol) of purified 7FPPO and 70 ml of 96% sulfuric acid were placed in a 250 ml of three-neck round bottom flask equipped with magnetic stirrer, nitrogen inlet with thermometer, and addition funnel with drying tube. Then, the solution was cooled to −5 °C with an ice/salt bath, followed by adding mixture of 2.4 ml fuming nitric acid and 10.5 ml sulfuric acid dropwise over a period of 3 h, while maintaining the temperature below −5 °C. Next, the solution was allowed to reach to RT and react for 12 h. Finally, the mixture was poured into 700 g of ice. Once the ice was melted, yellow organic material was extracted with chloroform and washed with aqueous sodium bicarbonate until it was neutral. The solution was dried over magnesium sulfate and solid was obtained by precipitation into chloroform/methanol mixture. Then, it was purified by recrystallization from absolute ethanol, providing pale yellow crystals.

Yield: 89%, mp 160.2–160.9 °C, FTIR (KBr): 1529 cm^{-1} (asym NO_2 s), 1350 cm^{-1} (sym NO_2 s), 1204 cm^{-1} (P=O s). ^{1}H NMR (300 MHz, $CDCl_3$): 8.71–8.66 ppm (double, 2H), 8.56–8.53 ppm (quartet, 2H), 8.38–8.31 ppm (quartet, 2H), 7.98–7.91 ppm (sixtet, 2H). ^{19}F NMR (282.65 MHz, $CDCl_3$): −58.13 ppm (tri, 3F), −127.20 ppm (m, 2F), −137.12 ppm (m, 2F). ^{31}P NMR (304 MHz, $CDCl_3$): 15.02 ppm.

2.4. Preparation of bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethyl phenyl phosphine oxide (*m*DA7FPPO)

Bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethyl phenyl phosphine oxide (*m*DA7FPPO) was obtained by hydrogenation of *m*DN7FPPO (Scheme 1) under H_2 atmosphere using Pd/C catalyst in a high pressure reactor (Parr Instrumental Co., USA). 12 g (0.0236 mol) of purified *m*DN7FPPO, 150 ml of absolute ethanol, and two spoonful of Pd/C catalyst (15 mg) were added into the pressure reactor. The reaction was carried out under 100 psi of hydrogen pressure at 50 °C for 24 h with constant stirring (200 rpm). The catalyst was removed from the reaction mixture by filtering right after reaction was completed. The solvent was then stripped off and the product was purified by column chromatography using ethylacetate and hexane for eluant solvent, affording light yellow crystals.

Yield: 83%, mp 187.3–187.6 °C, FTIR (KBr): 3500–3300 cm^{-1} (N–H s), 1630 cm^{-1} (N–H b), 778 cm^{-1} (N–H b), 1187 cm^{-1} (P=O s). ^{1}H NMR (300 MHz, $CDCl_3$): 7.22–7.15 ppm (sixtet, 2H), 6.96–6.91 ppm (doublet, 2H), 6.80–6.72 ppm (quartet, 4H), 5.49 ppm (s, NH). ^{19}F NMR (282.65 MHz, $CDCl_3$): −56.23 ppm (tri, 3F), −128.68 ppm (m, 2F), −140.38 ppm (m, 2F). ^{31}P NMR (304 MHz, $CDCl_3$): 22.03 ppm.

2.5. Characterization of monomer and its intermediates

7FPPO, mDN7FPPO and *m*DA7FPPO were characterized by FT-IR (IR 2000, Perkin–Elmer) using a KBr pellet and FT NMR (JEOL, JNM-LA 300 WB, 300 MHz) with $CDCl_3$ or dimethylsulfocide-d_6. Chemical shifts were calibrated by using tetramethylsilane ($(CH_3)_4Si$), hexafluorobenzene (C_6F_6) and phosphoric acid (H_3PO_4), as an internal reference for ^{1}H NMR, ^{19}F NMR and ^{31}P NMR, respectively. Melting temperature of compounds was measured by using electrothermal digital melting point apparatus (Model 1A9100, Fisher).

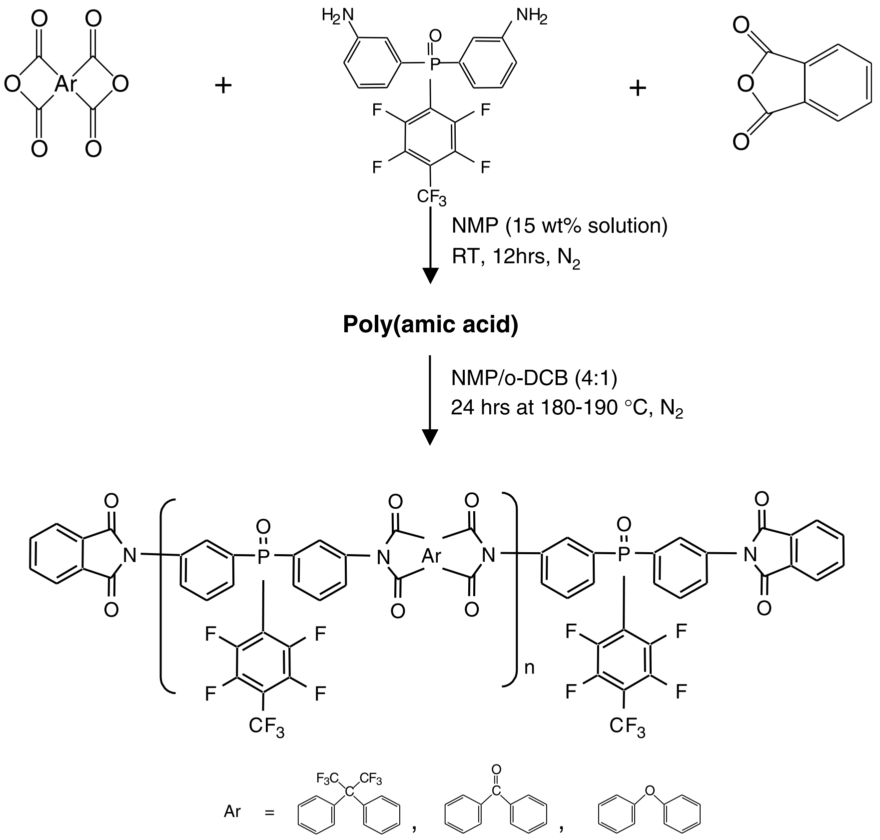
2.6. Synthesis and characterization of polyimides

The polyimides were synthesized with dianhydrides, such as 6FDA, BTDA and ODPA via conventional two-step reaction; preparation of poly(amic acid), followed by solution imidization (Scheme 2). The number average molecular weight of polyimides was controlled to 20,000 g/mol by off-stoichiometry and non-reactive end-groups were obtained by adding calculated amount of phthalic anhydride (PA). First, *m*DA7FPPO and distilled NMP were charged into a flame-dried three-neck round bottom flask equipped with mechanical stirrer, reverse Dean–Stark trap with condenser and drying tube, and nitrogen inlet with thermometer. After the complete dissolution of diamine, PA and dianhydride were added while stirring, and solid concentration was controlled to 15 wt%. Then, the mixture was reacted 12 h at RT, resulting in poly(amic acid) solution. For solution imidization, azeotropic agent, *o*-DCB (20 v/v%), was added into the poly(amic acid) and allowed to react at 180–190 °C for 24 h under a nitrogen flow. Finally, the polyimide solution was cooled to RT, followed by precipitation into water/methanol mixture (1:1 v/v%), filtering and drying in vacuum oven at 200 °C for 12 h.

2.7. Characterization of polyimides

The chemical structure of the polyimides were characterized by FT-IR (IR 2000, Perkin–Elmer) with KBr pellet and FT NMR (300 MHz JEOL JNM-LA 300 WB) using DMSO-d_6, while solubility of these was evaluated by dissolving polyimide films ($15\times15\times0.1$ mm^3) in solvents such as NMP, DMAc, tetrachloroethane, chloroform, THF, toluene, and acetone at the concentration of 10 wt% at RT for 24 h. Number average molecular weight was evaluated by GPC (Waters, M77251) in THF with a polystyrene standard and solution viscosity was measured with a Cannon-Ubbelohde viscometer in NMP at 25 °C.

Differential scanning calorimeter (DSC, TA-2910) and thermogravimetric analyzer (TGA, TA-2950) were utilized at 10 °C/min to measure T_g and thermal stability, respectively. The dielectric constants of polyimides were also evaluated via parallel-plate capacitor method at 1 MHz with Capacitance Meter (HP-4155), while Metricon Prism Coupler (Model 2010)



Scheme 2. Synthesis of polyimides with *m*DA7FPPO.

was used to measure in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of polyimides. For refractive index measurements, thin film (2.0–3.0 μm) on silicon wafer was utilized, which was prepared by spin coating of polyimide solution (15 wt% in TCE), followed by drying at T_g+20 °C.

3. Results and discussion

3.1. Synthesis and characterization of mDA7FPPO

A novel diamine, bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethyl phenyl phosphine oxide (*m*DA7PPO), containing perfluorinated phenyl pendent with trifluoromethyl (–CF_3) and phosphine oxide group, was successfully synthesized, and characterized by FT-IR, FT NMR and melting point analyzer. In the ^{1}H NMR (300 MHz, $CDCl_3$), 7FPPO exhibited three groups of peaks beside solvent peak. Upon nitration (*m*DN7FPPO), however, four groups of peaks appeared and the peaks shifted to down-field, while the peaks shifted up-field upon hydrogenation (*m*DA7FPPO) and four groups of peaks observed; three from protons of phenyl ring and one from amine moiety (Fig. 1). These behaviors can be attributed to the deshielding effect of electron-withdrawing nitro groups and the shielding effect of electron-donating amine groups. In addition, successful synthesis of *m*DA7FPPO was also confirmed by ^{19}F NMR analyses.

In FT-IR analysis, as shown in Fig. 2, 7FPPO exhibited aromatic C–F vibration absorption (1490 cm^{-1}), P=O stretching absorption (1195 cm^{-1}) and F-phenyl bending absorption (987 cm^{-1}). Upon nitration, new peaks at 1529 and 1350 cm^{-1} appeared, attributing to asymmetric and symmetric stretch of NO_2, respectively, besides P=O stretching and C–F vibration absorption peaks. After hydrogenation (*m*DA7FPPO), new peaks were observed; N–H stretching at 3500–3300 cm^{-1}, N–H primary bending at 1630 cm^{-1} and N–H out-of plane bending at 778 cm^{-1}. The P=O stretching peak shifted to 1187 cm^{-1} (*m*DA7FPPO) from 1204 cm^{-1} (*m*DN7FPPO) upon hydrogenation, owing to electron-donating effect of amine groups.

3.2. Synthesis and characterization of polyimides with mDA7FPPO

3.2.1. Characterization of polyimides

A novel monomer, *m*DA7FPPO was utilized to prepare polyimides with 6FDA, BTDA and ODPA, and their structures were analyzed by FT-IR and NMR, but discussion is made only with 6FDA–*m*DA7FPPO polyimide. As shown in Fig. 3, the characteristic absorption bands of imide ring were observed at 1789 cm^{-1} (C=O asymmetric stretching), 1727 cm^{-1} (C=O symmetric stretching), 1365 cm^{-1} (C–N stretching) and 717 cm^{-1} (C=O bending), but amide-carbonyl (C=O) peak at 1650 cm^{-1} was not observed, indicating successful

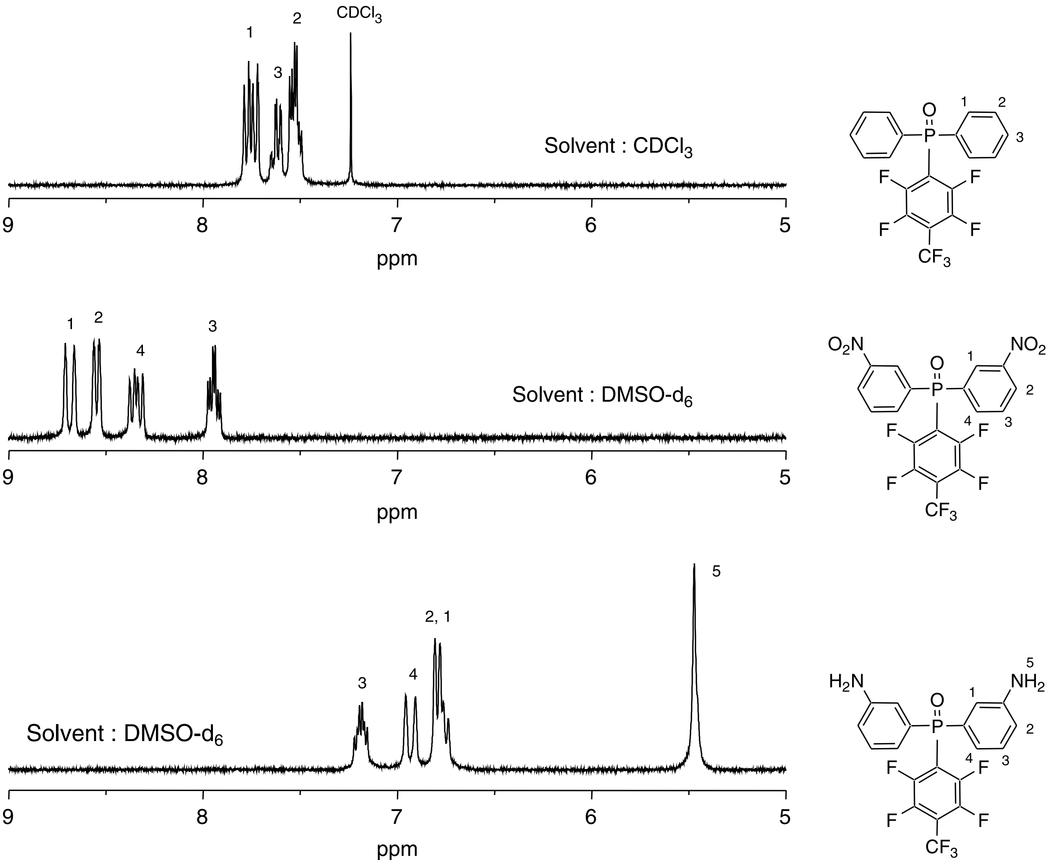


Fig. 1. ^{1}H NMR of *m*DA7FPPO and its intermediate compounds.

polyimide synthesis. In addition, P=O stretching absorption (1187 cm^{-1}), CF_3 stretching–bending absorption (1250–1090 cm^{-1}) and C–F ring vibration absorption (1475 cm^{-1}) were also observed, demonstrating presence of phosphine oxide and fluorine moieties as reported previously [13,14].

In ^{1}H NMR analysis of 6FDA–*m*DA7FPPO (300 MHz, $CDCl_3$), four groups of peaks were observed; two are from dianhydride moieties, while the other two are from diamine groups. Considering the electron withdrawing nature of imide, CF_3 and P=O groups, all protons were successfully assigned.

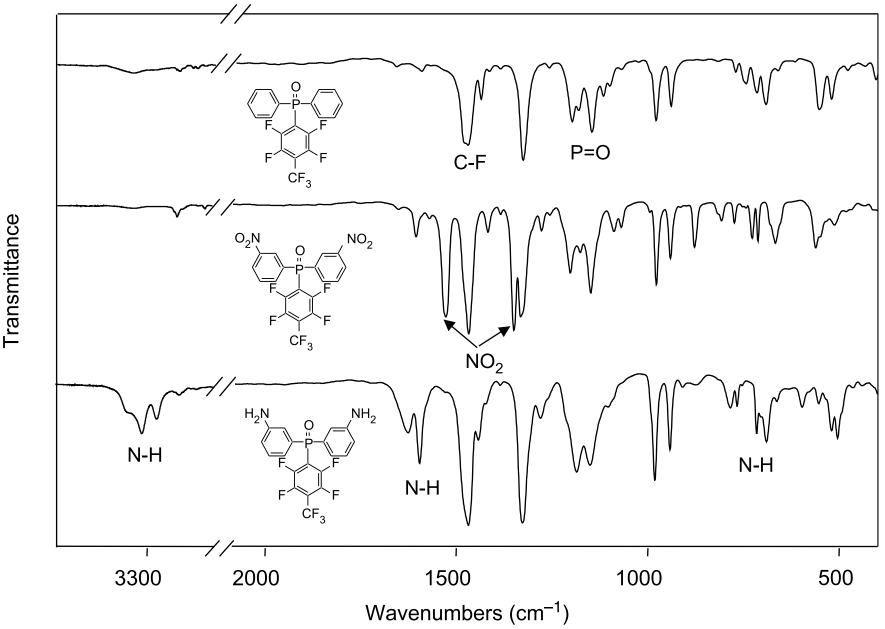


Fig. 2. FT-IR of *m*DA7FPPO and its intermediate compounds.

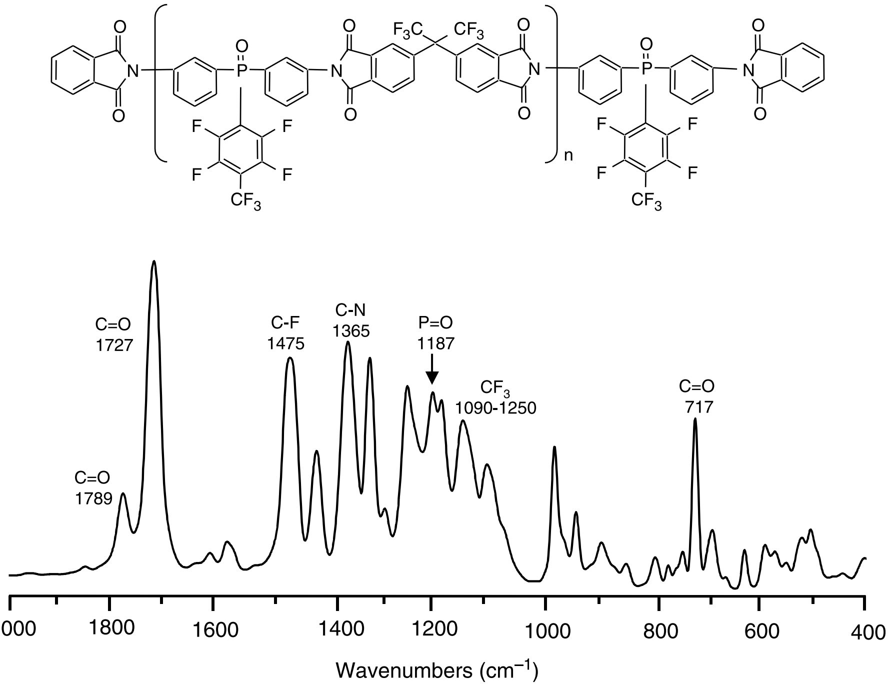


Fig. 3. FT-IR of polyimide from 6FDA–*m*DA7FPPO.

^{19}F NMR analysis (300 MHz, $CDCl_3$) revealed four peaks at −56.52 ppm (triplet, 3F), −63.23 (triplet, 6F) −127.97 ppm (multiplet, 2F) and −140.04 ppm (multiplet, 2F). Among them, three are from perfluoro-pendent groups of dimane moiety, while one (63.23 ppm) is from fluorines in 6FDA. As expected, single peak was shown at 17.79 ppm in ^{31}P NMR (300 MHz, $CDCl_3$), demonstrating only one type of phosphine in this polyimide. Consequently, based on the FT-IR and FT NMR results, it can be said that polyimides with *m*DA7FPPO was successfully synthesized.

3.3. Solubility and solution viscosity of polyimides

The *m*DA7FPPO-based polyimides exhibited good solubility in NMP, DMAc, TCE, $CHCl_3$ and THF regardless of dianhydrides used, but only selected samples were soluble in toluene and acetone. The excellent solubility of *m*DA7FPPO-based polyimides can be attributed to bulky perfluorinated phenyl pendant group including trifluoromethyl moiety, as discussed previously [13,14]. Since, all polyimides prepared in this study exhibited excellent solubility in NMP, intrinsic viscosity of *m*DA7FPPO-based polyimides was measured in NMP at 25 °C with a Cannon-Ubbelohde viscometer. As shown in Table 1, solution viscosities range from 0.22 to 0.25 dl/g, which are in reasonable rage considering the target molecular weight of 20,000 g/mol and these values are comparable to those reported earlier [13,14]. In addition, GPC analysis of these polyimides provided molecular weight of 18,300–21,100 g/mol, which are well matched to the target molecular weigh of 20,000 g/mol.

3.4. Thermal properties of polyimides

The 6FDA–*m*DA7FPPO polyimide provided T_g of 252 °C, followed by 247 and 229 °C with BTDA and ODPA-based polyimides, respectively (Table 1), which is well correlated to the stiffness/bulkiness of dianhydride moieties (6FDA > BTDA > ODPA). Compared to other polyimides, these values are similar to those with *m*DA6FPPO (228–252 °C), possibly owing to similar structure [13]. The polyimides with

Table 1
Characteristics of *m*DA7FPPO-based polyimides

Diamine	Dianhydride	[η] (dl/g)[a]	[M_n][b]	T_g (°C)[c]	T_d (°C)[d]		Residue (wt%)	
					In air	In N_2	In air	In N_2
mDA7FPPO	6FDA	0.25	21,100	252	504	515	7	47
	BTDA	0.25	18,300	247	511	523	7	58
	OPDA	0.22	19,200	229	517	529	12	55

[a] At 25 °C in NMP.

[b] By GPC in THF.

[c] By DSC, 10 °C/min.

[d] By TGA, 5 wt% loss, 10 °C/min.

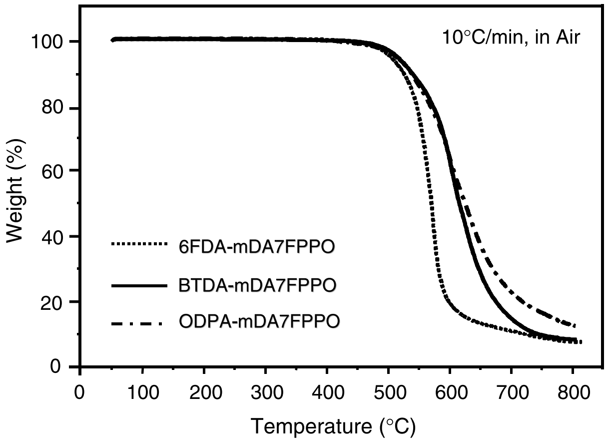


Fig. 4. TGA of *m*DA7FPPO-based polyimides in air.

*m*DA7FPPO also exhibited very high thermal stability, showing 5% weight loss temperature of 500 °C or higher. As shown in Fig. 4, the polyimides from BTDA and ODPA demonstrated a similar degradation behavior in air, while 6FDA–*m*DA7FPPO polyimide degraded rather rapidly around 550 °C, possibly owing to the poor thermal stability of CF_3 moiety. At 800 °C, high residue was observed with ODPA-based polyimides, over 10%, which is attributed relative weight percentage of phosphine oxide in ODPA–*m*DA7FPPO polyimide, compared to others.

3.5. Dielectric and optical properties of polyimides

As expected, the *m*DA7FPPO-based polyimides showed very low dielectric constants (2.65–2.81 at 1 MHz), owing to the perfluorinated phenyl pendent group with CF_3 moieties in *m*DA7FPPO (Table 2). Among those, the 6FDA–*m*DA7FPPO polyimide provided the lowest dielectric constant (2.65), as expected from bulky CF_3 moiety in 6FDA, followed by ODPA–*m*DA7FPPO (2.77) and BTDA–*m*DA7FPPO (2.81) polyimides. These values can be compared to 2.8 with *m*DA6FPPO–6FDA [13], demonstrating slightly lower dielectric constant of *m*DA7FPPO-based polyimides, possibly owing to slightly higher fluorine content (26.7 vs 28.8%). This can be compared to 2.3 with fluorine content of 30.1% [6].

In refractive index measurements, 6FDA–*m*DA7FPPO polyimide provided in-plane (n_{TE}) refractive index of 1.5209 and out-of plane (n_{TM}) refractive index of 1.5190, resulting birefringence of 0.0019 (Table 2). This very low value can be attributed to the bulky perfluorinated phenyl pendant, and the *meta*-substituted non-coplanar of *m*DA7FPPO. The other two polyimides also showed similar refractive indices and resultant birefringence were 0.0034 (with ODPA) and 0.0049 (with BTDA), reflecting the stiffness of dianhydride.

Table 2
Dielectric and optical properties of *m*DA7FPPO-based polyimides

Diamine	Dianhydride	*F* (wt%)	ε^a	n_{TE}	n_{TM}	Δn
*m*DA7F-PPO	6FDA	28.84	2.65	1.5209	1.5190	0.0019
	BTDA	18.06	2.81	1.5800	1.5751	0.0049
	ODPA	18.36	2.77	1.5806	1.5772	0.0034

[a] Measured at 1.55 μm; n_{TE}, refractive index of in-plane; n_{TM}, refractive index of out-of-plane; Δn, $n_{TE}-n_{TM}$.

4. Conclusions

1. A novel diamine, bis(3-aminophenyl)-2,3,5,6-tetrafluoro-4-trifluoromethylphenyl phosphine oxide (*m*DA7FPPO), was successfully synthesized via Grignard reaction and subsequent nitration and hydrogenation.
2. Polyimides prepared from *m*DA7FPPO and dianhydrides such as 6FDA, BTDA or ODPA exhibited excellent solubility, high T_g (252 °C) and good thermal stability ($>$ 500 °C).
3. The *m*DA7FPPO-based polyimides also provided low dielectric constant (2.65) and small birefringence($<$ 0.0019) because of the bulky perfluorinated phenyl pendent group and non-coplanarity of *m*DA7FPPO.

Acknowledgements

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