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New fluorinated aromatic poly(ether-amide)s derived from 2,2′-bis(3,4,5-trifluorophenyl)-4,4′-diaminodiphenyl ether and various dicarboxylic acids

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ABSTRACT

A new class of highly fluorinated aromatic poly(ether-amide)s was prepared through triphenyl phosphite-activated polycondensation of 2,2′-bis(3,4,5-trifluorophenyl)-4,4′-diaminodiphenyl ether (FPAPE) and four dicarboxylic acid comonomers. All the resulting polymers were thoroughly characterized by FT-IR, UV, and NMR spectroscopic methods. The effects of the fluorine atoms directly linked to the lateral phenyl rings as well as fluoro-containing phenyl groups attached to the macromolecular chains on some properties of the polymers were investigated by comparing with poly(ether-amide)s prepared from 4,4′-oxydianiline (4,4′-ODA) and 2,2′-diphenyl-4,4′-diaminodiphenyl ether (PAPE). The FPAPE-derived polymers exhibited excellent solubility in a variety of organic solvents. Results obtained from X-ray studies showed that the presence of the bulky fluoro-containing phenyl groups attached to the chains disrupts their structural order in a great amount, and leads to a decrease in crystallinity extent of the macromolecules. Furthermore, the highly fluorinated polymeric chains showed a significant enhancement in organo-solubility, heat-stability and T_g values when compared to their non-fluorinated counterparts.

1. Introduction

Aromatic polyamides are one of the most important classes of high-performance polymers. This family of materials along with aromatic polyimides plays a vital role in advanced technologies. For practical use in various recent applications, new aromatic polyamides possessing both high thermal stability and solubility in common organic solvents are required [1,2]. To obtain different properties and for different applications, various structural changes have been introduced in aromatic polyamide backbones [3–12]. Introduction of bulky substituents into the macromolecular chains is expected to decrease their orderly arrangement. With this kind of structural modification an enhanced organo-solubility and reduced chain crystallinity are subsequently resulted [13–16]. In recent years, however, considerable attention has been devoted to the fluorinated aromatic polyamides. Fluoro-containing aromatic polyamides have attracted much attention due to their outstanding properties. This class of engineering plastics exhibits highly thermal stability and chemical inertness. Among the modifications, fluorination might be one of the most promising procedures to achieve a good compromise in the desired properties [17–23]. Fluoro-containing substituents, including fluorine atoms or fluoroalkyl groups such as CF_3 possess large electronegativities and, thus, often endow fluoropolymers with good organo-solubility. Meanwhile, the thermal properties of the polymers can often be maintained because of the outstanding thermal and thermooxidative stability of the fluoro groups [24]. Compared with those aromatic polymers having $-CF_3$ groups attached to the macromolecular backbone, polymers possessing directly linked fluorine atoms to the aromatic main chain [25–28] exhibit much lower molar volume, and this class of polyfluorinated aromatic polyamides has been proposed to be used as coatings for optical waveguide fabrication [29].

In our previous study we successfully prepared a highly fluorinated aromatic diamine monomer namely 2,2′-bis(3,4,5-trifluorophenyl)-4,4′-diaminodiphenyl ether (FPAPE) via a two-step pathway starting from 2,2′-diiodo-4,4′-dinitrodiphenyl ether (DINPE) [30]. It is noticeable that the mentioned two-step pathway has been also utilized formerly to synthesize a diamine structurally similar to FPAPE by the name of 2,2′-bis(*p*-phenoxyphenyl)-4,4′-diaminodiphenyl ether (PPAPE), which was used to prepare the corresponding aromatic polyimides [31] and polyamides [32]. FPAPE has six fluorine atoms directly attached to the lateral phenyl rings instead of two *p*-phenoxy groups in the structure of PPAPE.

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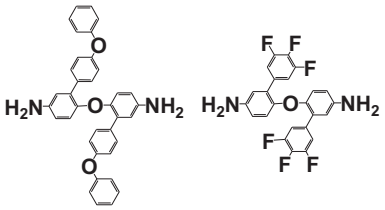


FPAPE was then used to prepare a number of fluoro-containing aromatic polyimides. In the present study, however, we will report the synthesis and characterization of novel highly fluorinated aromatic polyamides derived from diamine FPAPE and four simple diacid comonomers. Experimentally, to attain further results, polymers derived from 2,2′-diphenyl-4,4′-diaminodiphenyl ether (PAPE) possessing lateral phenyl rings but lacking any fluorine atom as well as polymers derived from 4,4′-oxydianiline (4,4′-ODA) lacking fluorinated phenyl lateral groups were also prepared to compare their characteristics with those of the polymers prepared from FPAPE. Solubility in common organic solvents, crystallinity of the macromolecular chains, intrinsic viscosity of the polymers solutions, and thermal stability were subsequently investigated.

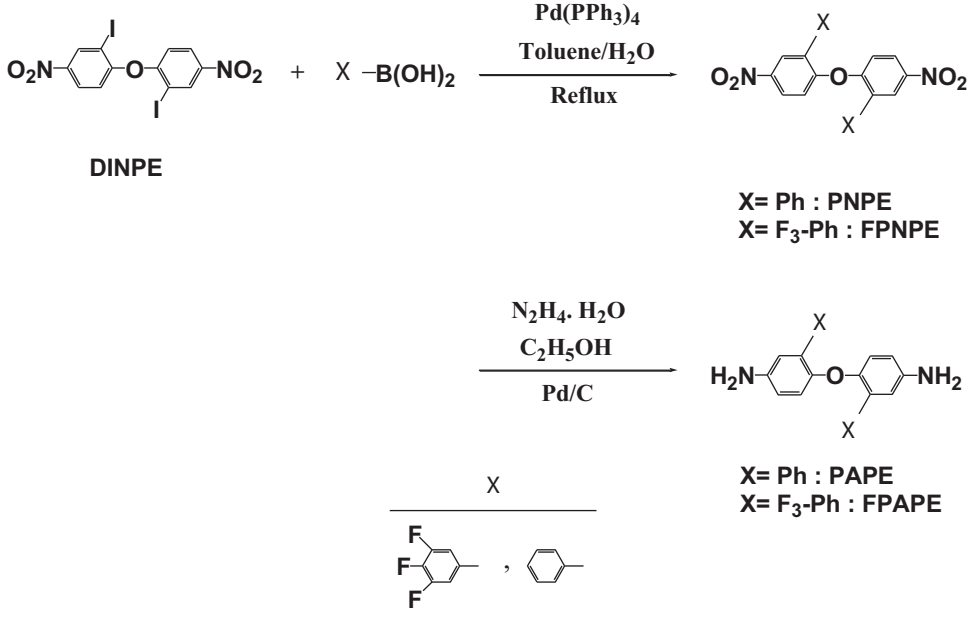
2. Results and discussion

2.1. Synthesis

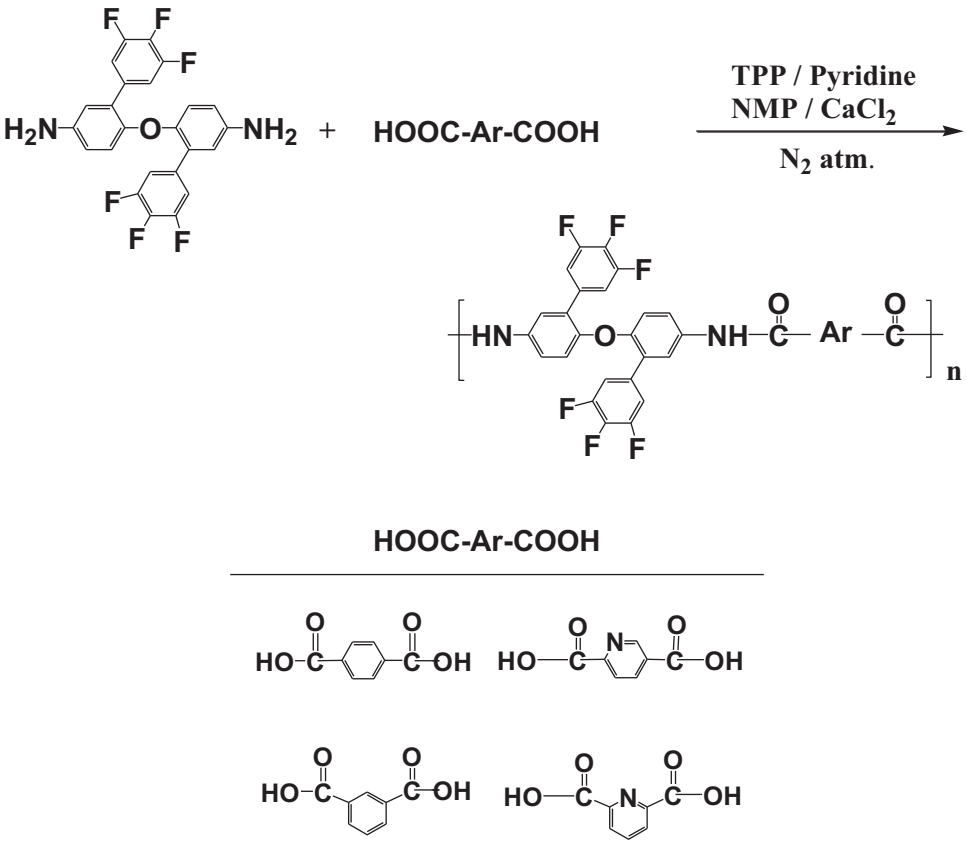
PAPE was synthesized starting from DINPE by a two-step manner. In the first step, DINPE was reacted with phenylboronic acid via a Suzuki coupling reaction affording yellow needles of 2,2′-diphenyl-4,4′-dinitrodiphenyl ether (PNPE). In the second step, PNPE was reduced to obtain pale yellow solids of PAPE. It should be noted that PAPE has been synthesized previously by Morikawa et al. [33] via a manner other than that of used by us. They synthesized PAPE via a more complicated method (a five-step pathway starting from 3-chloro-4-fluoronitrobenzene), and then applied it to prepare some aromatic polyimides (not polyamides). One of their synthesized polyimides, for example that of obtained from polycondensation of PAPE and pyromellitic dianhydride (PAPE/PDA) is discussed in a continuation to compare its characteristics with poly(ether-amide)s prepared here. In addition to PAPE/PDA, to investigate the effect of lateral group nature, a previously reported poly(ether-amide) having phenoxy groups attached to the lateral phenyl rings, i.e. PPAPE/IPA will be also addressed.

IR and NMR spectroscopy results of PNPE and PAPE obtained from our simple two-step method were thoroughly conformable to those reported beforehand. On the other hand, our strategy to synthesize FPAPE was similar to synthesis of PAPE. Synthesis of FPAPE has been stated elsewhere in depth [30]. Scheme 1 outlines the synthetic route to these diamines. Fluorinated diamine FPAPE was then utilized to prepare the corresponding poly(ether-amide)s through reacting with four aromatic diacid comonomers. The highly fluorinated all-aromatic poly(ether-amide)s including FPAPE/TPA, FPAPE/IPA, FPAPE/2,5-PDA, and FPAPE/2,6-PDA as well as their two non-fluorinated counterparts, i.e. PAPE/IPA (lacking fluorine atoms attached to the lateral phenyl rings) and ODA/IPA (lacking fluorinated phenyl lateral groups), were prepared by phosphorylation method, similarly. This method involves the one-pot polycondensation of aromatic diacids with aromatic diamines in the presence of an aryl phosphite such as triphenyl phosphite (TPP) and an organic base such as pyridine [34–36]. All the polyamidation reactions proceeded smoothly in homogeneous solutions with a high yield (over 90%). Scheme 2 shows the reaction route to prepare the resulting fluorinated polymers. The synthetic route to the reference poly(ether-amide)s (PAPE/IPA and ODA/IPA) is also shown in Scheme 3.

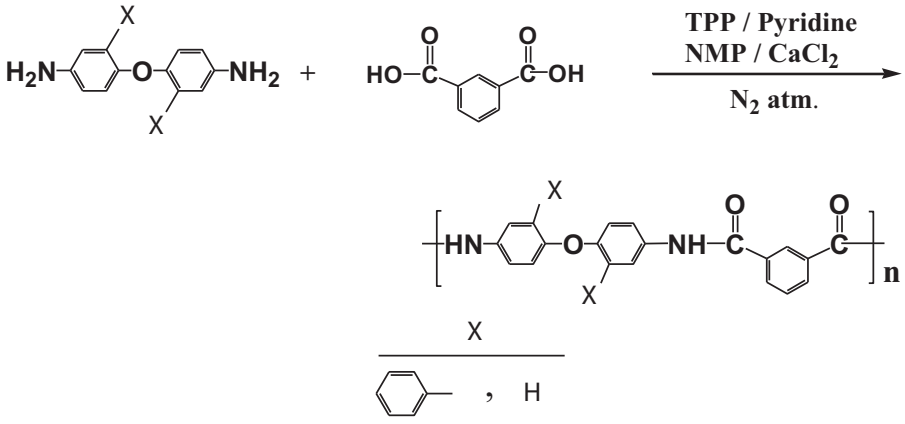
Some characteristics of the fluorinated and non-fluorinated poly(ether-amide)s including λ_{max} values by means of UV–vis spectroscopy and their apparent color are tabulated in Table 1. FT-IR and ^{1}H NMR spectroscopy were used to confirm the structure of the resulting poly(ether-amide)s. In the infrared spectra, the absorptions of amide groups appear at about 3350 cm^{-1} (N–H stretch) and 1650 cm^{-1} (C=O stretch). Fig. 1 (top) shows FT-IR spectrum of the polymer FPAPE/IPA. ^{1}H NMR spectra of the fluoro-containing polymers showed amide protons peak at about 10.55 ppm. Fig. 1 (bottom) shows proton-assigned ^{1}H NMR spectrum of the same polymer FPAPE/IPA. In this spectrum only the region of appearance of aromatic protons can be observed, instead all data obtained from ^{1}H NMR spectroscopy of the



Scheme 1. Synthetic route to diamines FPAPE and PAPE.



Scheme 2. Synthetic route to the fluorinated poly(ether-amide)s.



Scheme 3. Synthetic route to the reference non-fluorinated poly(ether-amide)s.

poly(ether-amide)s are tabulated in Table 2. In all cases, chemical shifts and integral values of the peaks are compatible with the type and the number of attributed hydrogens.

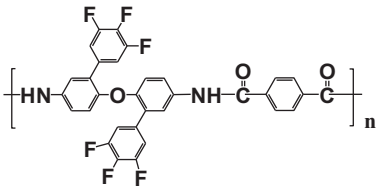
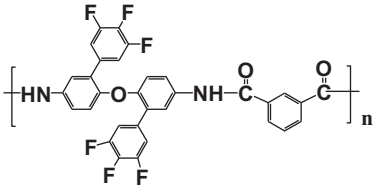
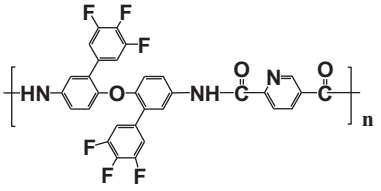
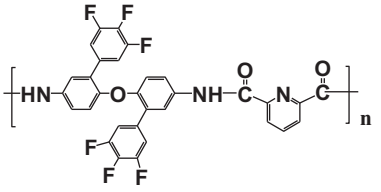
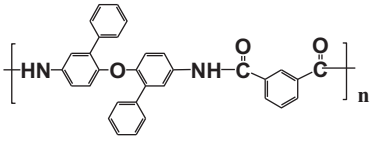
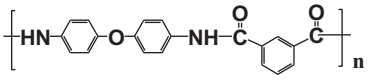
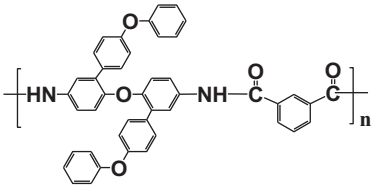
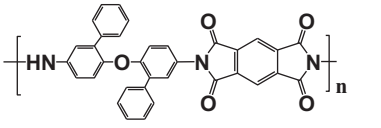
2.2. Solution viscosity

Solution viscosity can be used to estimate an average molecular weight because it is a general rule that the more extended any macromolecule is, the more viscose solution bearing it will be. For polymeric materials there is a definite relationship between molecular weight and solution viscosity [37]. The limited viscosity numbers ([η] values) were measured from their specific viscosities, η_{sp}, at concentrations 0.1, 0.2, 0.3, 0.4, and 0.5 g dL^{-1} in *N*,*N*-dimethylacetamide (DMAc) at 30 °C. The η_{sp} values were plotted against the concentrations used, and linear extrapolation was done. [η] was obtained as the *y*-axis intersect. In other word, these values for all polymeric solutions were determined through the extrapolation of the concentrations used to zero. The [η] values (intrinsic viscosities) in DMAc at 30 °C is tabulated in Table 1. The high molecular weights of the polymers might be confirmed by the high [η] values (up to 1.0 dL g^{-1}) as well as the absence of detectable end groups (NH_2 or COOH) in the FT-IR and ^{1}H NMR spectra of the resulting poly(ether-amide)s.

2.3. Organo-solubility

The solubility behavior of the resulting fluorinated poly(ether-amide)s was tested qualitatively in various organic solvents. Table 3 shows the results obtained from this part of our study. All fluoro-containing poly(ether-amide)s could be easily dissolved in polar

Table 1
Some characteristics of the resulting fluorinated and non-fluorinated poly(ether-amide)s, and poly(ether-imide).

Polymer	Chemical formula	λ_{max}[a] (nm)	Color	$[\eta]$[b] ($dL\,g^{-1}$)
FPAPE/TPA		277	Pale yellow	–[c]
FPAPE/IPA		265	Pale cream	1.11
FPAPE/2,5-PDA		274	Pale gray	1.07
FPAPE/2,6-PDA		269	White	1.01
PAPE/IPA		281	Cream	0.98
ODA/IPA		928	Pale brown	–[c]
PPAPE/IPA[d]		266	Brown	0.80
PAPE/PDA[e]		–[f]	–[f]	0.87[g]

[a] Measured in DMSO.
[b] Measured in DMAc at 30 °C.
[c] Was not dissolved in DMAc adequately.
[d] Data obtained from Ref. [31].
[e] Data obtained from Ref. [33].
[f] Not reported.
[g] Inherent viscosity of the related poly(amic acid) measured at 0.5 g dL^{-1} in NMP at 30 °C.

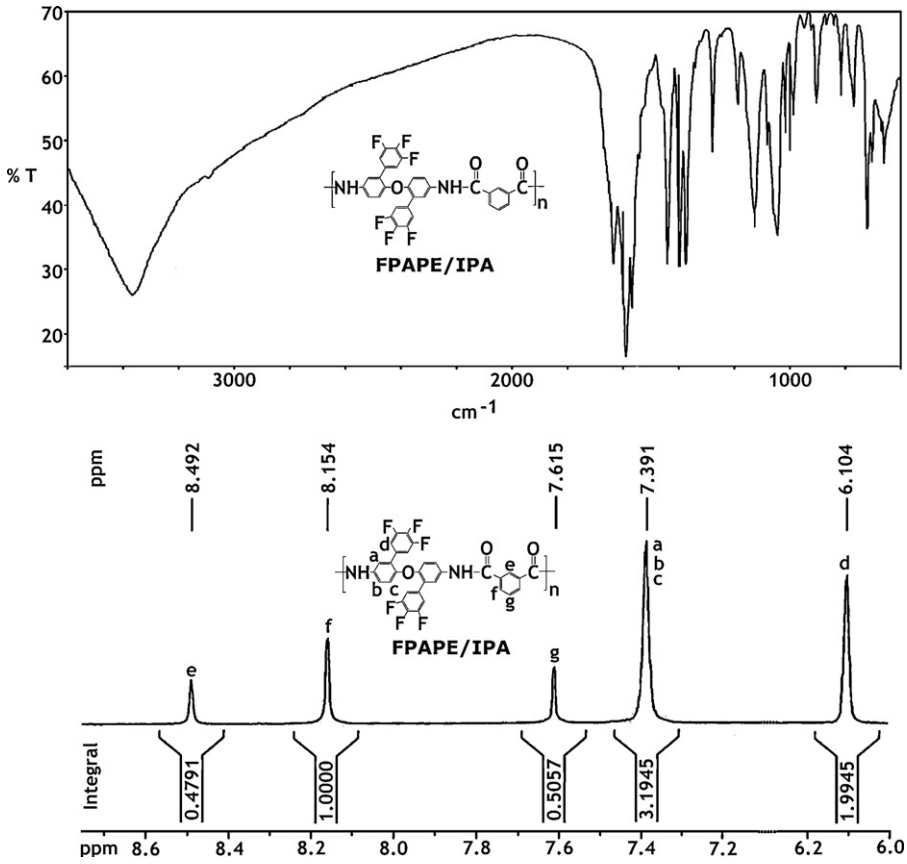


Fig. 1. IR (top) and ^{1}H NMR (bottom) spectra of the poly(ether-amide) FPAPE/IPA.

organic solvents such as dimethyl sulfoxide (DMSO), DMAc, *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP) at room temperature or upon heating at about 70 °C. This class of polymers was nearly dissolved even in less polar solvents including pyridine and tetrahydrofuran (THF) upon heating. Fluorine and fluoro-containing substituents endow a large amount of polarity due to the high electronegativity of fluorine atoms, and thereby fluoropolymers show good organo-solubility, particularly in polar solvents. Furthermore, the good solubility of these all-aromatic poly(ether-amide)s might be caused by an entropy advantage resulted from the bulky fluorinated phenyl groups that inhibited the close packing of the polymer chains. According to this, the highly fluorinated aromatic poly(ether-amide)s showed a further solubility in polar solvents when compared to their non-fluorinated counterparts. The order of 4,4′-ODA/IPA < PAPE/IPA < FPAPE/IPA ∼ PPAPE/IPA gives a qualitative indication of the trend in organo-solubility. Although bulky phenoxy lateral groups in PPAPE/IPA may disrupt order of the chains further in comparison with small fluorine atoms in FPAPE/IPA, the less steric effect of fluorine atoms is balanced by the extra organo-solubility in polar solvents gained from the electronic effects of the fluorine atoms. Moreover, some other trends could be also detected from the table, such as the order of FPAPE/TPA < FPAPE/IPA or PAPE/PDA < PAPE/IPA. Also, the pyridyl-based poly(ether-amide)s, i.e. FPAPE/2,5-PDA and FPAPE/2,6-PDA were somewhat more soluble than those of prepared from terephthalic acid (TPA) or isophthalic acid (IPA) diacid comonomers.

2.4. X-Ray diffraction patterns

In order to study the crystallinity amount of the fluorinated poly(ether-amide)s and to investigate the effect of fluoro-containing phenyl pendant groups on the crystallinity extent, wide-angle X-ray diffraction (WXRD) measurements at room temperature in the region of 2θ = 10–50° were done for poly(ether-amide)s FPAPE/IPA and 4,4′-ODA/IPA. The diffraction patterns are presented in Fig. 2. According to the diffractograms obtained, only one broad peak was observed in the range of 10–30°, and almost no crystal diffraction was detected for this class of new fluorinated aromatic poly(ether-amide)s. This amorphous diffraction pattern is reasonable because the presence of the bulky fluorinated phenyl groups attached to the macromolecular backbone induces looser chain packing and decreases the intermolecular forces between the polymer chains causing a decrease in crystallinity. In fact, introducing bulky substituents within the macromolecular chains decreases the well-organized arrangement of the chains. On the other hand, it seems to be a true statement that the enhancement of polarity of the chains endowed by fluorine atoms in these highly fluorinated poly(ether-amide)s enhances crystallite regions of them to a large extent by increasing intermolecular forces, causing a more crystallinity amount. However, the results obtained from the fluorinated poly(ether-amide)s clearly show that the steric factor caused by bulky fluorinated phenyl lateral groups outweighs the polarity factor derived from fluorine atoms. Hence, the steric effects are the dominant factor in crystallinity here, and only the minor effect with a opposite direction is believed to be electronic.

2.5. Thermogravimetric analysis (TGA)

Thermal stability of the resulting poly(ether-amide)s were evaluated by thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The results obtained from TGA analyses are tabulated in Table 4. TGA thermograms showed that the highly fluorinated poly(ether-amide)s obtained

Table 2
^{1}H NMR results of the resulting poly(ether-amide)s.

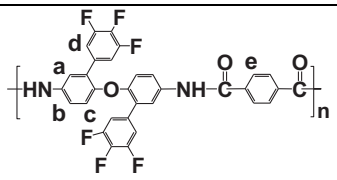
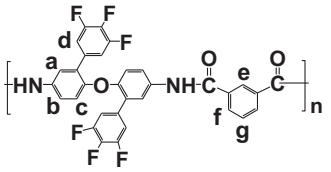
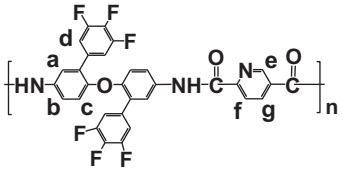
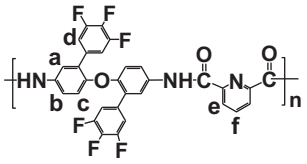
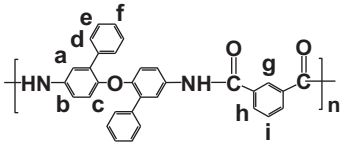
Polymer	Formula	^{1}H NMR results (ppm)
FPAPE/TPA		10.55 (2H, amide-H), 8.04 (4H, H_e), 7.39 (6H, H_a & H_b & H_c), 6.10 (4H, H_d)
FPAPE/IPA		10.53 (2H, amide-H), 8.49 (1H, H_e), 8.15 (2H, H_f), 7.61 (1H, H_g), 7.39 (6H, H_a & H_b & H_c), 6.10 (4H, H_d)
FPAPE/2,5-PDA		10.53 (2H, amide-H), 9.15 (1H, H_e), 8.43 (1H, H_f), 8.14 (1H, H_g), 7.39 (6H, H_a & H_b & H_c), 6.09 (4H, H_d)
FPAPE/2,6-PDA		10.54 (2H, amide-H), 8.23 (2H, H_e), 8.18 (1H, H_f), 7.38 (6H, H_a & H_b & H_c), 6.10 (4H, H_d)
PAPE/IPA		10.53 (2H, amide-H), 8.49 (1H, H_g), 8.14 (2H, H_h), 7.61 (1H, H_i), 7.25–7.47 (16H, H's$_{a-f}$)

Table 3
Solubility of the resulting fluorinated and non-fluorinated poly(ether-amide)s.

Solvent[a]	FPAPE/TPA	FPAPE/IPA	FPAPE/2,5-PDA	FPAPE/2,6-PDA	PAPE/IPA	4,4′-ODA/IPA	PPAPE/IPA[b]	PAPE/PDA[c]
DMSO	+	++	+	++	+	+	++	–[d]
DMAc	+	++	++	++	++	±	++	++
DMF	+	+	+	++	+	±	+	++
NMP	+	++	+	++	+	±	++	++
Pyridine	+	++	+	++	+	±	–[d]	++
THF	–	+	±	+	±	–	±	–
DCM	–	±	–	±	–	–	–[d]	–[d]
Toluene	–	–	–	±	–	–	±	–[d]

++, soluble at room temperature; +, soluble on heating; ±, partially soluble or swollen; and –, insoluble even on heating.
[a] Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent.
[b] Data obtained from Ref. [31].
[c] As a poly(ether-imide); data obtained from Ref. [33]. According to the paper cited in this reference, ++ means "soluble on heating".
[d] Not reported.

here were stable up to 450 °C. However, a poly(ether-imide) had a higher stability toward heat comparing with its poly(ether-amide) analog. The poly(ether-amide)s derived from pyridyl-based diacids, i.e. 2,5-pyridine dicarboxylic acid (2,5-PDA) and 2,6-pyridine dicarboxylic acid (2,6-PDA) were somewhat more stable toward heat than those of derived from TPA or IPA. From the order 4,4′-ODA/IPA < FPAPE/IPA, it will be readily revealed that the laterally attached fluoro-containing phenyl rings have somewhat an enhancing effect on the thermal stability of the poly(ether-amide)s. Furthermore, the order PAPE/IPA < FPAPE/IPA showed that the fluorine atoms directly linked to the phenyl rings have an increasing effect on thermo-stability. One of the most important factors for thermo-stability of fluorinated polyamides is bond energy of C–F. In fact, a strong C–F bond leads to high thermal and chemical stabilities

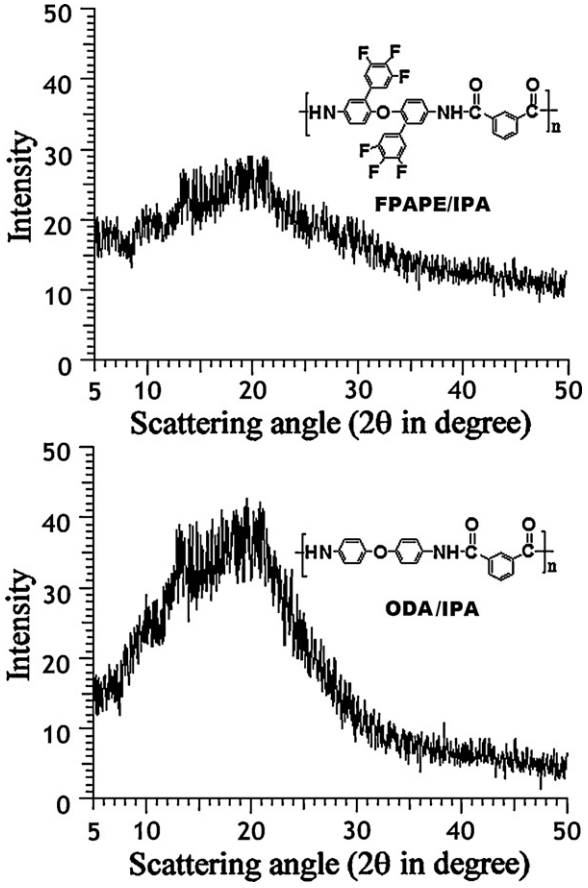


Fig. 2. X-ray diffraction patterns of the poly(ether-amide)s FPAPE/IPA (top) and ODA/IPA (bottom).

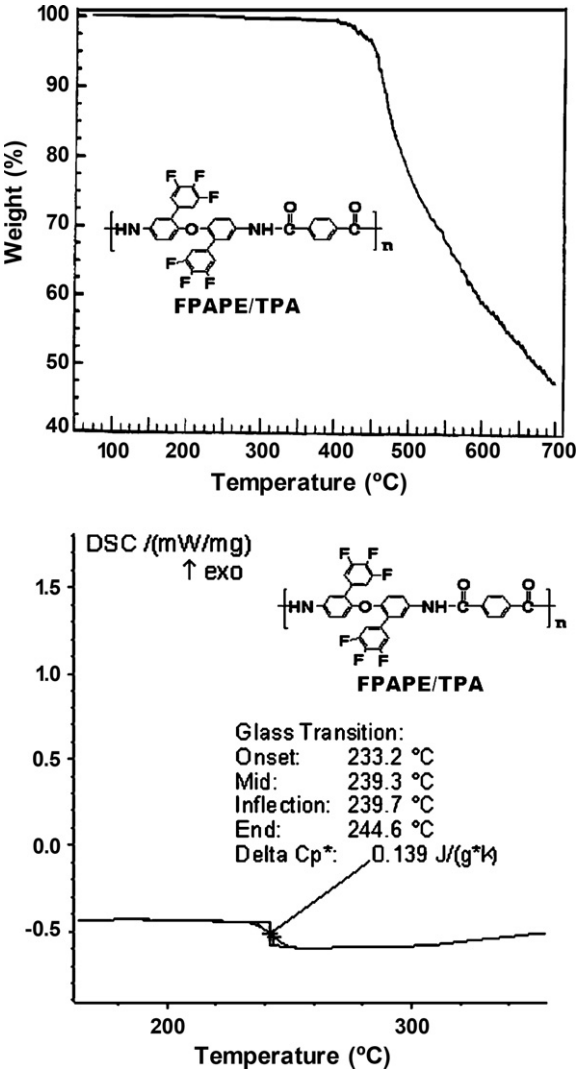


Fig. 3. TGA (top) and DSC (bottom) thermograms of the poly(ether-amide) FPAPE/TPA.

of fluorinated polymers [39]. A representative TGA thermogram for the fluorinated poly(ether-amide) FPAPE/TPA is presented in Fig. 3 (top). As the profile shows, the char yield at 700 °C for this polymer was over 45%, and the plateau region proceeded to about 450 °C.

2.6. Differential scanning calorimetry (DSC)

T_o (the "onset" temperature, defines the point at which the first deviation from the base line on the low temperature side is observed) and T_g ($T_{0.5}$, temperature of 50% transition) values of the four fluoro-containing aromatic poly(ether-amide)s and their two non-fluorinated analogs were determined by differential scanning calorimetry (DSC) measurements. These values for the two pyridyl-based poly(ether-amide)s FPAPE/2,5-PDA and FPAPE/2,6-PDA were about 10 °C grater than those of the other two fluoropolymers, i.e. FPAPE/TPA and FPAPE/IPA. This might be due to the presence of nitrogen heteroatoms in the heteroaromatic rings that limit free rotation of the macromolecular chains by forming excessive H-bond with hydrogen atoms of amide groups. This limitation in free rotation of the chains leads reasonably to an enhancement in T_o and T_g values. In addition to the mentioned excessive H-bonds caused by nitrogen heteroatoms, the order 4,4′-ODA/IPA < FPAPE/IPA revealed that the incorporation of bulky fluoro-containing phenyl pendant groups into the chemical structure of the polymers restricts the free rotation of their macromolecular chains and consequently leads to an enhanced T_g value. According to the results obtained, poly(ether-imide) PAPE/PDA showed T_g about 70 °C greater than poly(ether-amide) PAPE/IPA. This could be attributed to the presence of imide heterocyclic ring that increases rigidity of the chains. There is also a less dramatic but consistent trend which reveals that fluorine atoms attached to the phenyl lateral groups have more increasing effect on T_g values than phenoxy groups attached to them (PPAPE/

Table 4
Some characteristics of the resulting fluorinated and non-fluorinated poly(ether-amide)s, and poly(ether-imide).

Polymer	$T_{d5\%}$[a] (°C)	$T_{d10\%}$[b] (°C)	T_o[c] (°C)	T_g[d] (°C)
FPAPE/TPA	456	467	233	239
FPAPE/IPA	451	464	229	241
FPAPE/2,5-PDA	460	471	242	247
FPAPE/2,6-PDA	456	468	235	245
PAPE/IPA	443	452	228	235
4,4′-ODA/IPA	448	459 (450)[e]	227	232
PPAPE/IPA[f]	–[g]	525	–[g]	196
PAPE/PDA[h]	–[g]	622	–[g]	309

[a] Temperature at which 5% weight loss was recorded by TGA in N_2 atmosphere.
[b] Temperature at which 10% weight loss was recorded by TGA in N_2 atmosphere.
[c] Onset temperature, from the second heating traces of DSC measurements in N_2.
[d] Temperature of 50% transition, from the second heating traces of DSC measurements in N_2.
[e] Data obtained from Ref. [38].
[f] Data obtained from Ref. [31].
[g] Not reported.
[h] Data obtained from Ref. [33].

IPA < FPAPE/IPA). A more restriction in free rotation of the chains is caused by fluorine atoms relative to phenoxy groups. This restriction itself might arise from the enhancement in polarity and consequently in intermolecular attractions. The results obtained from the DSC analyses are tabulated in Table 4. A typical DSC plot for the same poly(ether-amide) FPAPE/TPA are presented in Fig. 3 (bottom).

3. Conclusions

FPAPE as a diphenyl ether-based diamine containing two fluorinated phenyl lateral groups in its chemical structure was successfully utilized to prepare some highly fluorinated aromatic poly(ether-amide)s. All fluoro-containing polymers were amorphous and had good solubility in polar organic solvents due to the presence of bulky phenyl groups possessing three directly attached fluorine atoms along the chains. The fluoro-containing poly(ether-amide)s synthesized from FPAPE had higher T_g values and thermal stability when compared to their non-fluorinated counterparts. Therefore, no noticeable drawback like insolubility, intractability, and thermal sensitivity that often limit utilities in various advanced technological applications was observed for the FPAPE-derived poly(ether-amide)s. The results obtained from this study clearly showed that the highly fluorinated diamine FPAPE as a structurally well-designed monomer can be considered as a good candidate to prepare the corresponding heat-resistant aromatic polymer. In addition, it can be concluded that good solubility, moderate T_g values and excellent thermal stability make these ether-hinged fluorinated polyamides promising as high-performance polymeric materials.

4. Experimental

4.1. Measurements

The limited viscosity number values of the polymers solutions were determined using an Ubbelohde viscometer. FT-IR spectra were recorded on a PERKIN ELMER RX I FT-IR spectrometer. The spectra of solids were obtained using KBr pellets. ^{1}H NMR spectra were recorded with a Bruker AVANCE 500 NMR operated at 500 MHz for proton using DMSO-d_6. Thermal gravimetric analysis (TGA) and DSC were performed on a METTLER TA 5000 system (Columbus, OH) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The DSC traces were obtained from heating, rapid cooling, and reheating of samples in a range of 50–400 °C. Ultraviolet maximum wavelength (λ_{max}) values were determined with a GBC model 916 ultraviolet–visible (UV–vis) instrument (GBC Scientific Equipment, Australia) in DMSO at a concentration of 0.1 mg mL^{-1}. WXRD patterns were performed at room temperatures with film specimens on a D8 ADVANCE BRUKER X-ray diffractometer with Ni-filtered Cu-K_α radiation (30 kV, 25 mA).

4.2. Materials

Phenylboronic acid (from MERCK, m.p. 216–219 °C) and 3,4,5-trifluorophenylboronic acid (from MERCK, m.p. 283–288 °C) were used as received. All diacid comonomers including TPA (from MERCK, m.p. 227–228 °C), IPA (from MERCK, m.p. 341–343 °C), 2,5-PDA (from MERCK, m.p. 256–258 °C), and 2,6-PDA (from MERCK, m.p. 248–250 °C) were used as received without further purification. 4,4′-ODA (from MERCK, m.p. 188–192 °C) was purified by recrystallization from ethanol before use. DINPE was synthesized from 4,4′-dinitrodiphenyl ether as reported previously [31]. Solvents used including NMP, DMAc, DMF, DMSO and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. THF and toluene were dried by sodium before use. Dichloromethane (DCM) was used without further purification.

4.3. Synthesis of 2,2′-diphenyl-4,4′-dinitrodiphenyl ether (PNPE)

DINPE (0.5120 g, 1 mmol), Pd(PPh_3)$_4$ (0.0346 g) and sodium carbonate (0.3921 g) were placed in a three-necked flask. A mixture of toluene/water (1:1) (7.5 mL) was added to the reaction vessel. Before the reaction took place, the solution was purged with a slow stream of nitrogen for 15 min and then phenylboronic acid (0.2682 g, 2.2 mmol) was introduced into the solution. The reaction mixture was stirred under reflux for 7 days. Upon cooling, the solution mixture formed two phases, a green solution phase and a brown oily solid phase. They were isolated from each other, and the brown oily phase was purified by ethyl acetate/*n*-hexane (1:2) to afford 0.3340 g PNPE as yellow solids precipitated at the bottom of the vessel (81% yield); m.p. 142–144 °C (Lit. 143–144) [33]. The fluorinated dinitro FPNPE was synthesized similarly.

4.4. Synthesis of 2,2′-diphenyl-4,4′-diaminodiphenyl ether (PAPE)

To a stirred suspension solution of PNPE (0.4124 g, 1 mmol) and 10% Pd/C (0.0060 g) in ethanol (2.5 mL), a solution of hydrazine monohydrate (1.1 mL) and ethanol (1.5 mL) was added dropwise at 70–80 °C over a period of 2 h. After complete addition, the mixture was heated at reflux temperature for another 24 h. The hot reaction solution was filtered to remove Pd/C, and the filtrate was then distilled using a rotary evaporator to remove the solvent. The crude product was purified by recrystallization from ethanol to give 0.2784 g of PAPE cream crystals (79% yield); m.p. 204–206 °C (Lit. 204–205) [33]. The fluorinated diamine FPAPE was synthesized similarly.

4.5. Preparation of the fluorinated poly(ether-amide)s

A typical example of the polyamidation reactions by phosphorylation method is as follows. A mixture of FPAPE (0.462 g, 1 mmol), IPA (0.166 g, 1 mmol), calcium chloride (0.350 g), TPP (0.8 mL), pyridine (1.2 mL) and NMP (4.0 mL) was refluxed for 3 h. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring to isolate polymer FPAPE/IPA. The precipitated polymer was separated by vacuum filtration and washed thoroughly with methanol (35 mL) and hot water (100 mL), and dried at 120 °C under vacuum for 24 h. The other fluorinated poly(ether-amide)s were synthesized in a similar manner. The yields of all polycondensation reactions were above 90%. The limited viscosity number values in DMAc at 30 °C as well as the ultraviolet λ_{max} values in DMSO were also measured and the data obtained along with subjects associated with IR, NMR, organo-solubility results, WXRD, TGA, and DSC analyses were reported and discussed in Section 2.

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