Journal of Fluorine Chemistry 131 (2010) 767–775

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and characterization of fluorinated polyimides derived from novel unsymmetrical diamines

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ARTICLE INFO

Article history:
Received 15 January 2010
Received in revised form 23 March 2010
Accepted 24 March 2010
Available online 31 March 2010

Keywords:
Fluorinated polyimide
Solubility
Unsymmetrical diamine

ABSTRACT

Two kinds of aromatic, unsymmetrical diamines with ether–ketone group, 3-amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone and 4-amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone, were successfully synthesized with two different synthetic routes. Then, they were polymerized with 4,4′-oxydiphthalic anhydride, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride, and 2,2′-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride to form a series of fluorinated polyimides via a conventional two-step thermal or chemical imidization method. The resulting polyimides were characterized by measuring their solubility, viscosity, mechanical properties, IR-FT, and thermal analysis. The results showed that the polyimides had inherent viscosities of 0.48–0.68 dl/g and were easily dissolved in bipolarity solvents and common, low-boiling point solvents. Meanwhile, the resulting strong and flexible polyimide films exhibited excellent thermal stability, e.g., decomposition temperatures (at 10% weight loss) are above 575 °C and glass-transition temperatures in the range of 218–242 °C. The polymer films also showed outstanding mechanical properties, such as tensile strengths of 86.5–132.8 MPa, elongations at break of 8–14%, and initial moduli of 1.32–1.97 GPa. These outstanding combined features ensure that the polymers are desirable candidate materials for advanced applications.

1. Introduction

Polyimides (PIs) represent a class of high performance polymers that combine high thermal stability, chemical resistance, excellent electrical and mechanical properties, and so they have been widely used in many applications such as aerospace, microelectronics, optoelectronics and composites [1,2]. For these applications it is desirable to use polyimides that are soluble in spin coating and casting processes. However, most of wholly aromatic polyimides have high melting or softening temperatures (Ts's), and are insoluble in most organic solvents because of the rigidity of the backbone and strong interchain interactions. Those properties make them generally intractable or difficult to process. Thus, many studies have focused on designing such chemical structures of the rigid aromatic backbone so as to obtain aromatic polymers that are processable by conventional techniques, while maintaining desirable properties. For example, bulky lateral substituents [3–5], flexible linkages [6–8], noncoplanar biphenyl moieties [9,10] as well as unsymmetrical structures [11–13] have been used to enhance the solubility of aromatic polymers make them processability.

Most of the approaches for soluble polyimides are aimed at reduction of several types of chain–chain interaction, such as chain packing (e.g., crystallinity), charge transfer and electronic polarization interactions. As well known, introduction of geometrically or molecularly unsymmetrical diamine components into the polyimide main chain has led to new polyimides with improved solubility, melt processability and other desirable properties [14–19]; additionally, fluorination is also known for increasing intermolecule space while enhancing the solubility, optical transparency and lower moisture absorption of polyimides [6,20,21].

In this work, we synthesize two kinds of new aromatic unsymmetrical diamine monomers, 3-amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone (*m*-AAFP) and 4-amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone (*p*-AAFP), which have been designed as potentially convenient condensation monomers for polyimides, capable of imparting solubility and good thermal properties at the same time. Then, a series of all-aromatic, organosoluble polyimides bearing unsymmetrical ether structure were synthesized from the two diamines with three different kinds of commercial dianhydrides. The characterizations of the two diamines and related intermediates, as well as the

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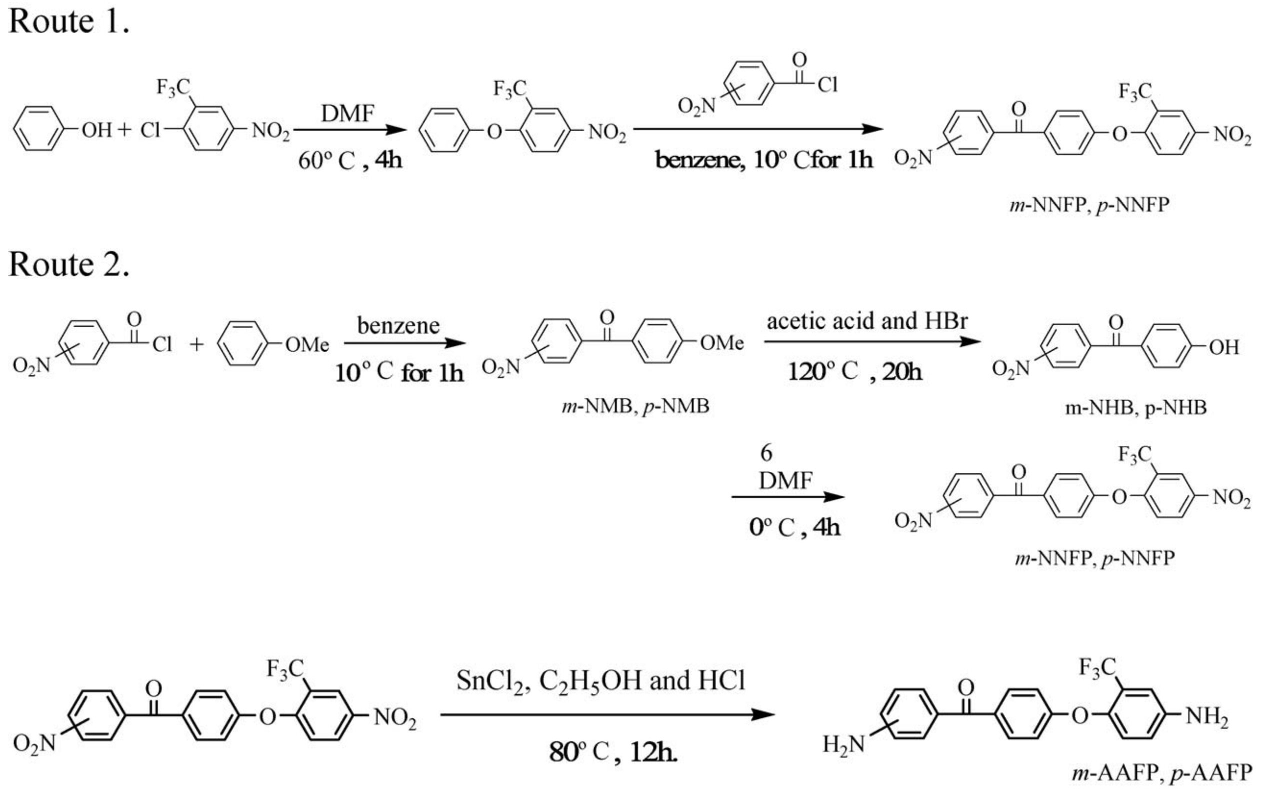
doi:10.1016/j.jfluchem.2010.03.014



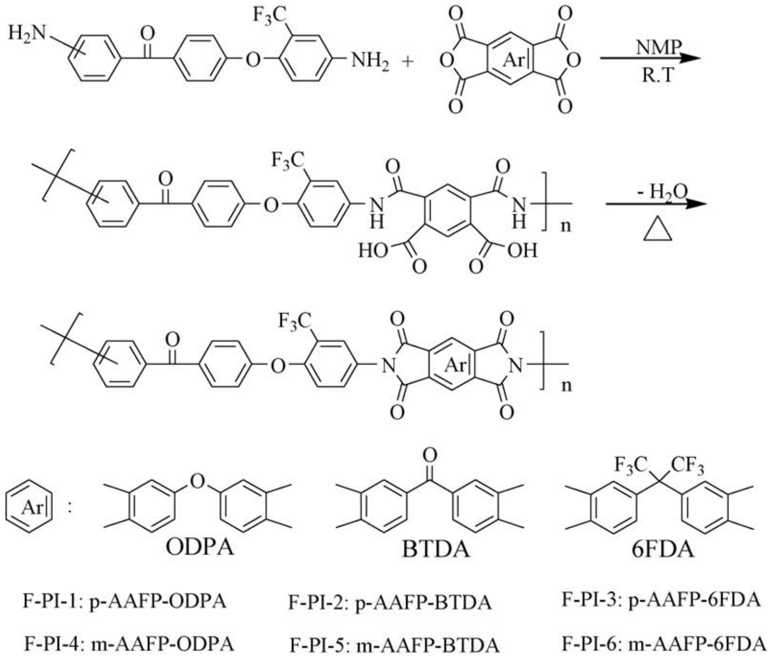
Scheme 1. Synthesis of diamine *m*-AAFP and *p*-AAFP.

resulting polyimides based on the two diamines were carried out by means of FT-IR, DSC, TGA and elemental analysis methods.

2. Results and discussion

2.1. Monomer synthesis

The diamines with the ether–ketone group, *m*-AAFP and *p*-AAFP, were prepared according to a well-developed method (Scheme 1). We designed two different routes to synthesize NNFP. *m*-NNFP and *p*-NNFP were successfully synthesized by the Friedel-Crafts reaction (route 1). In the route 2, the intermediate dinitro compound *m*-NNFP and *p*-NNFP were synthesized by a nucleophilic chloro-displacement reaction of 2-chloro-5-nitrotrifluoromethylbenzene with *m*-NHB or *p*-NHB in the presence of potassium carbonate in N,N-dimethylacetamide (DMAc). Both the para nitro-group and the ortho trifluoromethyl group activated the chlorine atom for displacement; therefore, the chlorine-displacement reaction of



Scheme 2. Synthesis of the polyimides.

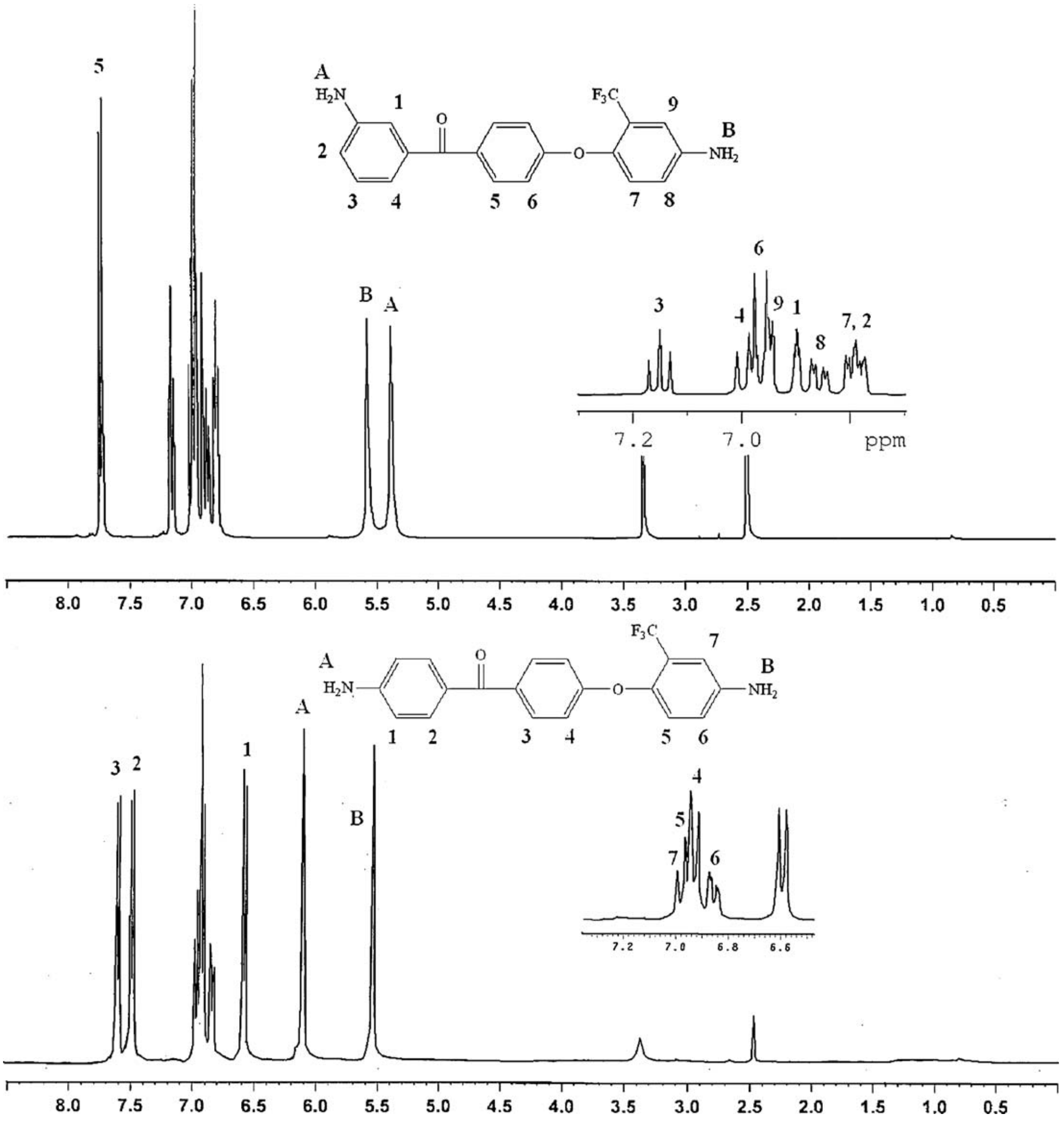


Fig. 1. ^{1}H NMR spectra of *m*-AAFP and *p*-AAFP.

2-chloro-5-nitrobenzotrifluoride by the phenoxide anion was readily carried out even at 80 °C. Diamine *m*-AAFP or *p*-AAFP was readily obtained in high yields by the reduction of NNFP with $SnCl_2$/HCl in refluxing ethanol.

NMR and MS analysis were used to confirm the structures of the intermediates and the diamine monomers, *m*-AAFP and *p*-AAFP. Fig. 1 shows ^{1}H NMR spectrum, the absorption signals of aromatic protons of *m*-AAFP or *p*-AAFP appeared in the range of 7.3–8.6 ppm. In the ^{13}C NMR spectrum (Fig. 2) the carbon 13 atoms in *m*-AAFP and *p*-AAFP showed 18 and 16 signals, respectively, which resonated in the regions of 110–195 ppm. For the 3F-diamine compound AAFP, the large quartet centered at about 123 ppm was due to the CF_3 carbon. The one-bond C–F coupling constant in this case was 273 Hz. The 3F-attached carbon also exhibited a clear quartet centered at about 120 ppm with a smaller coupling. All the spectroscopic data obtained agreed with the expected structures.

2.2. Polymer synthesis

New polyimides were prepared from *m*-AAFP or *p*-AAFP and commercially available aromatic dianhydrides, such as ODPA, BTDA and 6FDA, via a conventional two-step procedure as shown in Scheme 2. The polymerization was carried out by reacting stoichiometric amounts of diamine monomer AAFP with aromatic dianhydrides at a concentration of 15% solids in NMP. The ring-opening polyaddition at room temperature for 24 h yielded poly(amic acid)s (PAA), followed by sequential heating to 300 °C or mixture of Ac_2O/Py to obtain the corresponding polymers. Transformation from poly(amic acid) to polyimide was possible via the thermal or chemical cyclodehydration; the former were easy to handle and cast into thin films, and the latter was suited to prepare soluble polyimides. In general, it is well known that CF_3 groups can decrease the nucleophilicity of aromatic amines, thus, reaction rate is lower than corresponding nonfluorinated monomer. In our work, we rised temperature to 80 °C for another 4 h to compensate for the deficiency. The chemical structures of polyimides were characterized by FT-IR, and element analysis.

All of the polyimides could form tough and transparent films, and showed characteristic imide absorption bands at 1782–1776 cm^{-1} attributed to the asymmetrical carbonyl stretching vibrations, and 1725–1718 cm^{-1} attributed to the symmetrical carbonyl stretching vibrations. The absorption at 1383–1374 cm^{-1} was assigned to C–N stretching, and the C–O multiple stretching absorptions were also detected in the range of 1300–1100 cm^{-1}. There was no existence of the characteristic absorption bands of

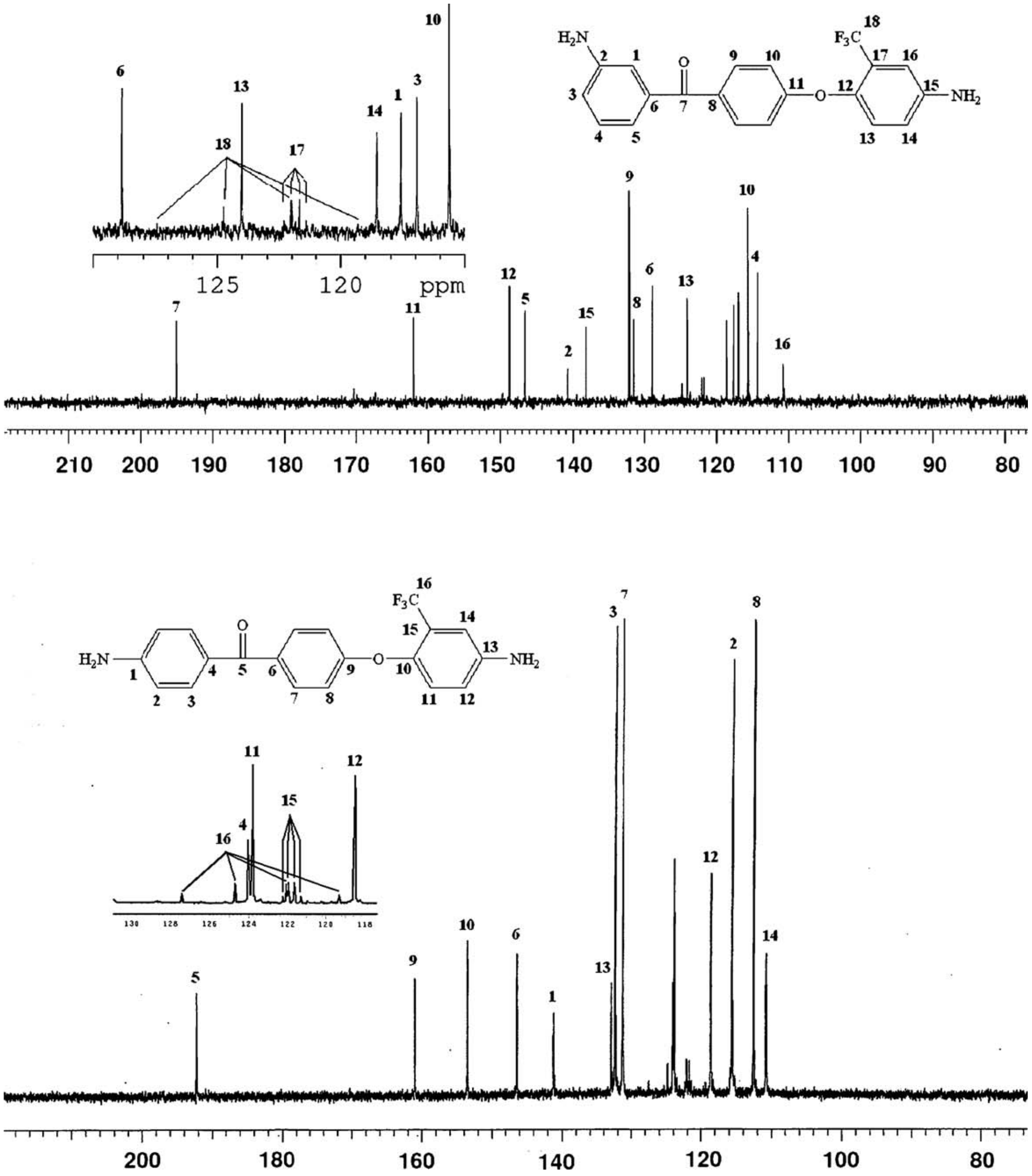


Fig. 2. ^{13}C NMR spectra of *m*-AAFP and *p*-AAFP.

Table 1
Physical properties and elemental analysis of the polyimides.

Polyimide	Yield (%)	Inherent viscosity(dl/g)	Composition of repeating unit	Elemental analysis (%)			
					C	H	N
F-PI-1	97	0.52	$C_{36}H_{17}F_3N_2O_7$	Calcd.	66.88	2.65	4.33
				Found	66.75	2.73	4.35
F-PI-2	96	0.58	$C_{37}H_{17}F_3N_2O_7$	Calcd.	67.48	2.60	4.25
				Found	67.53	2.64	4.41
F-PI-3	98	0.68	$C_{39}H_{17}F_9N_2O_6$	Calcd.	60.01	2.20	3.59
				Found	59.81	2.24	3.57
F-PI-4	98	0.48	$C_{36}H_{17}F_3N_2O_7$	Calcd.	66.88	2.65	4.33
				Found	66.94	2.59	4.29
F-PI-5	97	0.62	$C_{37}H_{17}F_3N_2O_7$	Calcd.	67.48	2.60	4.25
				Found	67.57	2.64	4.19
F-PI-6	97	0.51	$C_{39}H_{17}F_9N_2O_6$	Calcd.	60.01	2.20	3.59
				Found	60.12	2.17	3.50

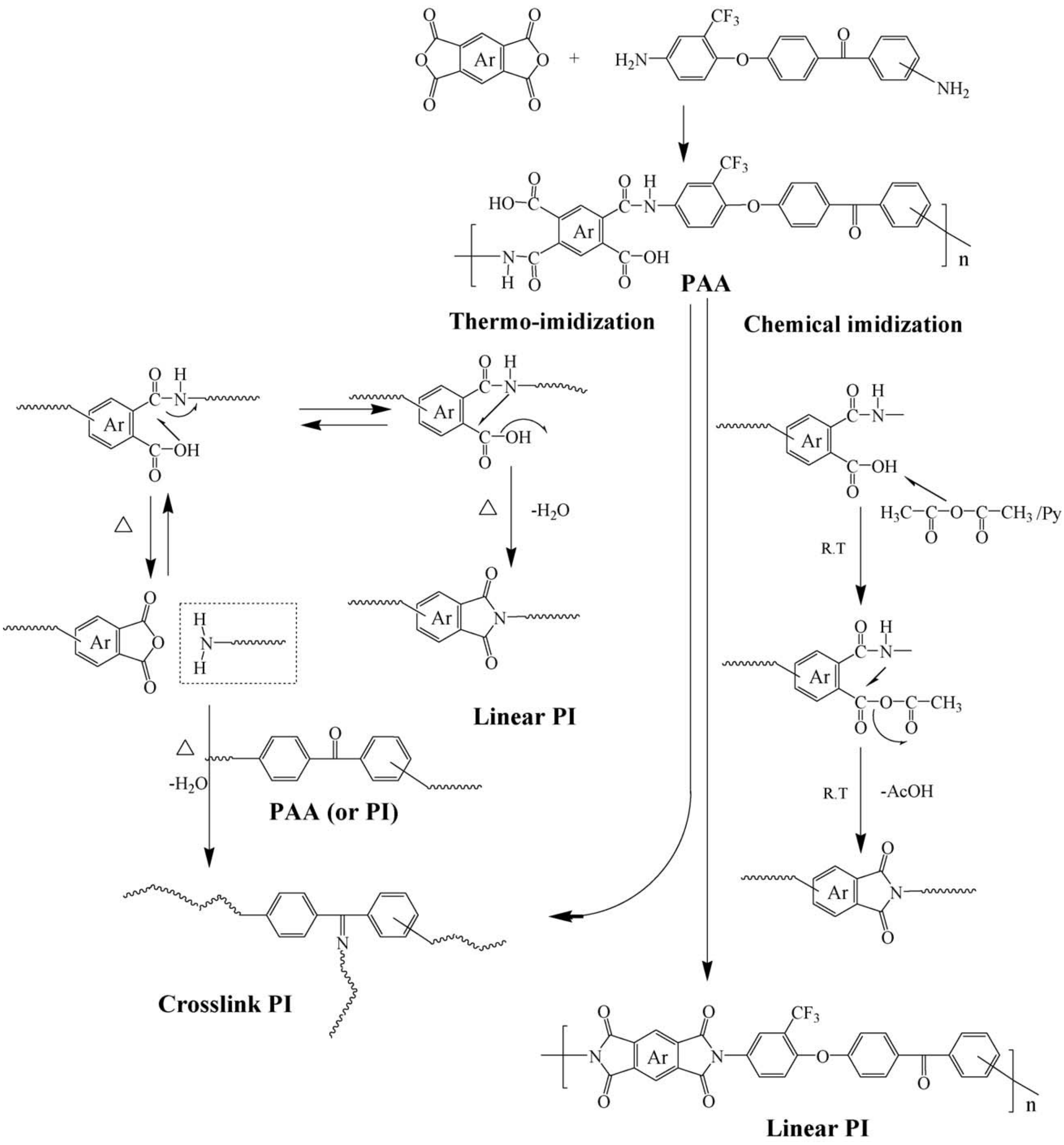


Fig. 3. Mechanism of thermal and chemical imidization.

Table 2
Solubility of the polyimides.

Solvents	Polyimides[a]					
	F-PI-1	F-PI-2	F-PI-3	F-PI-4	F-PI-5	F-PI-6
NMP	++	++	++	++	++	++
DMAc	++	++	++	++	+	++
DMF	++	++	++	++	++	++
DMSO	++	+	++	++	++	++
THF	+	+	+	+	+–	+
$CHCl_3$	+–	+–	+–	+	+	+–
Toluene	+	+–	+	+	+	++

[a] Measured by chemical cyclization polyimide derived from the corresponding poly(amic acid)s. Qualitative solubility was determined with as 10 mg of polymer in 1 ml of solvent. ++, soluble at room temperature; +, soluble on heating; +–, partial soluble on heating; –, insoluble on heating.

the amide group near 3200–3363 (N–H stretching) and 1650–1674 (C=O stretching) cm^{-1}. In addition to the IR spectra, the elemental analysis values of the polymers generally agreed well with the calculated values for the proposed structures. Table 1 shows the element analysis data for the new polyimides, which are in good agreement with the calculated values for the proposed chemical structures.

As shown in Fig. 3 the difference of PI between thermal and chemical imidization can be explained by the imidization reaction mechanism. PAA was synthesized by dianhydride and diamine via a polyaddition reaction in the amidetype polar solvent at room temperature. This kind of PAA was an unstable polymer; the hydroxyl group of the carboxylic acid group and amino group of amide in PAA caused a nucleophilic substitution reaction to take place with the carbonyl group of PAA at room temperature or in the heating process. The former was a reversible reaction, which could reduce to form anhydride and amine, and the latter was an irreversible reaction, which would dehydrate to form imide. At room or low temperature, the equilibrium of the former becomes PAA solution with little chance to occur later. Although PAA solution was heated, the reversible and irreversible reactions increased with temperature, and more anhydride ends and amine ends in PAA were produced. These ends of anhydride and amine still could regenerate to amic acid. However, the ketone group was an electrophilic group, which condensed to the amine group to form an imine group; therefore, PAA with the ketone group is connected with imine linkage to form nonlinear or cross-linking PI during thermal imidization. The cross-linking reaction increased with a higher concentration of PAA after most solvents were volatilized in the imidization. If PAA is tested with Ac_2O/Py via chemical imidization, causing the Ac_2O to react with amic acid to form amide–anhydride, then the imide is formed by a nucleophilic reaction of the amide–anhydride group with separating acetic acid. According to the preceding description, this type of cross-linking was due to the ketone group of PAA being connected with the imine group by thermal imidization.

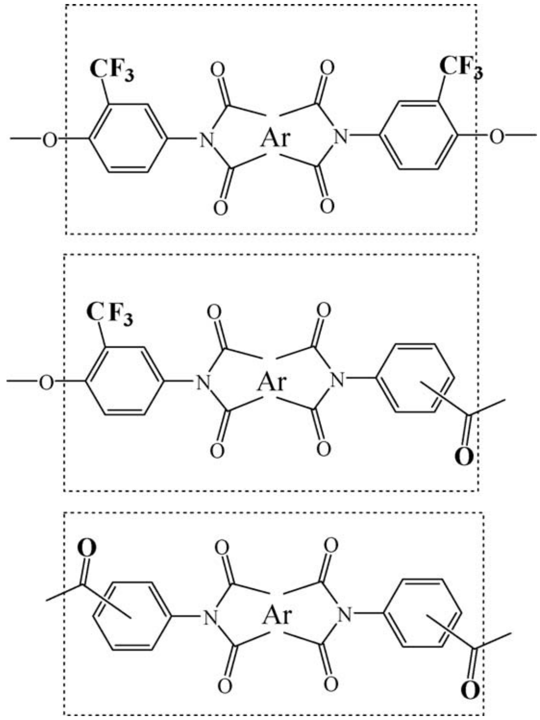


Fig. 4. Three different triad structures.

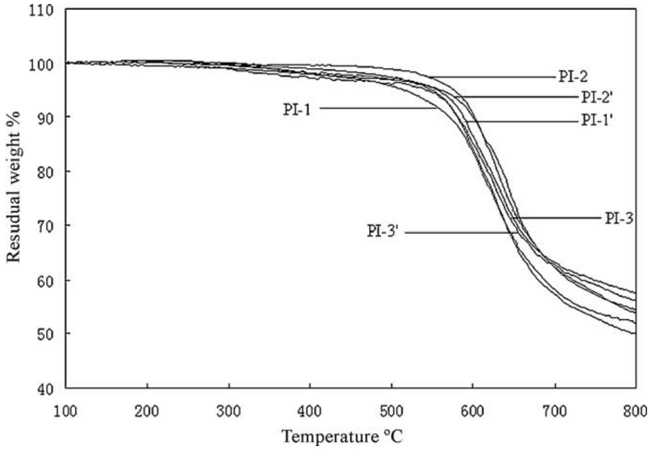


Fig. 5. TGA curve of the polyimides.

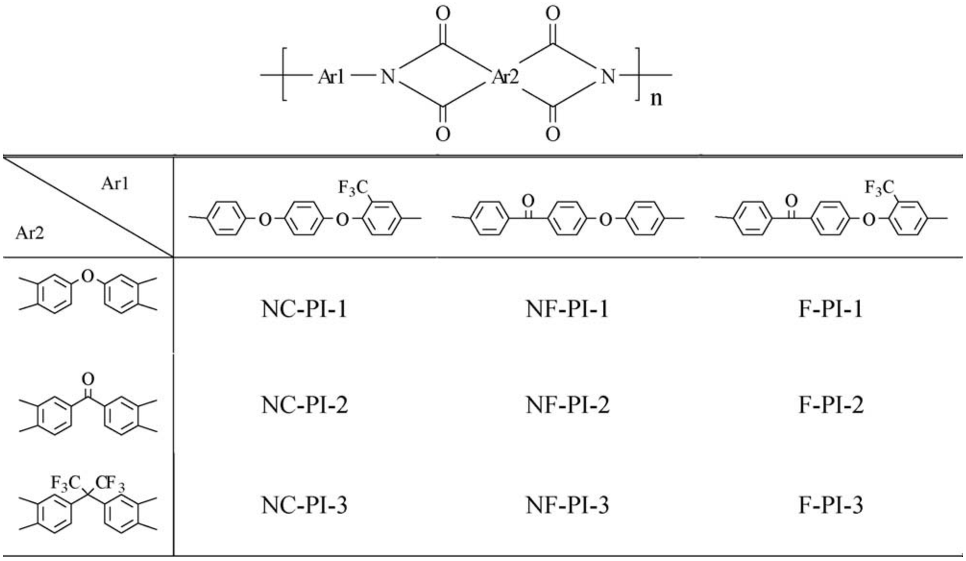
2.3. Solubility

The solubilities of the resulting polyimides by chemical imidization were investigated for the samples in different organic solvents. The solubility behavior of these polymers in different solvents is presented in Table 2. These polymers from *m*-AAFP and *p*-AAFP exhibited good solubility behavior in polar solvents such as DMSO, DMF, DMAc, NMP, THF and toluene. The good solubility might be attributed to the more bent chain structure of the polyimides. The bulky CF_3 groups could loosen the packing of the polyimide backbone chains, resulting in the increase of free volume in the polymers. On the other hand, the unsymmetrical structure could result in the random head-to-tail, head-to-head and tail-to-tail triad orientation in consecutive repeating units along the polymer main chain (Fig. 4). These three structures are naturally different in rigidity and degree of bending, but because they all should be present mixed up along polymer chains, they lead to backbone randomization. This backbone randomization should make a contribution to the high solubility of polymers. In summary, the bulky CF_3 groups and the unsymmetrical structure could increase the disorder in the chains and hinder dense chain stacking, thus reducing the chain–chain interactions to enhance solubility. It should be noted that good solubility in low-boiling-point solvents is critical for preparing polyimide films or coatings at a relatively low processing temperature, which is desirable for advanced microelectronics manufacturing applications.

Table 3
DSC and TGA of the non-cross-linked polyimides, nonfluorinated polyimides and fluorinated polyimides.

Polyimide[a]	Thermal properties				
	T_g[b] (°C)	T_d[c] (°C)	T_5[c] (°C)	T_{10}[c] (°C)	R_w[c] (%)
F-PI-1	231	577	567	590	50
F-PI-2	238	590	584	603	54
F-PI-3	218	567	568	589	58
F-PI-4	224	552	564	575	52
F-PI-5	242	586	575	600	54
F-PI-6	222	560	572	582	56
NC-PI-1	232	546	545	570	17
NC-PI-2	237	540	538	561	31
NC-PI-3	260	525	523	535	5
NF-PI-1	248	588	582	608	56
NF-PI-2	251	575	573	618	48
NF-PI-3	242	564	558	582	50

[a] Measured samples were obtained by thermal imidization method.
[b] T_g was measured by DSC at a heating rate of 10 °C/min in nitrogen.
[c] T_d, decomposition-starting temperature; T_5 and T_{10}, temperature at a 5 or 10% weight loss. R_w, residual weight (%) at 800 °C in nitrogen.



Scheme 3. Synthesis of the non-cross-linked polyimides, nonfluorinated polyimides and fluorinated polyimides.

2.4. Thermal properties and mechanical properties

DSC and TGA methods were applied to evaluate the thermal properties of the polyimides; the TGA curves of the polyimides are shown in Fig. 5, and thermal analysis data from the TGA and DSC curves of the polyimides are summarized in Table 3. DSC revealed that rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so that T_g of the polymer could be easily read in the second heating trace of DSC. The T_g values of PI-1 to PI-6 were in the range of 218–242 °C. As we expected, the T_g values of these polyimides depend on the structure of the different component and decreased with increasing flexibility of the polyimide backbones according to the applied structure of the monomer. For the thermal stability of the polyimides, Table 3 gives the temperatures of the initial decomposition and 5 and 10% gravimetric losses in nitrogen. The temperatures of the initial decomposition were determined to be in the range of 552–590 °C for all polyimides tested. The temperatures of 10 and 5% gravimetric losses of the polyimides reached 564–575 and 575–603 °C in nitrogen. Also, the char yields at 800 °C for all the polymers were in the range of 50–58 wt%. As shown in Table 3 and Scheme 3, the thermal stabilization of non-cross-linked polyimides (NC-PI-1–NC-PI-3) is worse than cross-linked polyimides (F-PI-1–F-PI-3 and NF-PI-1–NF-PI-3). But the thermal stabilization of nonfluorinated polyimides (NF-PI-1–NF-PI-3) and fluorinated polyimides (F-PI-1–F-PI-3) did not show significant difference, generally, the thermal stabilization of fluorinated polyimides is better than nonfluorinated polyimides because of the existing of CF_3, we think it may attribute to two reasons: (1) it is well known that CF_3 groups can decrease the nucleophilicity of aromatic amines due to their strong electronegativity, thus, the nonfluorinated monomer has better nucleophilicity than fluorinated monomer, the molecular weight of nonfluorinated polyimides are higher than fluorinated polyimides and (2) the cross-linking reaction play an important role in thermal stabilization of polymer. As shown in Table 4, all the polyimides can be processed into clear, flexible and tough films, the polyimide films had tensile strengths of 86.5–132.8 MPa, elongations at break of 8–14% and tensile modulus of 1.32–1.97 GPa, which indicated strong and tough materials.

Table 4
Mechanical properties and water absorption of the polyimides.

Polymer	Tensile strength (MPa)	Elongation (%)	Modulus (GPa)	Water absorption (%)
F-PI-1	126.6	12	1.46	0.44
F-PI-2	132.8	8	1.78	0.44
F-PI-3	117.5	10	1.32	0.67
F-PI-4	116.5	13	1.37	0.52
F-PI-5	86.5	11	1.97	0.63
F-PI-6	104.2	14	1.74	0.41

2.5. Moisture uptakes

Polyimide materials usually show higher moisture uptakes than the hydrocarbon polymers because of the presence of imide groups. The moisture absorption of aromatic polyimides can be up to 3.0–3.5% depending on the chemical structures of polymer and the relative humidity of the surrounding environments, which have a significant influence on the dielectric properties of polymers. For instance, polyimides derived from PMDA or 6FDA with ODA show moisture uptakes of 2.3–2.7 wt% and 1.3–1.64 wt%, respectively. Also, some fluorinated polyimides were reported to absorb moisture of <1%. However, there was not a quantitative linear relationship between the fluorine content and moisture uptake for polyimide materials. Table 4 compares the moisture uptakes of the polyimides derived from diamine *m*-AAFP or *p*-AAFP with three dianhydrides. The moisture uptakes of polyimides were measured at 0.41–0.67%. The moisture absorption of polyimides might be related to several factors including the chemical structures, the introduction of fluorinated groups and of other functional groups, the geometrical packing of the polymer chains as well as film-processing parameters, and so forth in which the chemical structure and the presence of functional groups in polymer might be the major concern factors. The trifluoromethyl groups possess amphiprotoc features, which inhibit the absorption of moisture molecules on the surface of the fluorinated polymers. On the other hand, the bulky trifluoromethyl groups could loosen the packing of the polyimide backbone chains, resulting in the increase of free volume in the polymers that ensure the polymer to entrap some of the water molecules. These two opposing effects of the trifluoromethyl groups are offsetted, to some extent, resulting in fluorinated polyimides with lower moisture absorption than the corresponding polyimides derived from unfluorinated diamines. Fig. 5 shows the moisture uptakes of non-cross-linked polyimides

Table 5
The water absorption comparison of non-cross-linked polyimides, nonfluorinated polyimides and fluorinated polyimides.

Polyimides	Non-cross-linked polyimides			Nonfluorinated polyimides			Fluorinated polyimides		
	NC-PI-1	NC-PI-2	NC-PI-3	NF-PI-1	NF-PI-2	NF-PI-3	F-PI-1	F-PI-2	F-PI-3
Water absorption (%)	0.32	0.63	0.41	1.08	1.32	0.86	0.44	0.44	0.67

(NC-PI-1–NC-PI-3), nonfluorinated polyimides (NF-PI-1–NF-PI-3) and fluorinated polyimides (F-PI-1–F-PI-3). The fluorinated polyimides and non-cross-linked polyimides shown lower moisture uptakes than of nonfluorinated polyimides, it indicates that the CF_3 group plays a main role in moisture uptakes (Table 5).

3. Conclusions

Two kinds of aromatic unsymmetrical diamines with CF_3 group, 3-amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone and 4-amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone, were successfully synthesized by two different synthetical routes and polymerized with various aromatic tetracarboxylic acid dianhydrides. The resulting polyimides exhibit good solubility, excellent thermal stability and balanced mechanical properties. The introduction of unsymmetrical structures and trifluoromethyl groups in polyimides results in dramatic changes in their properties, especially in the improvement of solubility and lowered moisture uptakes.

4. Experimental

4.1. Materials

Commercially available 2-chloro-5-nitrotrifluoromethylbenzene, m-nitrobenzoyl chloride, p-nitrobenzoyl chloride (Shanghai Chemical Reagents Corp., China), phenol, phenyl methyl ether (Fuchen Chemical Reagents Corp., Tianjin, China). 4,4′-Oxydiphthalic anhydride (ODPA, Shanghai Nanxiang Chemical Co., China), 3-nitro-benzoyl chloride, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, Beijing Chemical Reagents Corp., China) and 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA, Aldrich) were recrystallized from acetic anhydride before use. N,N-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were purified by distillation under reduce pressure over calcium hydride and stored over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

4.2. Measurements

The inherent viscosities of the resulting polyimides were measured with an Ubbelohde viscometer at 30 °C. FT-IR spectra (KBr) were recorded on a Nicolet Nexus 670 FT-IR spectrometer. ^1H NMR and ^{13}C NMR spectra were measured on a JEOLEX-300 spectrometer with tetramethylsilane as the internal reference. Elemental analyses were determined with a PerkinElmer model 2400 CHN analyzer. DSC testing was performed on a PerkinElmer DSC 7, differential scanning calorimeter at a scanning rate of 10 °C/min in flowing nitrogen (30 cm^3/min), and the T_g values were read at the DSC curves at the same time. TGA was conducted with a TA Instruments TGA 2050, and the experiments were carried out with approximately 10 mg samples in flowing air (flow rate = 100 cm^3/min) at a heating rate of 20 °C/min. The mechanical properties were measured on an Instron 1122 tensile apparatus with 100 mm × 5 mm specimens in accordance with GB 1040-79 at a drawing rate of 100 mm/min.

4.3. Monomer synthesis

4.3.1. (4-Nitro-2-trifluoromethylphenoxy)-phenoxy ether (NFPP)

2-Chloro-5-nitrotrifluoromethylbenzene (9.02 g, 0.04 mol) and phenol (3.76 g, 0.04 mol) were first dissolved in 40 ml of DMF in a 100-ml flask with stirring. After the mixture was completely dissolved, potassium carbonate (5.56 g, 0.04 mol) was added to it in one portion. After 30 min of stirring at room temperature, the mixture was heated at 60 °C for 4 h. The obtained mixture was poured into 300 ml of distilled water. The precipitated solid was collected by filtration and dried in vacuo at 60 °C for 12 h. The crude product was purified by column chromatography over silica gel (4:1 petroleum ether/ethyl acetate), 10.52 g was obtained (92%). ^1H NMR ($CDCl_3$, ppm): 8.60 (s, 1H), 8.32–8.29 (dd, 1H), 7.50–7.46 (t, 2H), 7.34–7.31 (t, 1H), 7.14–7.12 (d, 2H), 6.95–6.93 (d, 2H). Low MS (*m*/*e*) 282.2, Calcd. 283 for $C_{13}H_8F_3NO_3$.

4.3.2. 3-Nitro-4′-methoxy-benzophenone (m-NMB) and 4-nitro-4′-methoxy-benzophenone (p-NMB)

18.5 g (0.1 mol) of m-nitrobenzoyl chloride was gradually added to a mixture of 60 ml of benzene, 10.8 g (0.1 mol) of phenyl methyl ether and 16.0 g (0.12 mol) of anhydrous aluminum chloride at 10–12 °C with continuous stirring. After addition, the mixture was slowly heated to 40 °C and stirred for 2 h. Finally, the resulting reaction mixture was allowed to cool to room temperature and poured into 500 ml of a water solution of hydrochloric acid (5%) to precipitate out white solids. The solids was collected by filtrating, and washed with hot methanol to give 23.0 (92%) g of white powder. ^1H NMR ($CDCl_3$, ppm): 8.63 (s, 1H), 8.47–8.44 (dd, 1H), 8.16–8.14 (d, 1H), 7.82–7.80 (d, 2H), 7.74–7.70 (t, 1H), 7.57–7.55 (d, 2H). Low MS (*m*/*e*) 257.07, Calcd. 257 for $C_{14}H_{11}NO_4$.

p-NMB was prepared from p-nitrobenzoyl chloride in CH_2Cl_2. ^1H NMR ($CDCl_3$, ppm): 8.35–8.32 (d, 2H), 7.90–7.87 (d, 2H), 7.83–7.80 (d, 2H), 7.01–6.98 (d, 2H), 3.91 (t, 3H). Low MS (*m*/*e*) 257.07, Calcd. 257 for $C_{14}H_{11}NO_4$.

4.3.3. 3-Nitro-4′-hydroxy-benzophenone (m-NHB) and 4-nitro-4′-hydroxy-benzophenone (p-NHB)

A 500 ml one-necked flask equipped with stir bar and reflux condenser was charged with 12.8 g (0.05 mol) of *m*-NMP, 160 ml of glacial acetic acid and 60 ml of HBr (48%). This solution was refluxed for 20 h till only one spot in TLC and allowed to cool to room temperature. The orange solution was extracted with 200 ml of CH_2Cl, the organic layer was washed with 150 ml of water and dried over $MgSO_4$. The solvent was removed, to give 10.1 (93%) g of white powder of compound 3-nitro-4′-hydroxy-benzophenone (*m*-NHB). ^1H NMR ($CDCl_3$, ppm): 8.58 (s, 1H), 8.44–8.42 (dd, 1H), 8.11–8.09 (d, 1H), 7.83–7.81 (d, 2H), 7.72–7.68 (t, 1H), 7.01–6.98 (d, 2H). Low MS (*m*/*e*) 243.05, Calcd. 243 for $C_{13}H_9NO_4$.

p-NHB: ^1H NMR ($CDCl_3$, ppm): 8.35–8.32 (d, 2H), 7.90–7.87 (d, 2H), 7.79–7.76 (d, 2H), 6.95–6.92 (d, 2H). Low MS (*m*/*e*) 243.05, Calcd. 243 for $C_{13}H_9NO_4$.

4.3.4. 3-Nitro-4′-(4-nitro-2-trifluoromethylphenoxy)-benzophenone (m-NNFP) and 4-nitro-4′-(4-nitro-2-trifluoromethylphenoxy)-benzophenone (p-NNFP)

2-Chloro-5-nitrotrifluoromethylbenzene (9.02 g, 0.04 mol) and *m*-NHB (7.72 g, 0.04 mol) were first dissolved in 100 ml of DMF in a

250-ml flask with stirring. After the mixture was completely dissolved, potassium carbonate (5.56 g, 0.04 mol) was added to it in one portion. After 30 min of stirring at room temperature, the mixture was heated at 60 °C for 4 h. The obtained mixture was poured into 300 ml of distilled water. The precipitated solid was collected by filtration and dried in vacuum at 60 °C for 12 h. The crude product was purified by column chromatography over silica gel (4:1 petroleum ether/ethyl acetate), 15.52 g was obtained (90%).

9.7 g (0.05 mol) of m-nitrobenzoyl chloride was gradually added to a mixture of 60 ml of benzene, 14.2 g (0.05 mol) of NFPP and 8.0 g (0.06 mol) of anhydrous aluminum chloride at 10–12 °C with continuous stirring. After addition, the mixture was slowly heated to 40 °C and stirred for 2 h. Finally, the resulting reaction mixture was allowed to cool to room temperature and poured into 500 ml of a water solution of hydrochloric acid (5%) to precipitate out white solids. The solids were collected by filtrating, and washed with hot methanol to give 15.32 g (71%) of yellow powder. ^{1}H NMR (DMSO-d6, ppm): 8.63 (s, 1H), 8.62 (s, 1H), 8.49–8.47 (dd, 1H), 8.43–8.40 (d, 1H), 8.17–8.15 (d, 1H), 7.94–7.92 (d, 2H), 7.77–7.73 (t, 1H), 7.26–7.24 (d, 2H), 7.15–7.13 (d, 1H). Low MS (*m*/*e*) 432.31, Calcd. 432 for $C_{20}H_{11}F_3N_2O_6$.

p-NNFP was prepared by the similar method. ^{1}H NMR (DMSO-d6, ppm): 8.63 (s, 1H), 8.62 (s, 1H), 8.49–8.47 (dd, 1H), 8.43–8.40 (d, 1H), 8.17–8.15 (d, 1H), 7.94–7.92 (d, 2H), 7.77–7.73 (t, 1H), 7.26–7.24 (d, 2H), 7.15–7.13 (d, 1H). Low MS (*m*/*e*) 432.31, Calcd. 432 for $C_{20}H_{11}F_3N_2O_6$.

4.3.5. 3-Amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone (m-AAFP) and 4-amino-4′-(4-amino-2-trifluoromethylphenoxy)-benzophenone (p-AAFP)

A mixture consisting of 21.6 g (0.05 mol) of *m*-NNFP, 58.0 g (0.3 mol) of anhydrous $SnCl_2$ and 500 ml of 95% C_2H_5OH was put into a reaction flask, with stirred while 20 ml of concentrated HCl was added slowly. After addition of hydrochloric acid was finished, the mixture was refluxed for 12 h. Excess ethanol was evaporated, and the remaining solution was poured into 400 ml of distiller water, the mixing solution was basified with 15% NaOH solution to form a precipitate, and the precipitate was filtrated off, washing with water and methanol, recrystallized from toluene to get a yellow product 16.4 g (88%). ^{1}H NMR (DMSO-d6, ppm): 7.74–7.72 (d, 2H), 7.18–7.14 (t, 1H), 7.02–7.00 (d, 1H), 6.98–6.96 (d, 2H), 6.95 (s, 1H), 6.91 (s, 1H), 6.88–6.86 (dd, 1H), 6.82–6.78 (m, 2H). ^{13}C NMR (DMSO-d6, ppm): 195.0, 162.0, 148.8, 146.6, 140.7, 138.1, 132.0, 131.4, 128.8, 124.0, 118.5, 117.6, 116.9, 115.6, 114.3, 110.,7. Low MS (*m*/*e*) 372.34, Calcd. 372 for $C_{20}H_{15}F_3N_2O_2$. FT-IR(KBr): 3419, 3333 (NH stretch), 1271, 1238, 1159, 1122 cm^{-1} (C–O and C–F stretch).

p-AAFP was prepared by the similar method. ^{1}H NMR (DMSO-d6, ppm): 7.62–7.59 (d, 2H), 7.51–7.48 (d, 2H), 6.99–6.83 (m, 6H), 6.83–6.80 (d, 2H). ^{13}C NMR (DMSO-d6, ppm): 192.3, 161.1, 153.6, 146.5, 141.1, 132.9, 132.5, 131.4, 124.0, 123.9, 118.6, 115.6, 122.6, 110.7. Low MS (*m*/*e*) 372.34, Calcd. 372 for $C_{20}H_{15}F_3N_2O_2$. FT-IR(KBr): 3448, 3359 (NH stretch), 1263, 1232, 1168, 1127 cm^{-1} (C–O and C–F stretch).

4.4. Polymer synthesis

The polyimides were synthesized from various dianhydrides and diamine AAFP via a two-step method. The synthesis of polyimide PI-1 (ODPA–*m*-AAFP) is used as an example to illustrate the general synthetic route used to produce the polyimides. To a solution of 0.3722 g (1.0 mmol) of diamine AAFP in 5.0 ml of CaH_2-dried NMP, 0.3099 g (1.0 mmol) of ODPA was added in one portion. The solution was stirred at room temperature under N_2 for 24 h to yield a viscous poly(amic acid) (PAA) solution. PAA was converted into a polyimide with thermal or chemical imidization methods. For the thermal imidization method, the PAA solution was cast onto a clean glass plate and heated (80 °C/3 h, 120 °C/30 min, 150 °C/30 min, 180 °C/30 min, 210 °C/30 min, 250 °C/30 min, 300 °C/1 h) to produce a fully imidized polyimide film. Chemical imidization was carried out by the addition of an equimolar mixture of acetic anhydride and pyridine to the aforementioned PAA solution (with mechanical stirring) at the ambient temperature for 30 min and via heating at 80 °C for 4 h. The polyimide solution was poured into methanol. The precipitate was collected by filtration, washed thoroughly with methanol, and dried at 80 °C in vacuo to give the following.

PI-2 (BTDA and *m*-AAFP), PI-3 (6FDA and *m*-AAFP), and PI-1′ (ODPA and *p*-AAFP), PI-2′ (BTDA and *p*-AAFP), PI-3′ (BTDA and *p*-AAFP) were synthesized by a similar method.

Acknowledgement

The authors acknowledge the financial support of the Research Foundation of the State Key Laboratory of Applied Organic Chemistry.

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