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Ming Kang¹, and Yuhong Huang²

Abstract

To overcome insoluble and low transmittance of the traditional polyimides (PIs), two kinds of novel fluorosilicone PIs were prepared. First, 1,4-bis (4-amino-2-trifluoromethylphenoxy) benzene, compound **3a**, and 4,4'-bis(4-amino-2-trifluoromethylphenoxy)diphenyl ether, compound (**3b**), with 2-chloro-5-nitrobenzotrifluoride and *p*-hydroquinone or 4,4'-dihydroxydiphenyl ether were prepared. Second, hydrosilylation of nadic anhydride (NA) with 1,1,3,3-tetramethyldisiloxane (TMDS) yielded 5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl) bisnorbornane-2,3-dicarboxylic anhydride, compound (**4**). Initially, the conditions of the synthesis reaction such as reaction temperature, catalyst dosage, molar ratio of TMDS/NA, and reaction time on yield of compound **4** by the single factor approach were studied. The optimal reaction conditions were reaction temperature: 90°C, catalyst dosage: 1 ml (Pt% = 0.37%), molar ratio of TMDS/NA: 1/1.8, and reaction time: 3 h. The yield was 74.6%. Finally, two kinds of new organosoluble, light-colored, and good thermal stable fluorosilicone PI compounds (**5a-5b**) were synthesized from compounds **3a-3b** and **4** and 4,4'-hexafluoroisopropylidenedipthalic anhydride, prepared through a typical two-step polymerization method. The solubility of the novel fluorosilicone PI films of compounds **5a-5b** and the traditional PI film (4,4'-diaminodiphenyl ether (ODA)-biphenyltetracarboxylic dianhydride, DIY) were contrasted. The result showed that the fluorosilicone PI films have good solubility. These PIs were soluble in amide polar solvents and even in less polar solvents. The glass transition temperatures of compounds **5a-5b** were 229.1 and 186.7°C and the 5% and 10% weight-loss temperatures were 519.8°C and 539°C, respectively. These films had cutoff wavelengths of 331.8 and 318.6 nm. Due to these properties, these PIs could be used as aerospace, photoelectric, and microelectronic materials.

Keywords

Fluorosilicone polyimides, solubility, optical transparency, thermal stability

Introduction

Aromatic polyimides (PIs) are well known as a class of high-performance polymers because of their outstanding properties, such as high thermal stability, high mechanical performance, good chemical resistance, and excellent electrical properties.^{1–6} Therefore, they have been widely used in aerospace and electrical and electronic applications.⁷ At the same time, optical transparency of PI films is of special importance in some applications, such as flexible solar radiation protectors, orientation films in liquid-crystal display devices, optical waveguides for communication interconnects, and optical half-wave plates for planar lightwave circuits.⁸ However, applications may be rather limited due to their high softening or melting temperatures and insoluble nature in most organic solvents.⁹ Furthermore, the

standard wholly aromatic PIs often have strong absorption in the visible region of their ultraviolet–visible (UV-Vis) spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer complex (CTC) formation.¹⁰ To overcome these drawbacks, modifications

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of PI structures are often used, for example, by introduction of flexible aryl-ether linkages,^{1,11,12} nonsymmetrical structures,^{13–15} or bulky substitutes^{16–18} into the polymer¹⁴ backbones.

Ether linkages are the most popular, flexible linkages introduced into PI backbones. It is generally recognized that an aryl-ether linkage imparts properties such as better solubility and melt-processing characteristics and improved toughness in comparison with those of polymers without an aryl-ether linkage. Meanwhile, some researches revealed that incorporation of siloxane and alicyclic¹⁹ segments proved effective to increase transparency, water ingress resistance, electrical property, and solubility of PIs.

PIs containing hexafluoroisopropylidene or pendent trifluoromethyl groups are of²⁰ special interest. It was found that the incorporation of CF₃ into polymer backbones resulted in an enhanced solubility and optical transparency together with a lowered dielectric constant, which attributed to low polarizability of the C–F bond and the increase in free volume. The fluorinated PIs also provided other merits such as good thermal and low moisture absorption.

In this work, we synthesized two kinds of aromatic symmetrical diamine monomers, 1,4-bis (4-amino-2-trifluoromethylphenoxy)benzene (compound **3a**) and 4,4'-bis (4-amino-2-trifluoromethylphenoxy)diphenyl ether (compound **3b**) and one kind of dianhydride,^{1,7,9,21} 5,5-(1,1,3,3-tetramethyl disiloxane-1,3-diyl)-bis-norborane-2,3-dicarboxylic anhydride (compound **4**)²², which have been designed as potentially convenient condensation monomers for PIs, capable of imparting solubility and good thermal properties at the same time. The conditions of the synthesis reaction such as reaction temperature, catalyst dosage, molar ratio of TMDS/NA, and reaction time on yield of compound **4** were first discussed by the single-factor approach. Then, two kinds of new organosoluble fluorosilicone PI compounds **5a–5b** were synthesized from the two diamine compounds **3a–3b** with the dianhydride compound **4** and 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA). The solubility of the novel fluorosilicone PI film compounds **5a–5b** and the traditional PI film (ODA-biphenyltetracarboxylic dianhydride (BPDA), DIY) were contrasted. The characterizations of the two diamines, the dianhydride, and related intermediates, as well as the resulting PIs based on the two diamines and the dianhydride were carried out by means of Fourier transform infrared (FTIR), elemental analyses, proton nuclear magnetic resonance (¹H NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and UV-Vis spectra.

Experimentation

Materials

Hydroquinol (Kelong, China), 4,4'-dihydroxydiphenyl ether (4,4'-oxydiphenol, Maya Reagent, Zhejiang, China),

2-chloro-5-nitrobenzotrifluoride (Maya Reagent), 5% palladium/carbon (Pd/C, DIY), hydrazine hydrate (Chengdu Union Chemical Industry Reagent Research Institute (CUICR), Chengdu, China), nadic anhydride (NA) (Maya Chemicals), 1,1,3,3-tetramethyldisiloxane (TMDS, Aladdin Reagents, China), *N,N*-dimethylformamide (DMF, Guanghua, Guangdong Province, China), potassium carbonate (K₂CO₃), toluene, ethanol absolute, methanol, and acetic anhydride (CUICR), diethyl ether (Kermel, China), and petroleum ether (Zhiyuan, Tianjin, China).

Measurements

FTIR spectra were obtained using a Nicolet-5700 (PE; Thermo Electron Scientific Instruments Corporation, Madison, Wisconsin, USA) instrument from 500 to 4000 cm⁻¹ on potassium bromide (KBr) pellets. Elemental analysis was analyzed using an Vario EL CUBE (Elementar Analysensysteme GmbH). ¹H NMR was analyzed using an Avance (Bruker, Billerica, Massachusetts, USA) 600 MHz ¹H spectrometer. TGA was conducted using an STA 449 C (NETZSCH, Germany) analyzer. Experiments were carried out on 2–4 mg film samples heated in flowing nitrogen (50 cm³ min⁻¹) at a heating rate of 5°C min⁻¹. DSC traces were measured on an STA 449 C (NETZSCH) at a heating rate of 5°C min⁻¹ in flowing nitrogen (50 cm³ min⁻¹). Glass transition temperatures (*T*_{gs}) were read as the midpoint of the heat capacity jump. UV-Vis spectra of the polymer films were recorded on a UV-3150 UV-Vis spectrophotometer (Shimadzu, Tokyo, Japan).

Monomer synthesis

Synthetic routes for the diamine monomers, the dianhydride monomer, and the fluorosilicone PIs are shown in Figures 1 to 3, respectively.

Synthesis of diamine compounds 3a–3b. Hydroquinol, compound **1a** (11.01 g, 0.10 mol) and 2-chloro-5-nitrobenzotrifluoride (45.67 g, 0.20 mol) were first dissolved in 100 ml of DMF in a flask with stirring.^{1,7,9,21} After the mixture was completely dissolved, K₂CO₃ (24.18 g, 0.17 mol) was added to it in one portion. After 30 min of stirring at room temperature, the mixture was heated at 100°C for 12 h. The obtained mixture was poured into methanol/water (volume ratio 10/1) to give a solid, which was collected, washed thoroughly with methanol and hot water, and dried under vacuum at 60°C. The crude product was recrystallized from DMF/methanol to give fine crystals (46.12 g). DSC measurements at a scan rate of 5°C min⁻¹ showed yield: 1,4-bis (4-nitro-2-trifluoromethylphenoxy)benzene, compound **2a**, 94.5%, 4,4'-Bis(4-nitro-2-trifluoromethylphenoxy)diphenyl ether, compound **2b**, 89.0% and melting point (m.p.): compound **2a**, 215.0°C, compound **2b**, 157.5°C.

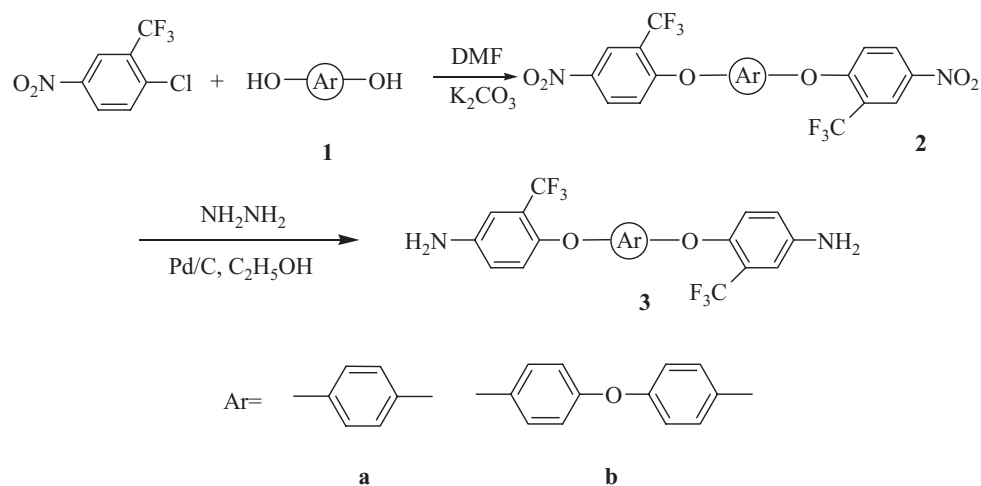


Figure 1. Synthesis of the fluorinated diamine monomers.

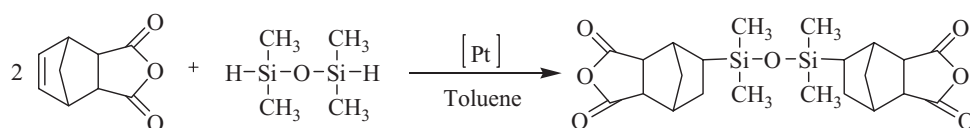


Figure 2. Synthesis of the silylnorbornane anhydride monomer.

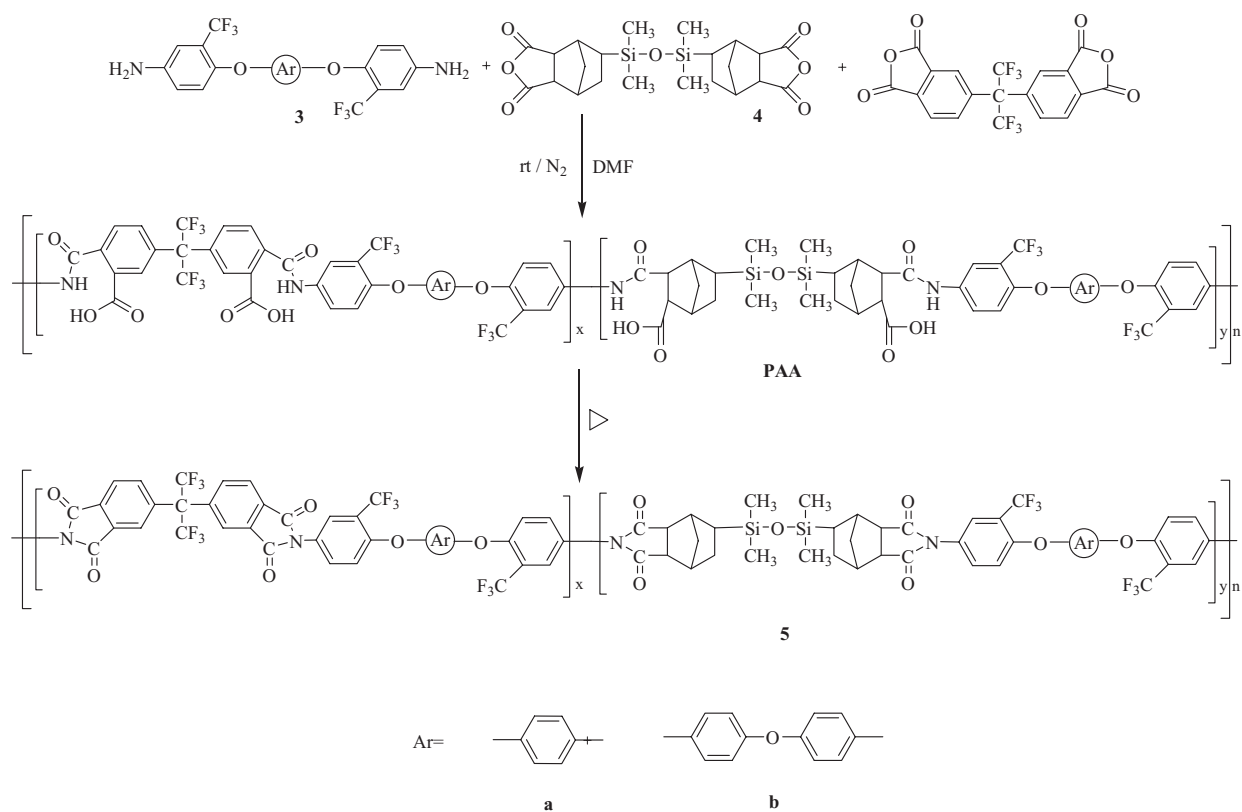


Figure 3. Synthesis of polyimides.

Compound **2a** (4.88 g, 0.01 mol) and 5% Pd/C (0.09 g) were suspended in 70 ml of ethanol in a flask. The suspension solution was heated to reflux, and hydrazine monohydrate 80% (6.82 ml) was added dropwise to the mixture. After a further 12 h of reflux, darkened solution was filtered hot to remove Pd/C, and the filtrate was distilled to remove some solvent. The obtained mixture was poured into stirring water, giving rise to a precipitate that was isolated by filtration (4.02 g). DSC measurements at a scan rate of $5^{\circ}\text{C min}^{-1}$ showed yield: compound **3a**, 93.8%, compound **3b**, 91.2%; m.p.: compound **3a**, 127.8°C , compound **3b**, 76.0°C .

Compound **2a**: IR (KBr): 1530, 1331 cm^{-1} (NO_2 stretch), 1292, 1272, 1179, 1150, 1121 cm^{-1} (C–F and C–O stretch). Elemental analysis calculated for $\text{C}_{20}\text{H}_{10}\text{F}_6\text{N}_2\text{O}_6$ (488.32): C, 49.18%; H, 2.05%; N, 5.74%. Found: C, 49.21%; H, 2.09%; N, 5.70%. $^1\text{H NMR}$ (600 MHz, deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$), ppm) δ : 8.535, 8.530 (2H, H_a), 8.483–8.463 (2H, H_b), 7.402 (4H, H_d), 7.259, 7.243 (2H, H_c).

Compound **2b**: IR (KBr): 1530, 1331 cm^{-1} (NO_2 stretch), 1292, 1263, 1179, 1141, 1092 cm^{-1} (C–F and C–O stretch). Elemental analysis for $\text{C}_{26}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_7$ (580.42): calculated: C, 53.80%; H, 2.44%; N, 4.83% and found: C, 53.85%; H, 2.41%; N, 4.79%. $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$, ppm) δ : 8.515, 8.511 (2H, H_a), 8.477–8.457 (2H, H_b), 7.310–7.212 (8H, H_d), 7.162, 7.147 (2H, H_c).

Compound **3a**: IR (KBr): 3500, 3387 cm^{-1} (N–H stretch), 1258, 1219, 1160, 1121 cm^{-1} (C–O and C–F stretch). Elemental analysis for $\text{C}_{20}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_2$ (428.36): calculated: C, 56.06%; H, 3.30%; N, 6.54% and found: C, 56.02%; H, 3.34%; N, 6.48%. $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$, ppm) δ : 6.894, 6.889 (2H, H_a), 6.842 (4H, H_d), 6.821 (2H, H_c), 6.797–6.778 (2H, H_b), 5.404 (4H, NH_2).

Compound **3b**: IR (KBr): 3461, 3387 cm^{-1} (N–H stretch), 1258, 1219, 1160, 1121 cm^{-1} (C–O and C–F stretch). Elemental analysis for $\text{C}_{26}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_3$ (520.46): calculated: C, 60.00%; H, 3.49%; N, 5.38% and found: C, 60.08%; H, 3.43%; N, 5.33%. $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$, ppm) δ : 6.965, 6.950 (4H, $\text{H}_{a,c}$), 6.900–6.840 (8H, H_d), 6.804–6.785 (2H, H_b), 5.418 (4H, NH_2).

Synthesis of compound 4. Karstedt's catalyst (1 ml, Pt% = 0.37%) was added to a stirred mixture of NA (7.38 g, 0.045 mol), TMDS (3.35 g, 0.025 mol), and dry toluene (50 ml).²² The resulting mixture was heated with stirring at 90°C for 3 h. After cooling, carbon black (1–2 g) was added, and the solution was stirred for 1 h at room temperature. Filtration, removal of the solvent at 70°C with a vacuum pump, and addition of dry diethyl ether resulted in the precipitation of a white crystalline solid. Based on the method of preparation, the product obtained was 5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)bisorbornane-2,3-dicarboxylic anhydride (8.63 g) with an yield of 74.6% and m.p. of 127.1°C , by DSC analysis at a scan rate of $5^{\circ}\text{C min}^{-1}$.

In this section, the conditions of the synthesis reaction such as reaction temperature, catalyst dosage, molar ratio of TMDS/NA, and reaction time on yield of compound **4** were first discussed by the single-factor approach. It showed that the optimal reaction conditions were reaction temperature of 90°C , catalyst dosage of 1 ml (Pt% = 0.37%), molar ratio of TMDS/NA of 1/1.8, and reaction time of 3 h. The yield was 74.6%.

Compound **4**: IR (KBr): 2964, 2875 cm^{-1} (C–H stretch), 1850, 1781 cm^{-1} (C=O stretch), 1258 cm^{-1} (Si–Me stretch), 1080 cm^{-1} (Si–O–Si stretch). Elemental analysis for $\text{C}_{22}\text{H}_{30}\text{Si}_2\text{O}_7$ (462.70): calculated: C, 57.10%; H, 6.55% and found: C, 57.18%; H, 6.49%. $^1\text{H NMR}$ (600 MHz, deuterated chloroform, ppm) δ : 0.073–0.053 (12H, H_c), 0.678, 0.675 (2H, H_d), 1.685–1.547 (8H, H_e), 2.875–2.760 (4H, H_b), 3.466–3.396 (4H, H_a).

Polymer synthesis

The fluorosilicone PI compound **5a** was synthesized from 100% (mole) diamine compound **3a**, 5% (mol) dianhydride compound **4**, and 95% (mol) 6FDA by a conventional two-step procedure of ring opening polyaddition at room temperature to form poly acrylic acid (PAA) and sequential heating to 250°C (thermal imidization, T) to obtain the corresponding PI.

Compound **5a**: IR (KBr): 1789, 1735 cm^{-1} (imide C=O stretch), 1379 cm^{-1} (C–N stretch), 1092, 721 cm^{-1} (imide ring deformation), 1262 cm^{-1} (Si–CH₃ stretch), 1048 cm^{-1} (Si–O–Si stretch) and some stronger peak of C–O and C–F stretch was in the range 1100–1300 cm^{-1} . $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$, ppm) δ : 8.205, 8.192 (2H, H_c), 7.976, 7.964 (2H, H_g), 7.915 (2H, H_f), 7.722 (2H, H_a), 7.704 (2H, H_b), 7.265 (4H, H_d), 7.232, 7.217 (2H, H_c), 3.312 (4H, H_h ; H_2O (impurity)), 2.497–2.491 (18H, $\text{H}_{i,j,k}$, $\text{DMSO}-d_6$), 0.008 (12H, H_l).

Compound **5b**: IR (KBr): 1789, 1730 cm^{-1} (imide C=O stretch), 1379 cm^{-1} (C–N stretch), 1101, 721 cm^{-1} (imide ring deformation), 1257 cm^{-1} (Si–CH₃ stretch), 1048 cm^{-1} (Si–O–Si stretch) and some stronger peak of C–O and C–F stretch was in the range 1100–1300 cm^{-1} . $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$, ppm) δ : 8.199, 8.185 (2H, H_c), 7.971, 7.958 (2H, H_g), 7.719 (2H, H_a), 7.701, 7.686 (2H, H_b), 7.211, 7.196 (2H, H_c), 7.150, 7.135 (8H, H_d), 3.312 (4H, H_h ; H_2O (impurity)), 2.497–2.491 (18H, $\text{H}_{i,j,k}$, $\text{DMSO}-d_6$), 0.007 (12H, H_l).

Results and discussion

Monomer synthesis

The CF_3 -containing diamine compounds **3a–3b** were prepared in two steps according to a well-developed method (Figure 1). The intermediate dinitro compounds **2a–2b** were synthesized from the aromatic nucleophilic substitution of

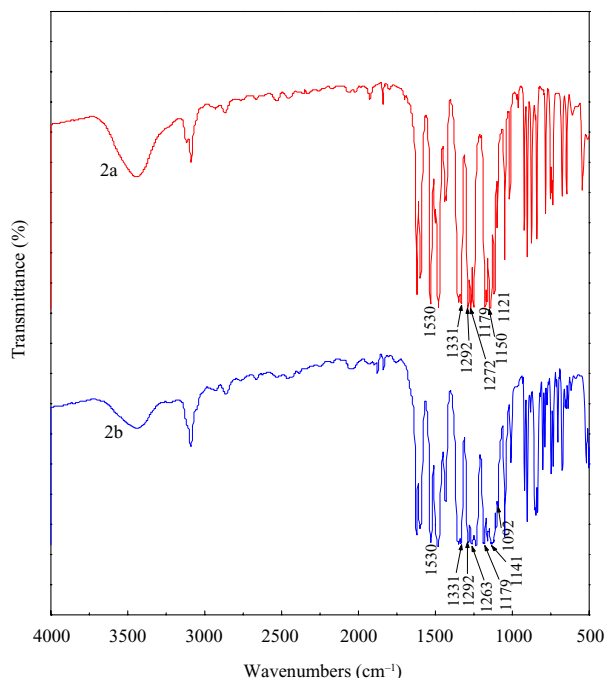


Figure 4. FTIR spectra of 3F-dinitro compound **2a**, 3F-dinitro compound **2b**. FTIR: Fourier transform infrared.

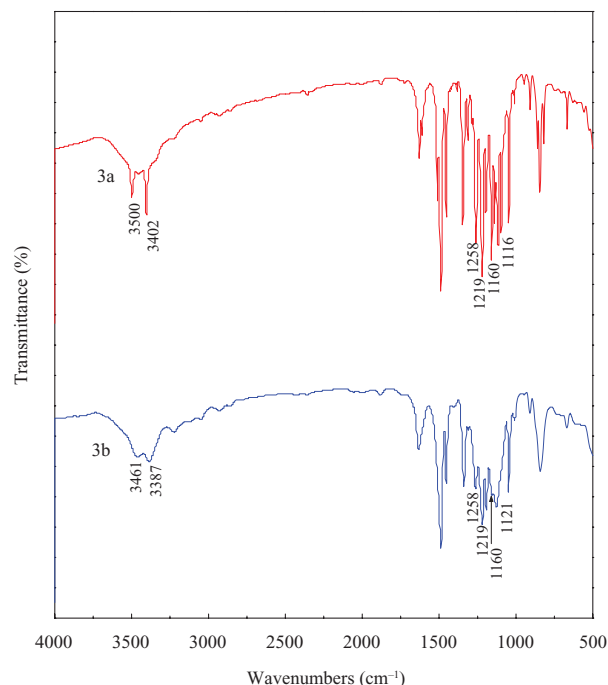


Figure 5. FTIR spectra of 3F-diamine compound **3a**, 3F-diamine compound **3b**. FTIR: Fourier transform infrared; **3a**: 1,4-bis (4-amino-2-trifluoromethylphenoxy) benzene; **3b**: 4,4'-bis (4-amino-2-trifluoromethylphenoxy)diphenyl ether.

2-chloro-5-nitrobenzotrifluoride with hydroquinol and 4,4'-dihydroxydiphenyl ether compounds **1a-1b** in the presence of K_2CO_3 . Diamine compounds **3a-3b** were readily obtained in high yields by the catalytic reduction of compounds **2a-2b** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. FTIR, 1H NMR, and DSC analyses were used to confirm the structures of the intermediate compounds **2a-2b** and the diamine monomer compounds **3a-3b**. Figures 4 and 5 show the FTIR spectra of dinitro compounds **2a-2b** and diamine compounds **3a-3b**. The nitro group of compounds **2a-2b** gave two characteristic bands at 1530 and 1331 cm^{-1} (NO_2 asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed a pair of N–H stretching bands in the region of 3300–3500 cm^{-1} .

TMDS and 5-norbornene-2,3-dicarboxylic acid anhydride were utilized to synthesize dianhydride compound **4** (Figure 2). Figure 6 shows the FTIR spectra of dianhydride compound **4**. The compound gave two characteristic bands at 1850 and 1781 cm^{-1} (C=O stretching). Meanwhile, it gave two other characteristic absorption peaks at cm^{-1} (Si–Me stretching) and 1080 cm^{-1} (Si–O–Si stretching).

Figure 7 presents the 1H NMR spectra of dinitro compounds **2a-2b** and diamine compounds **3a-3b**. The absorption signals of aromatic protons of compounds **2a-2b** appeared in the region of 8.535–7.147 ppm and those of compounds **3a-3b** shifted to a higher field between 6.965 and 6.778 ppm. In the 1H NMR spectrum of **2a-2b**, the

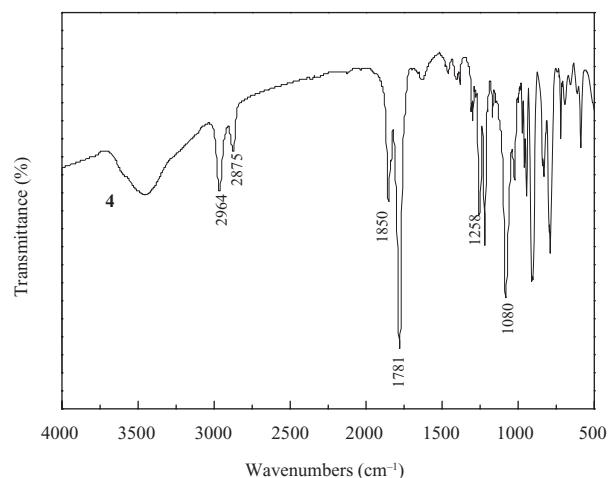


Figure 6. FTIR spectrum of siloxane-containing monomer compound **4**. FTIR: Fourier transform infrared; **4**: 5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl) bisnorbornene-2,3-dicarboxylic anhydride.

protons H_a and H_b appeared in the downfield due to the inductive effect of the electron withdrawing $-NO_2$ and $-CF_3$ groups; the protons H_c and H_d *ortho*-oriented to aromatic ether appeared in the upfield due to the conjugation effect. After reduction, the protons H_a and H_b of compounds **3a-3b** shifted to the upfield due to the electron donating property of the amino groups.

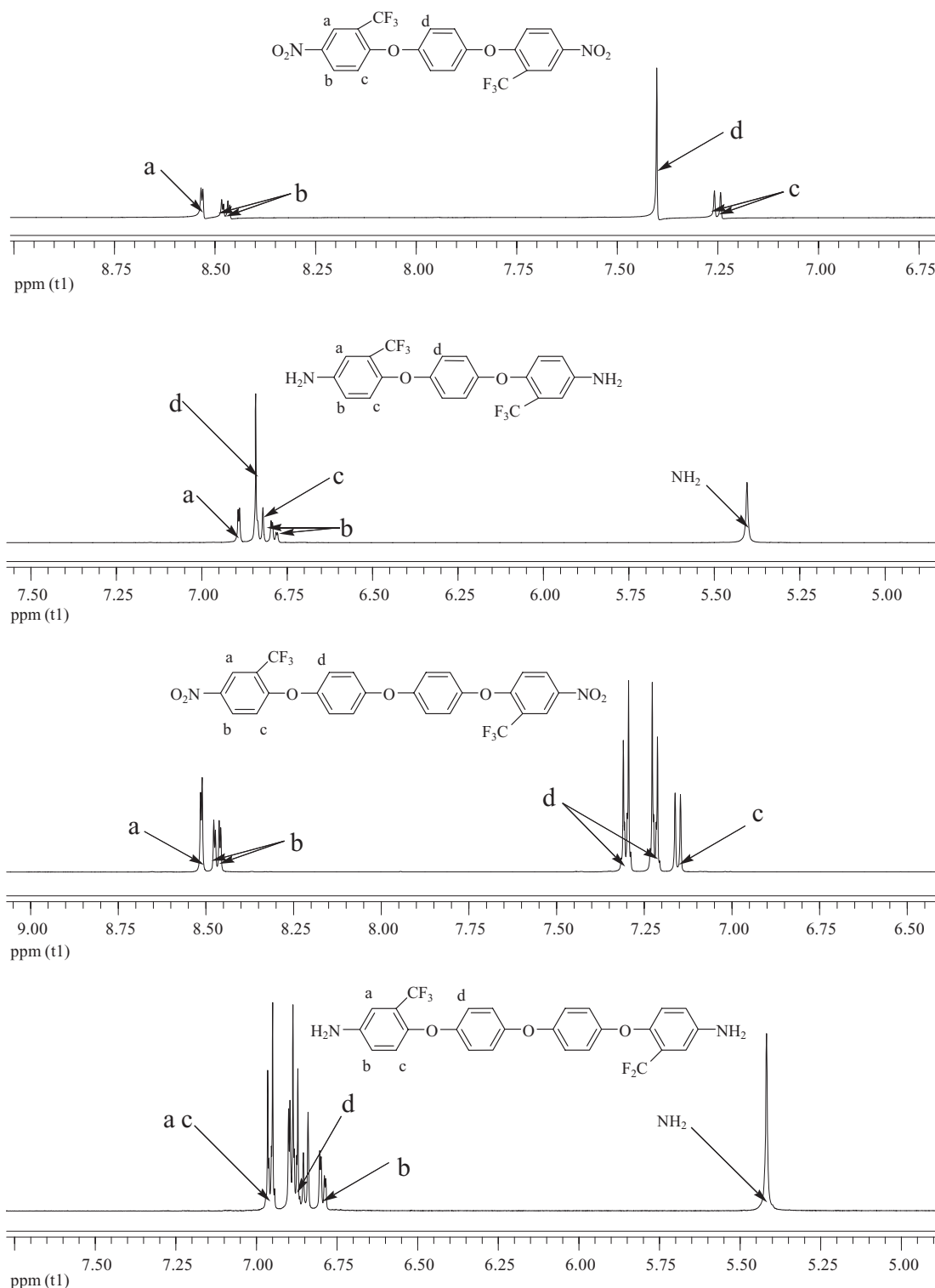


Figure 7. The ^1H NMR spectra of 3F-dinitro compounds **2a-2b** and 3F-diamine compounds **3a-3b** in DMSO- d_6 . ^1H NMR: proton nuclear magnetic resonance; DMSO- d_6 : deuterated dimethyl sulfoxide; **3a**: 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene; **3b**: 4,4'-bis(4-amino-2-trifluoromethylphenoxy)diphenyl ether.

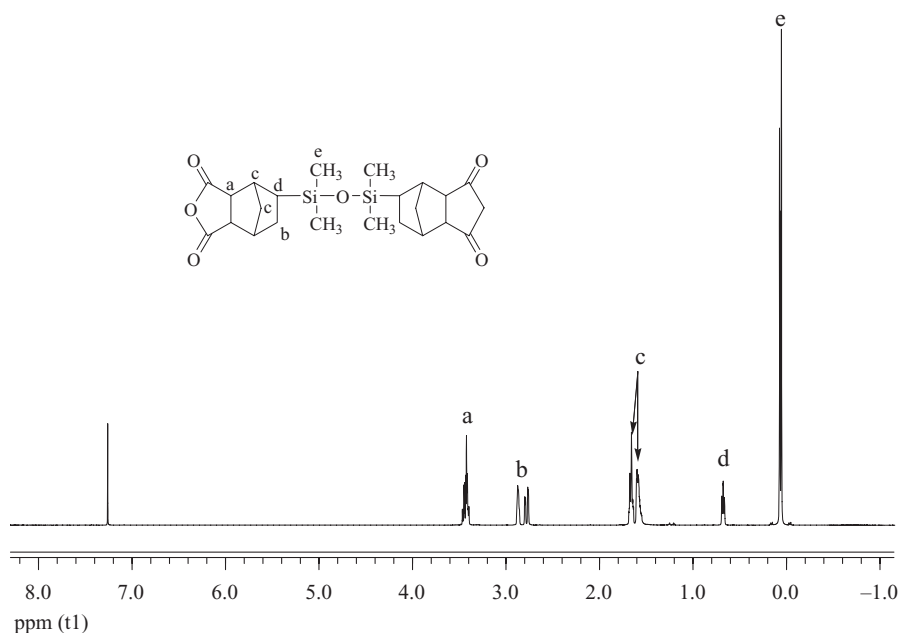


Figure 8. The ^1H NMR spectrum of dianhydride compound **4** in CDCl_3 . ^1H NMR: proton nuclear magnetic resonance; CDCl_3 : deuterated chloroform; **4**: 5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl) bisnorbornane-2,3-dicarboxylic anhydride.

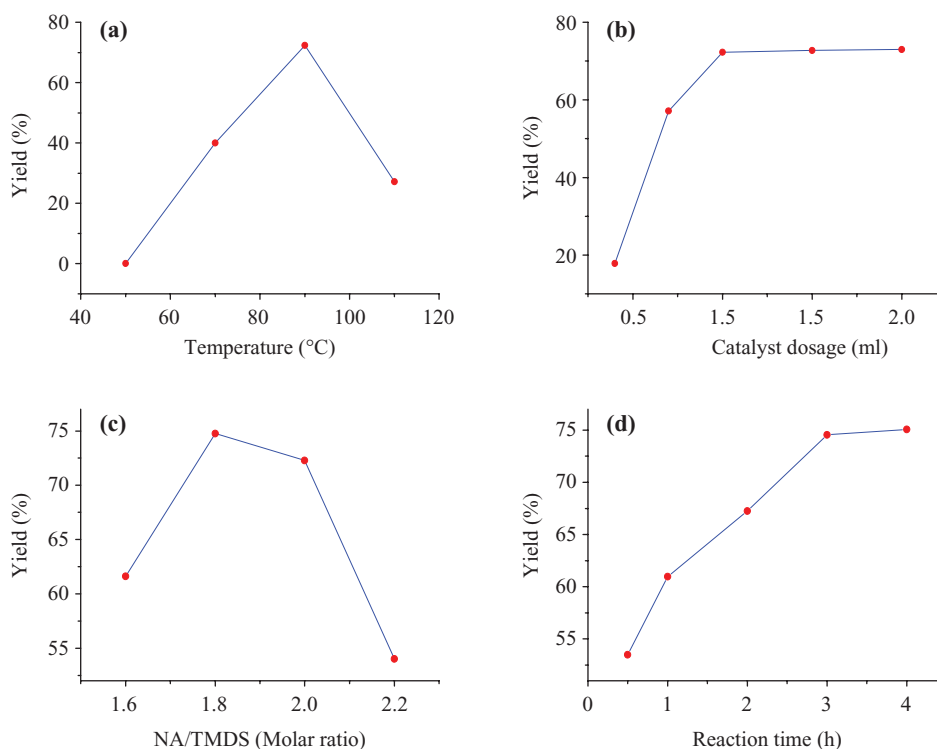


Figure 9. Effects of the conditions of the synthesis reaction such as reaction temperature, catalyst dosage, molar ratio of TMDS/NA, and reaction time on yield of compound **4**. (a) catalyst dosage = 1 ml (Pt% = 0.37%), NA/TMDS = 2:1, reaction time = 24 h; (b) NA/TMDS = 2:1, reaction time = 24 h, temperature = 90°C ; (c) reaction time = 24 h, temperature = 90°C , catalyst dosage = 1 ml (Pt% = 0.37%); and (d) temperature = 90°C , catalyst dosage = 1 ml (Pt% = 0.37%), NA/TMDS = 1.8:1. NA: nadic anhydride; TMDS: 1,1,3,3-tetramethyldisiloxane; **4**: 5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl) bisnorbornane-2,3-dicarboxylic anhydride.

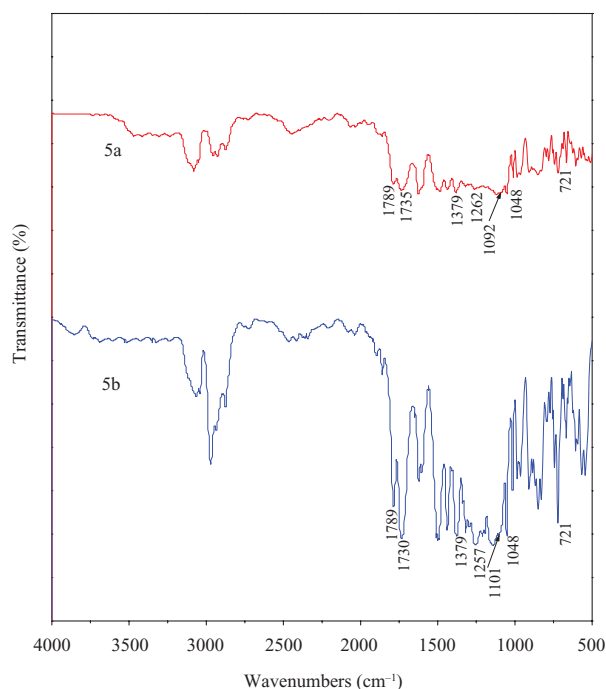


Figure 10. FTIR spectra of polyimides **5a-5b**. FTIR: Fourier transform infrared.

The ^1H NMR spectra of compound **4** are shown in Figure 8. In the ^1H NMR spectrum, the proton H_c appeared in the region of 0.073–0.053 ppm and the proton H_d appeared at 0.678 and 0.675 ppm. The above-cited results evidenced that compound **4** had been synthesized successfully.

Figure 9 shows that the optimal reaction conditions are reaction temperature of 90°C , catalyst dosage of 1 ml ($\text{Pt}\% = 0.37\%$), molar ratio of TMDS/NA of 1/1.8, and reaction time of 3 h. The yield was 74.6%. As the reaction temperature gradually increased, the reaction activity of Si–H increased gradually. But the reaction temperature was too high, it was prone to self-cross-linking reaction of Si–H.

The conversion rate increased with increasing amount of catalyst. However, when the dosage of the catalyst was more than 1 ml ($\text{Pt}\% = 0.37\%$), the conversion rate was not improved obviously. Therefore, the optimum catalyst dosage was 1 ml ($\text{Pt}\% = 0.37\%$) considering the economic benefit. The conversion rate increased with increasing molar ratio of NA/TMDS. When the molar ratio of NA/TMDS was more than 1.8, the conversion rate decreased. This is because TMDS was easy to volatilize, so the optimum molar ratio of NA/TMDS was <2 . The yield of compound **4** did not change after the reaction time reached 3 h. Thus, the optimum reaction time was 3 h.

Polymer synthesis

The polymer compounds **5a-5b** were synthesized from diamine compounds **3a-3b** with dianhydride compound **4** and

dianhydride 6FDA, by a conventional two-step procedure ring-opening polyaddition at room temperature to PAA, followed by sequential heating to 250°C to obtain the corresponding PIs, as shown in Figure 3. The typical IR spectrum of compound **5a-5b** is shown in Figure 10. All PIs exhibited characteristic imide group absorptions around 1789 and 1730–1735 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretch), 1379 cm^{-1} (C–N stretch), and 1092–1101 and 721 cm^{-1} (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm^{-1} due to the C–O and C–F stretching. Meanwhile, it gave the characteristic absorption peaks at 1262 and 1257 cm^{-1} (Si–Me stretching). The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the PAA precursors into PIs.

The ^1H NMR spectra of compounds **5a-5b** are shown in Figure 11. In the ^1H NMR spectrum, the $\text{H}_{c,d}$ shifted to the downfield due to the electron withdrawing property of carbonyl.

Optical transparency

Thin films were measured for optical transparency with UV-Vis spectroscopy. Figure 12 shows the UV-Vis absorption spectra of the PI films prepared via thermal imidizations, and cutoff wavelength (absorption edge, λ_0) value, and the percentage transmittance at 500 nm from these spectra are listed in Table 1. The PIs had shorter λ_0 than 350 nm and they exhibited high optical transparency of 85–90%.

The light colors of the PIs with the CF_3 groups in their diamine moieties and 6FDA could be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing CF_3 group was effective in reducing the CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron donating property of the diamine moieties). Moreover, the CF_3 group might weaken chain-to-chain cohesive force due to lower polarizability of the C–F bond. The decrease in intermolecular CTC formation is understandable also from the significant solubility of the PIs prepared from diamine. Consistent with the effect of CF_3 group, the flexible ether group was also sufficiently effective in reducing CTC formation.

Solubility

The solubility of these PIs was tested, and the results are summarized in Table 2. As seen in Table 2, the solubility of compounds **5a-5b** were better than the traditional PI film (ODA-BPDA, DIY). Compounds **5a-5b** showed excellent solubility in aprotic polar solvents such as DMF and DMSO and were also soluble in less polar solvents like tetrahydrofuran. This is due to the fact that the main chain phenylenes of compounds **5a-5b** contain the bulky trifluoromethyl substitute groups, producing a steric hindrance, which prevent

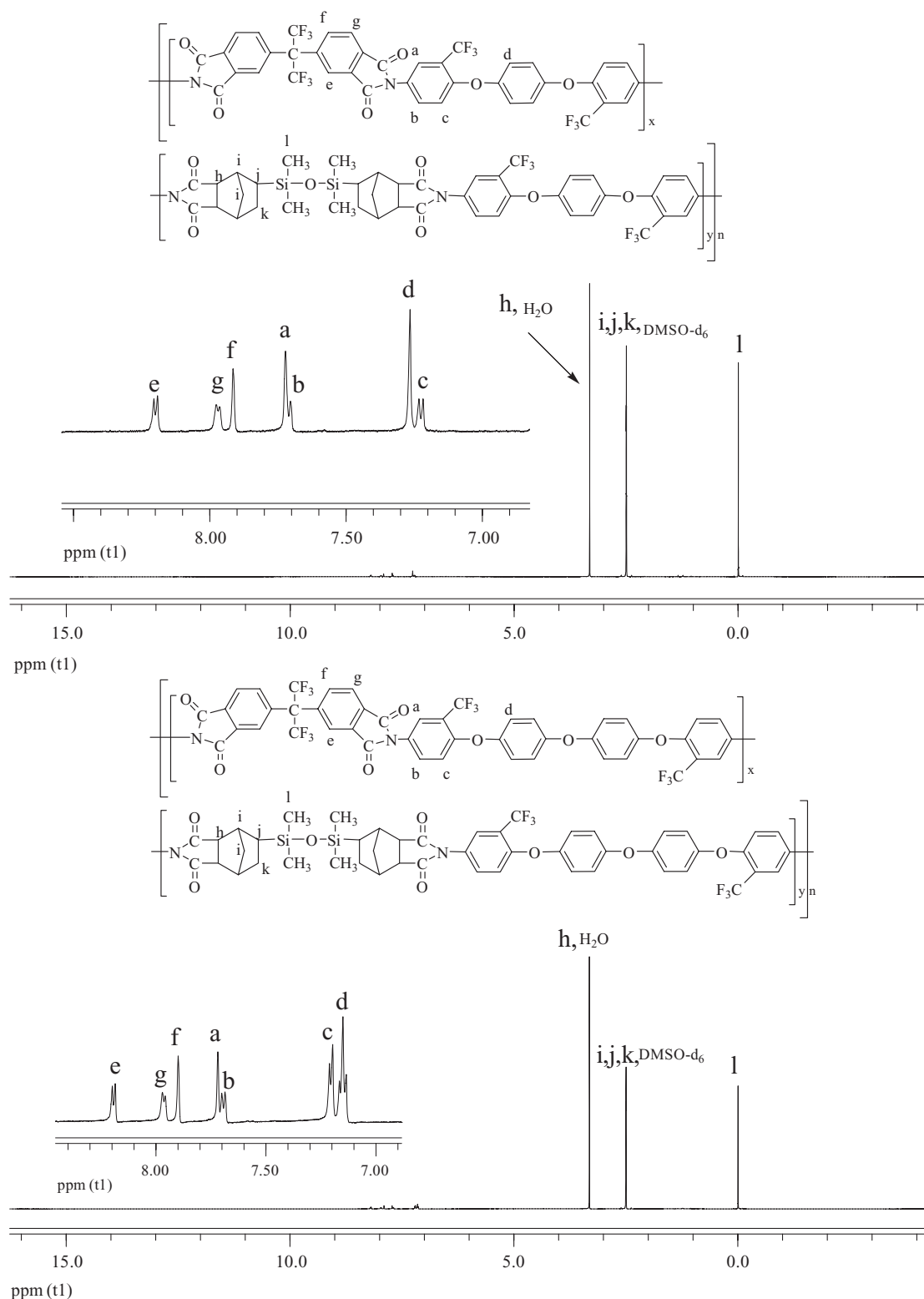


Figure 11. The ^1H NMR spectra of polyimides **5a-5b** in $\text{DMSO}-d_6$. ^1H NMR: proton nuclear magnetic resonance; DMSO: dimethyl sulfoxide.

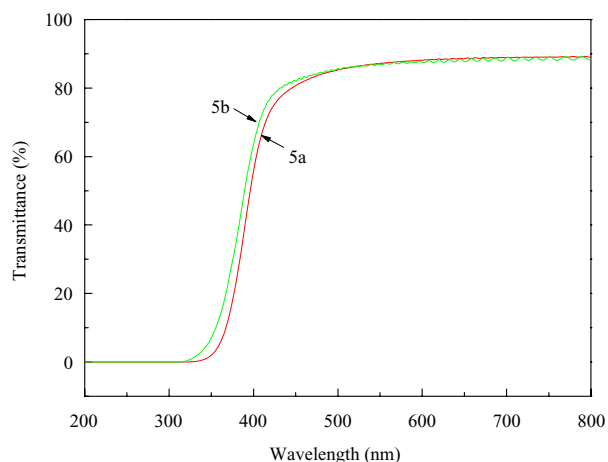


Figure 12. UV-visible spectra of the polyimide compounds **5a-5b**. UV: ultraviolet.

Table 1. Optical properties of polyimides.

Polymer	Film thickness(μm)	λ_0 (nm)	UV transmittance at 500 nm (%)
Compound 5a	30	331.8	85.3
Compound 5b	26	318.6	85.5

λ_0 : cutoff wavelength; UV: ultraviolet.

Table 2. Solubility behavior of polyimides.^a

Polymers	Solvents					
	DMF	CHCl_3	THF	Acetone	DMSO	Ethanol
Compound 5a	+	+	+	+	+	–
Compound 5b	+	+	+	+	+	–
ODA-BPDA	+	–	–	–	–	–

DMF: *N,N*-dimethylformamide; CHCl_3 : chloroform; THF: tetrahydrofuran; DMSO: dimethyl sulfoxide; BPDA: biphenyltetracarboxylic dianhydride.

^aPolyimide film (ODA-BPDA, DIY). Solubility: (+) soluble at room temperature, (–) insoluble at room temperature.

close-chain packing and allow the solvent molecules to diffuse into the polymer chains. Siloxane segments that are flexible groups were introduced into the PI backbone to increase the PI molecular flexibility. At the same time, the bulky alicyclic structures and the affinity and steric effect of silicon atoms to solvents reduce the intermolecular interactions to enhance solubility.

Thermal properties

DSC and TGA were used to evaluate the thermal properties of the PI films (Figures 13 and 14). The thermal behavior data of all the PIs were given in Table 3. T_g values of the PIs were obtained from DSC measurements. PI compounds

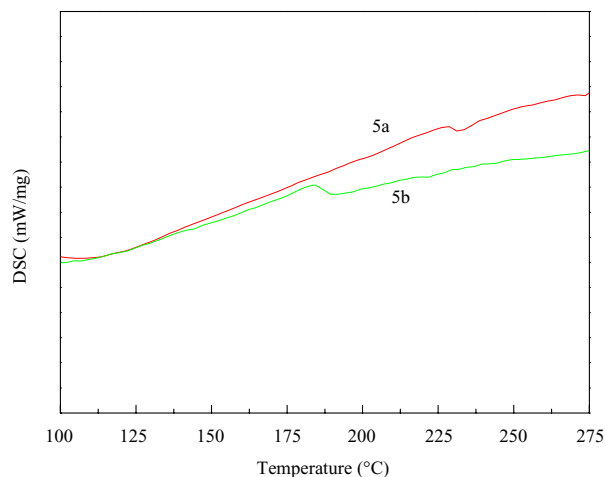


Figure 13. DSC curves of PI compounds **5a-5b** at a heating rate of 5°C min^{-1} . DSC: differential scanning calorimetry; PI: polyimide.

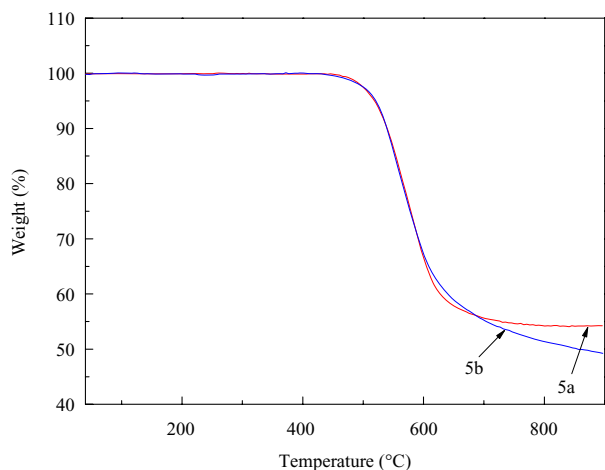


Figure 14. TGA curves of PI compounds **5a-5b** at a heating rate of 5°C min^{-1} . TGA: thermogravimetric analysis; PI: polyimide.

Table 3. Thermal properties of polyimides.

Polymer	DSC	TGA		
	T_g ($^\circ\text{C}$)	$T_{5\%}$ ($^\circ\text{C}$)	$T_{10\%}$ ($^\circ\text{C}$)	Char yield (%)
Compound 5a	229.1	519.8	539	54.3
Compound 5b	186.7	519.8	539	49.5

DSC: differential scanning calorimetry; TGA: thermogravimetric analysis; T_g : glass transition temperature; $T_{5\%}$: 5% weight-loss temperature; $T_{10\%}$: 10% weight-loss temperature.

5a-5b showed T_g values in the range of $186.7\text{--}229.1^\circ\text{C}$. When the two PI compounds were compared, the PI compound **5a** generally revealed slightly higher T_g value than that of compound **5b**. This could be attributed to more toughness in compound **5a** compared with compound **5b**, which has more aryl-ether linkages coming from diamine **3b**.

The thermal stabilities of these PIs were evaluated by TGA under nitrogen atmosphere with 5% and 10% weight-loss temperature ($T_{5\%}$ and $T_{10\%}$) for comparison. These are summarized in Table 3. The decomposition temperatures at 5% and 10% weight loss of PI compounds **5a-5b** were recorded as 519.8°C and 539°C under nitrogen atmosphere. These PIs exhibited high $T_{5\%}$ and $T_{10\%}$ values, and this may be a result of relatively higher rigidity of the molecular chains.

All the PIs left more than 49.5% char yields at 900°C under nitrogen atmosphere. The TGA results showed an excellent thermal stability of these PIs, even though they revealed high solubility and optical transparency.

Conclusions

Fluorinated diamine compounds **3a-3b** were synthesized via a high-yielding two-step procedure. Siloxane-containing dianhydride compound **4** was synthesized via a high-yielding one-step procedure. The optimal reaction conditions are reaction temperature of 90°C, catalyst dosage of 1 ml (Pt% = 0.37%), molar ratio of TMDS/NA of 1/1.8, and reaction time of 3 h. The yield of compound **4** was 74.6%. A series of designed novel organosoluble and colorless fluorosilicone PI compounds **5a-5b** were obtained successfully from compounds **3a-3b** and **4** with 6FDA by thermal imidization method. The obtained PIs displayed better solubility than the traditional PI film (ODA-BPDA), fantastic optical properties, and high thermal stability. As a result, we confirmed that PI compounds **5a-5b** showed light color and great transparency that is nearly equal to the colorless PI. These PIs may be the most promising, processable high-temperature materials for applications in micro-electronics and optical devices.

Conflict of interest

The authors declared no conflicts of interest.

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