



# Preparation and characterization of organic soluble polyimides with low dielectric constant containing trifluoromethyl for optoelectronic application

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## ABSTRACT

Polyimide (PI) films have excellent comprehensive properties and bright prospects in the next generation of optoelectronic and microelectronic applications. PIs were synthesized by aromatic diamines and alicyclic dianhydrides considered to be the most effective method for preparing polyimides with high light transmittance and low dielectric constant. In order to improve the overall performance of polyimide, the introduction of a large trifluoromethyl group into the main chain is also considered a powerful strategy. In this article a novel diamine containing 6 trifluoromethyl groups has been designed and synthesized by Suzuki reaction. Afterwards, PIs were synthesized with fluorinated aromatic dianhydride and alicyclic dianhydride through a two-step method. The two PIs have excellent solubility: PI-a and PI-b exhibited excellent solubility in common polar solvents. Such as DMF, DMAc, NMP and DMSO at room temperature, and PI-a was soluble in low-boiling solvents such as ethyl acetate,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  at room temperature. PI-b was soluble in low-boiling solvents acetone and  $\text{CHCl}_3$  at room temperature, which was rarely seen in other aromatic polyimides. Soluble in common organic solvents, especially low boiling point solvents, made these polymers easy to process and suitable for processing technology in solution. This was an important modification for PIs. They also showed good high temperature resistance: the decomposition temperature ( $T_{5\%}$ ) of two PIs were 520 °C and 475 °C. In addition, the residual rate at 790 °C was 50% and 49% respectively. Two PI films had a very low dielectric constant 2.26 and 2.24, respectively, which was attributed to the hyperbranched structure and strong electron-withdrawing fluorine-containing groups. PI-a and PI-b also had low water absorption of 0.66% and 0.72%, respectively. The transmittance of PI-a and PI-b high transparent films at 450 nm were 74% and 82%, respectively. The significant optical modification was mainly due to the weak electron-accepting alicyclic unit and the large trifluoromethyl electron withdrawing group. This work mainly provided an effective strategy for synthesizing comprehensive excellent performance PIs with high transmittance, excellent solubility, low water absorption, high heat resistance and low dielectric constant.

## 1. Introduction

With the advent of the 5G era and the development of microelectronics and integrated circuits, flexible substrates have become one of the hottest research directions [1,2]. Lightweight, bendable and even foldable flexible products are favored by people: such as flexible thin film transistors, flexible displays, multilayer flexible printed circuit boards, etc [3–6]. As a traditional transparent substrate material, glass can no longer meet people's requirements. In order to meet the application requirements of flexible displays and flexible substrates, it is necessary to develop materials with high transparency, easy processing,

high temperature resistance, low dielectric constant and stable chemical properties. Because the aromatic polyimide films have excellent high temperature resistance, chemical resistance, scalability and excellent mechanical properties [7–9], PIs are considered to be the most suitable polymers for flexible materials, mainly used in polyimide films [10–13], adhesives [14], composite materials [15], flexible display [16,17], liquid crystal alignment layer [18], engineering plastics [19], etc. However, the fully aromatic polyimides have rigid chain interaction, and charge transfer complex (CTC) is easily formed in the highly conjugated molecular chain, which make polymers insoluble, refractory and in darker color [20,21], they also have a higher dielectric constant. Poor

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solubility makes the polymer difficult to process and the film is easily brittle. These defects greatly limit the wide application of PIs in the advanced optoelectronic and microelectronics fields. Therefore, developing PIs with outstanding overall performance such as high heat resistance, excellent optical transparency, low dielectric and good processability features is still a great challenge.

In order to meet the needs of advanced optoelectronics and microelectronics applications, extensive reports [22–26] focused on the structural modification, such as the introduction of asymmetric monomers, flexible groups, fluorine-containing groups and bulky side group substituents to improve the solubility of polyimides. In 2019, Zhiming Mi [27] synthesized diamines containing twists and ether bonds, and synthesized PIs with 6FDA that were not only soluble in polar solvents DMF and DMAc at room temperature, but also soluble in low-boiling solvents  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , but the optical transmittance and thermal stability were average. For optical properties, it was reported that when the dianhydride structure is fixed, the optical properties of PIs were determined by the electron donating ability of the diamine. Researchers introduced large pendant substituents, flexible bond or electron-withdrawing functional groups into the polymer backbone to inhibit charge transfer to obtain transparent PIs [28–30], such as fluorine-containing groups and alicyclic structures. Due to the unique structure of fluorine atoms, the introduction of fluorine atoms can make PIs have many excellent properties. Such as trifluoromethyl, with low molar polarization and high electronegativity [31]. Researchers have developed many fluorine-containing PIs and find that fluorine-containing PIs not only have excellent optical properties, but also have better solubility in organic solvents [32–34]. However fluorinated PIs may reduce the thermal stability, it was reported that the trifluoromethyl group can achieve the purpose of modification without reducing thermal stability. At the same time in terms of coloring, the introduction of trifluoromethyl ( $-\text{CF}_3$ ) units in diamines is also considered as an effective method to obtain PIs with high optical properties. This is because the bulky trifluoromethyl group improves the flexibility of polymer molecular chains, and weakens the electronic interaction between polymer chains [35–37], thereby reducing CTC effect. In addition, PIs containing  $\text{CF}_3$  groups also have lower moisture absorption and low dielectric constant [38]. In the same way, if the alicyclic structure is keyed into the polymer, the conjugated structure of the polymer material can be destroyed to a large extent, the free flow of charges is inhibited, and the absorption of visible light by the polymer material is reduced, thereby obtaining high light transmittance and low dielectric constant polyimide materials. According to the reports among these strategies, the synthesis of semi-alicyclic polyimides from aromatic diamines and alicyclic dianhydrides were considered to be the best choice for obtaining polyimides with high light transmittance and low dielectric constant.

In this paper, a novel diamine ( $\text{N}^1$ -(4-aminophenyl)- $\text{N}^1$ -(5'-(3,5-bis(trifluoromethyl)phenyl)-2,3',5,5'-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl)benzene-1,4-diamine)(3) contained 6 trifluoromethyl groups had been designed and synthesized by Suzuki reaction. Contained multiple branches was to improve the flexibility of the PIs molecular chain and reduced the intermolecular force, thereby improved the solubility and dielectric constant. Then, a two-step method was used to synthesize polyamic acid (PAA) with fluorinated aromatic dianhydride 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) and alicyclic dianhydride Cyclobutanetetracarboxylic dianhydride (CBDA) in DMAc solution, finally dehydrated into organic soluble hyperbranched PIs at high temperature under pyridine/acetic anhydride. The solubility, dielectric constant and optical transparency of polymers were improved by functional trifluoromethyl groups ( $-\text{CF}_3$ ). Both of two PIs were characterized by hydrogen nuclear magnetic spectroscopy, infrared spectroscopy, elemental analysis, ultraviolet spectroscopy, GPC, XRD, TGA, and dielectric constant. It mainly provided an effective strategy for synthesizing hyperbranched PIs with comprehensive excellent performance. Such as high transmittance, easy processing, low dielectric constant, high temperature resistance and low

moisture absorption. These comprehensive excellent properties of PIs and multiple branched high fluorine-containing diamine monomers were rarely reported.

## 2. Experimental

### 2.1. Materials

2,4,6-Tribromoaniline, 4-fluoronitrobenzene, purchased from Aladdin Chemical Reagent Company, 3,5-bis(trifluoromethyl)phenylboronic acid, 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), Cyclobutanetetracarboxylic dianhydride (CBDA), N,N-dimethylacetamide (DMAc) were purchased from Energy Chemical. Purify DMAc solution by vacuum distillation. All other reagents were directly used for analysis after purchasing.

### 2.2. Characterization

Deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) was used as the solvent to analyze H nuclei at a resonance frequency of 400 MHz by Bruker Advance 400 NMR spectroscopy, and analyzed C nuclei at a resonance frequency of 101 MHz, and TMS as an internal standard. The infrared test was carried out with a Thermo Scientific Nicolet iS5 Fourier transform infrared spectrometer. Elemental analysis was determined by Elementar Vario EL cube analyzer. The melting point was determined by WRS-1B digital melting point instrument. Using DMF (flow rate of 1.0 mL/min) as the mobile phase and monodisperse polystyrene as the molecular weight standard, the number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) were determined by gel permeation chromatography. The organic solubility was measured in different organic solvents (10 mg polyimide/1.0 mL organic solvent) at room temperature (20 °C). UV-3600 ultraviolet spectroscopy was used to measure the transmittance of polyimide film with a thickness of about 20  $\mu\text{m}$ . Using Mettler TGA/SDTA 851e thermogravimetric analyzer under nitrogen atmosphere, the thermal stability of 30 °C–790 °C was analyzed at a heating rate of 10 °C/min. Using Q200 analyzer under nitrogen atmosphere, the DSC of 50 °C–390 °C was analyzed at a heating rate of 20 °C/min, secondary heating eliminated the influence of solvents and thermal history. An electronic tensile testing machine (HS-30048-S) was used to test the mechanical properties of films with the thickness about 50  $\mu\text{m}$ . Agilent4294A was used to test the dielectric constant of the polymer films at room temperature. The crystalline state of the powder was measured by the Rigaku Smartlab instrument, and the scanning angle ranges were 5° ~ 90° (2 $\theta$  value). The SL200B contact angle meter was used to study the hydrophobic properties of the films. The thickness of films was measured by the thickness tester C640 mechanical contact method.

### 2.3. Monomer synthesis

#### 2.3.1. Synthesis of 2,4,6-tribromo-N, N-bis(4-nitrophenyl)aniline (1)

2,4,6-tribromoaniline (10.1 g, 0.03 mol),  $\text{K}_2\text{CO}_3$  (13.96 g, 0.1 mol) and p-fluoronitrobenzene (11.5 g, 0.08 mol) dissolved in 120 mL of DMSO were heated to 120 °C and stirred for 8 h under the nitrogen atmosphere. After cooling, filtered and extracted with  $\text{CH}_2\text{Cl}_2$  for several times and condensed. Ethanol and water were used to recrystallize. Then, filtered and dried by suction filtration to obtain 8.7 g of product, Yield: 51%. Melting point: 235–237 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 8.25 (s, 2H, ArH), 8.22 (d,  $J = 9.2$  Hz, 4H, ArH), 7.21 (d,  $J = 9.2$  Hz, 4H, ArH).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 148.4, 142.4, 139.7, 136.6, 126.9, 125.7, 123.8, 120.5. Anal. calcd. for  $\text{C}_{18}\text{H}_{10}\text{O}_4\text{N}_4\text{Br}_3$ : C, 37.76%; H, 1.75%; N, 7.34%; Found: C, 38.01%; H, 1.82%; N, 7.04%.

### 2.3.2. Synthesis of $N^1$ -(4-aminophenyl)- $N^1$ -(2,4,6-tribromophenyl) benzene-1,4-diamine (2)

Compound (1) (3.5 g, 6 mmol), iron powder (2.8 g, 0.05 mol), ethanol (14 mL), water (7 mL), and glacial acetic acid (15 mL) were heated to 68 °C under the nitrogen atmosphere, the mixture changed from yellow to brown and stirred for 5 h. After cooling, the reaction mixture was filtered and extracted with  $\text{CH}_2\text{Cl}_2$  for several times, the pH was adjusted to alkaline by ammonia. Then the mixture was filtrated again. Condensed to obtain crude product, and then purified by column chromatography using ethyl acetate: n-hexane (v/v, 1:4) to obtain 2.75 g of product. Yield: 90%. Melting point: 245–248 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 7.96 (s, 2H, ArH), 6.49 (d,  $J$  = 31.7 Hz, 8H, ArH), 4.75 (s, 4H,  $-\text{NH}_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 143.6, 143.1, 136.1, 135.3, 128.0, 121.6, 119.8, 114.8. Anal. calcd. for  $\text{C}_{18}\text{H}_{14}\text{N}_3\text{Br}_3$ : C, 42.18%; H, 2.73%; N, 8.20%; Found: C, 42.05%; H, 2.79%; N, 7.96%.

### 2.3.3. Synthesis of $N^1$ -(4-aminophenyl)- $N^1$ -(5'-(3,5-bis(trifluoromethyl)phenyl)-2,3',5,5'-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl) benzene-1,4-diamine (3)

Compound (2) (1.03 g, 2 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (2.06 g, 8 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.048 g, 0.04 mmol) and anhydrous  $\text{K}_2\text{CO}_3$  (1.4 g, 10 mmol) in 20 mL of toluene and 10 mL of distilled water were heated to 110 °C under the  $\text{N}_2$  atmosphere. The reaction produced a lot of bubbles. Filtered with suction after cooling. The crude product was purified by column chromatography using ethyl acetate: n-hexane (v/v, 1:2) to obtain 1.2 g of product. Yield: 66%. Melting point: 235–238 °C. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3430 and 3376 ( $-\text{NH}_2$ ), 1282 (C-N), 1139 (C-F).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 8.56 (s, 2H, ArH), 8.00 (s, 3H, ArH), 7.80 (s, 6H, ArH), 6.28 (d,  $J$  = 8.0 Hz, 4H, ArH), 6.15 (d,  $J$  = 7.7 Hz, 4H, ArH), 4.62 (s, 4H,  $-\text{NH}_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 143.8, 143.6, 142.2, 142.1, 138.1, 136.6, 133.8, 131.8, 131.1, 130.3, 130.0, 129.7, 128.1, 125.0, 122.3, 122.1, 120.7, 114.4. Anal. calcd. for  $\text{C}_{42}\text{H}_{23}\text{N}_3\text{F}_{18}$ : C, 55.32%; H, 2.53%; N, 4.61%; Found: C, 54.76%; H, 2.76%; N, 4.41%.

## 2.4. Polymer synthesis

Under the protection of  $\text{N}_2$ , compound (3) (0.456 g, 0.5 mmol), 6FDA (0.228 g, 0.5 mmol), and 5 mL DMAc were added to a 25 mL of three-necked flask and stirred for 24 h at room temperature. Then added 3 mL DMAc to dilute the solution, and the equimolar mixture of pyridine/ $\text{Ac}_2\text{O}$  was added in the solution with the temperature heated to 110 °C and stirred for 5 h. After cooling, the reaction solution was slowly poured into 40 mL methanol and collected by suction filtration, washed the filter cake several times with methanol and water. Then dried under vacuum at 90 °C for 12 h to obtain PI-a product 0.60 g. Yield: 90%. The Mn and Mw of PI-a measured by GPC were 26,338 and 43850, respectively, and the polydispersity index (PDI) was 1.66. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1727 (C = O), 1277 (C-N), 1134 (C-F).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 8.63 (d,  $J$  = 6.9 Hz, 2H, ArH), 8.21 – 7.71 (m, 15H, ArH), 7.08 – 6.87 (m, 8H, ArH). Anal. calcd. for  $\text{C}_{61}\text{H}_{25}\text{N}_3\text{O}_4\text{F}_{24}$ : C, 55.49%; H, 1.90%; N, 3.18%; Found: C, 54.96%; H, 2.12%; N, 3.01%.

Under the protection of  $\text{N}_2$ , compound (3) (0.456 g, 0.5 mmol), CBDA (0.10 g, 0.5 mmol), and 5 mL DMAc were added to a 25 mL of three-necked flask and stirred for 24 h at room temperature. Then added 3 mL DMAc to dilute the solution, and the equimolar mixture of pyridine/ $\text{Ac}_2\text{O}$  was added in the solution with the temperature heated to 110 °C and stirred for 5 h. After cooling, the reaction solution was slowly poured into 40 mL methanol and collected by suction filtration, washed the filter cake several times with methanol and water, then dried under vacuum at 90 °C for 12 h to obtain PI-b product 0.47 g. Yield: 87%. The Mn and Mw of PI-a measured by GPC were 24,218 and 44,943 respectively, and the polydispersity index (PDI) was 1.85. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1729 (C = O), 1278 (C-N), 1134 (C-F).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 8.66 (s, 2H, ArH), 8.23 (s, 2H, ArH), 8.14 (s, 1H, ArH), 7.93 (d,  $J$  = 23.7 Hz, 6H, ArH), 7.08 (s, 4H, ArH), 6.88 (s, 4H, ArH), 3.55 (s, 4H,

ArH). Anal. calcd. for  $\text{C}_{50}\text{H}_{23}\text{N}_3\text{O}_4\text{F}_{18}$ : C, 56.02%; H, 2.15%; N, 3.92%; Found: C, 55.19%; H, 2.28%; N, 3.93%.

The polyimide films were prepared by dissolving polyimide powder in a DMAc solution used a solution casting method and casted on a glass substrate, and then 80 °C/2h, 100 °C/1h, 200 °C/1h. The film was obtained by immersed the glass substrate in deionized water, peeled off and dried.

## 3. Results and discussion

### 3.1. Monomer synthesis

Scheme 1 showed the specific synthetic route. There were 8 kinds of peaks in the NMR carbon spectrum of compound 1, and compound 2 had a  $-\text{NH}_2$  peak at 4.75 ppm. All nuclear magnetic and infrared spectroscopy data were consistent with the expected structure. In addition, the results of elemental analysis were consistent with the theoretical values. In summary, the new diamine monomer 3 had been successfully synthesized.

As shown in Scheme 2, the synthesized diamine (3) was used to synthesize polyimides PI-a and PI-b in two steps with the dianhydride 6FDA and CBDA, respectively. First, diamine and dianhydride were polymerized in DMAc at room temperature to form polyamic acid (PAA), and then pyridine/acetic anhydride was dehydrated at 110 °C to form PIs. The proton nuclear magnetic resonance spectrum and infrared spectra were shown in Fig. 1 and Fig. 2, respectively. There was no  $-\text{NH}_2$  peak near 5 ppm in the proton nuclear magnetic resonance spectrum, and no  $-\text{COOH}$  peak at 11–12.5 ppm. The infrared spectrum was C = O at 1729  $\text{cm}^{-1}$ . The tensile vibration peak of C-N was near 1277  $\text{cm}^{-1}$  and there was almost no  $-\text{NH}_2$  peak at 3200–3400  $\text{cm}^{-1}$ , and the results of elemental analysis were consistent with the theoretical values, which proved that the raw material had been successfully synthesized into PIs.

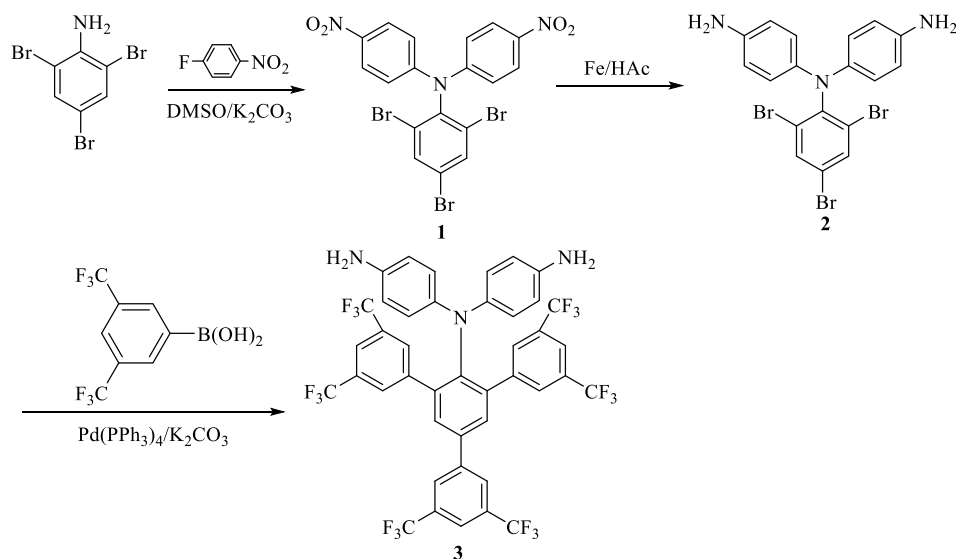
### 3.2. Solubility and morphology of polyimides

The results of the organic solubility were measured in different organic solvents (10 mg polyimide/1.0 mL organic solvent) at room temperature (20 °C) were shown in Table 1. As shown in Table 1, PIs exhibit excellent solubility in common polar solvents: such as DMF, DMAc, NMP and DMSO at room temperature, and PI-a was soluble in low-boiling solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and ethyl acetate at room temperature. PI-b also was soluble in low-boiling solvent acetone and  $\text{CHCl}_3$  at room temperature, which was rarely seen in other aromatic polyimides [39]. The good solubility could attribute to the trifluoromethyl electron withdrawing group and hyperbranched structure, which improved the flexibility of the molecular chain, effectively weakened the intermolecular action force [40]. Soluble in common organic solvents, especially low boiling point solvents, makes these polymers easy to process and suitable for solution processing technology [41]. In short, this was an important modification for PIs.

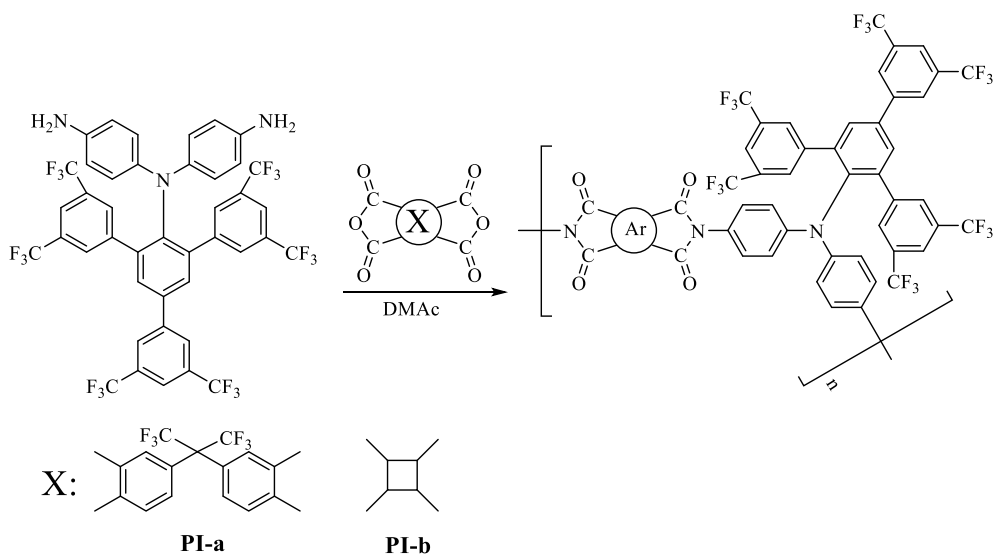
The polymer powders were characterized by XRD diffraction. There no obvious diffraction peaks in the Fig. 3, indicating that the PIs were amorphous. This also showed that the polymer had good solubility. In addition, PI-b had some crystallinity from the result compared to PI-a, because of the alicyclic structure was bonded to the polymer, the conjugated structure of the polymer material may be destroyed, which improved the flexibility of the molecular chain, thereby improved the crystallization ability.

### 3.3. Thermal stability

The results of the thermal properties of two PIs at 50–790 °C were tested by thermogravimetric analysis under nitrogen atmosphere were shown in Fig. 4. The decomposition temperature ( $T_{5\%}$ ) of two PIs were 520 °C and 475 °C, respectively. The mass fraction reduced by 10% were 545 °C and 495 °C, the residual rated at 790 °C were 50% and 49%,



Scheme 1. Synthetic route of monomers.



Scheme 2. Synthetic route of PIs.

respectively.

The  $T_g$  was one of the characteristic temperatures of polymer materials, which directly affects the use performance and processing performance of the material. The DSC of two PIs at 50–390 °C were tested by Q200 analyzer at a heating rate of 20 °C/min. The DSC curves of two PIs were shown in Fig. 5. The  $T_g$  of two PIs were 338 °C and 336 °C, respectively. The results of thermogravimetric analysis and DSC showed that the synthesized polyimides had good thermal stability and could withstand the high-temperature environment requirements of microelectronics manufacturing and high-tech applications of optoelectronic materials.

### 3.4. Dielectric properties and contact angle of polyimide film

The results of the dielectric constant of the PI films were measured at a frequency of 1KHz to 1 MHz at 20 °C and 50–60% relative humidity were shown in Fig. 5. Both of PI-a (fluorine content: 34.6%) and PI-b (fluorine content: 31.9%) films had a very low dielectric constant of 2.26 and 2.24(1 MHz), respectively. The excellent dielectric constant of two PIs was attributed to the strong electron withdrawing group of

trifluoromethyl, hyperbranched structures and the alicyclic structure. The hyperbranched structure increased the distance between molecules and reduced the force between molecules. And alicyclic structure could largely destroy the conjugated structure of polymer materials and inhibited the free flow of charges. Thus, the introduction of trifluoromethyl group, alicyclic structure and hyperbranched structure were an effective strategy to obtain low dielectric constant.

As shown in Fig. 6, the contact angles of two PI films were 101.49° and 83.57°, respectively. Especially the surface contact angle of PI-a film was hydrophobic. It was reported that the water droplet angle of the material is greater than 75°, then it can be proved that the water and oxygen barrier properties of the polymer material are relatively strong [42], which could ensure that the dielectric constant small in a humid environment better. In addition, as shown in Table 2, PI-a and PI-b had low water absorption, about 0.66% and 0.72%, which was attributed to the high fluorine content.

### 3.5. Mechanical properties of polyimides

The results of the mechanical properties of the films with a thickness

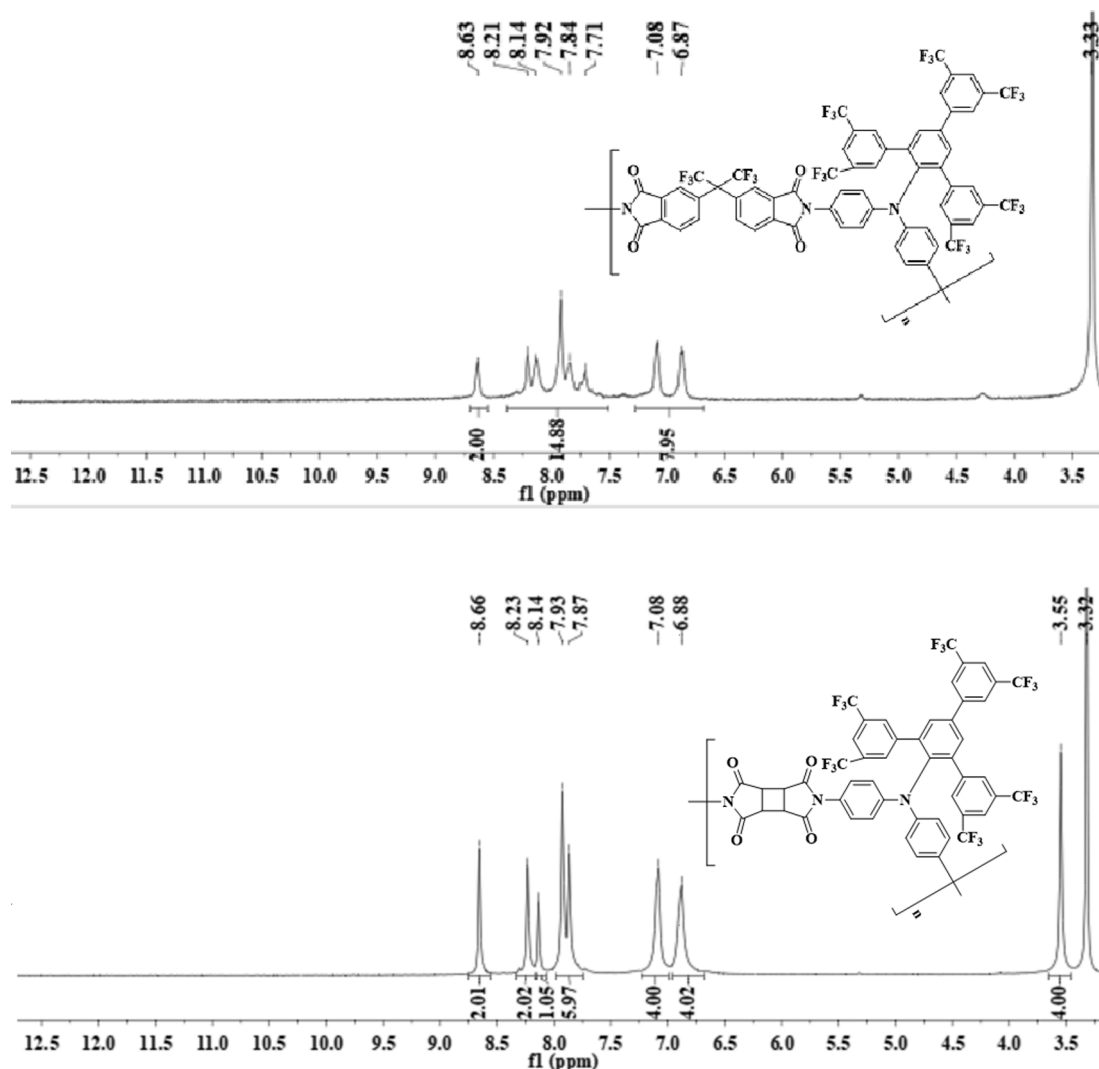


Fig. 1.  $^1\text{H}$  NMR spectra of PI-a and PI-b in  $\text{DMSO}-d_6$ .

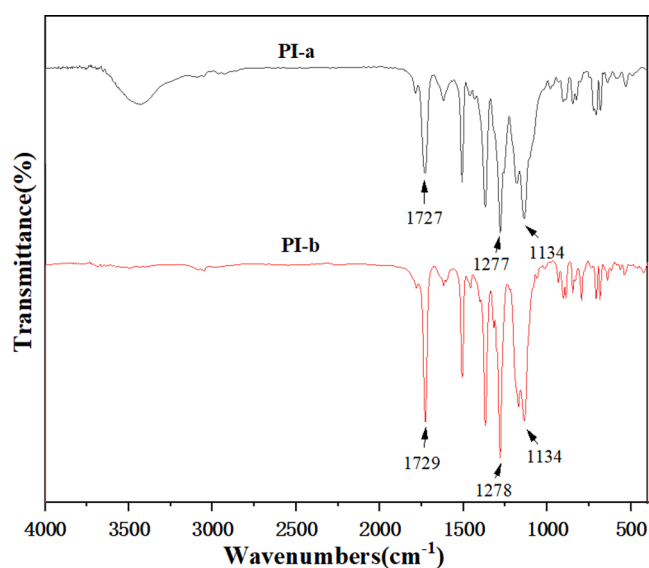


Fig. 2. FT-IR spectra of PI-a and PI-b.

of about 50  $\mu\text{m}$  and a width of 10 mm were tested are shown in Tab 2. The tensile strengths of two PIs were 59.8 and 48.4 MPa, respectively, and both PIs had smaller modulus. The elongation rate is 7.2% and 4.2%, which showed that the films had the characteristics of high hardness and good flexibility.

### 3.6. Optical properties of polyimides

Fig. 7 showed the transmittance of the PI-a and PI-b films at different wavelengths in the ultraviolet–visible spectrum at a thickness of  $20 \pm 3 \mu\text{m}$ . The transmittance of two PIs at 450 nm were 74% and 82%, respectively. The cut-off wavelengths are 395 nm and 390 nm, respectively. Strong electron-withdrawing fluorine-containing groups and alicyclic fragments effectively weakened the intermolecular and intramolecular CTC effect [43]. Compared with the reported transmittance of wholly aromatic polyimide, it had been greatly modified. Fig. 8.

## 4. Conclusion

Based on trifluoromethyl and alicyclic structure had greatly modified the optical, electrical properties and solubility of polyimides, this article mainly synthesized a new diamine monomer containing 6 trifluoromethyl groups by Suzuki reaction. Afterwards, two PIs with 34.6% and 31.9% fluorine content were synthesized with fluorinated aromatic



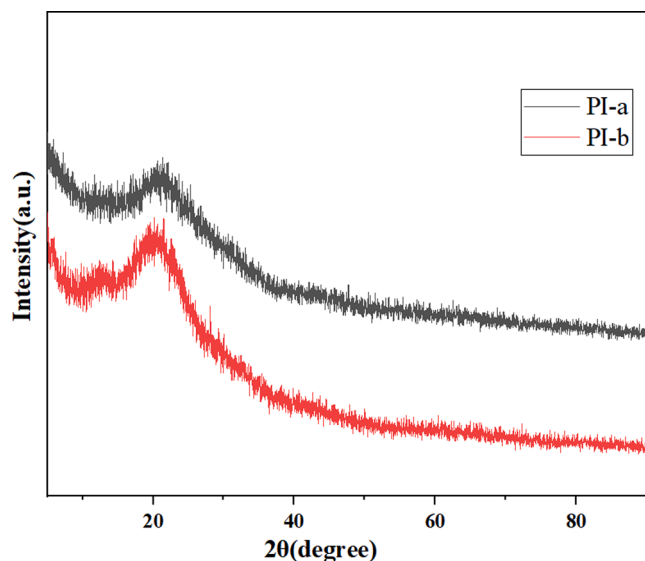
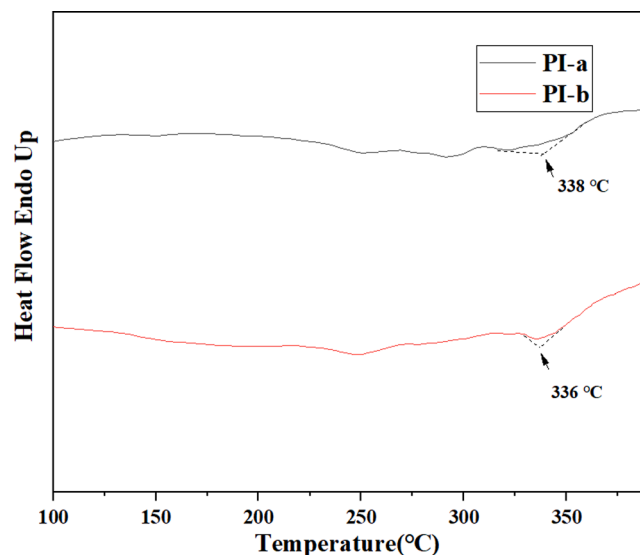
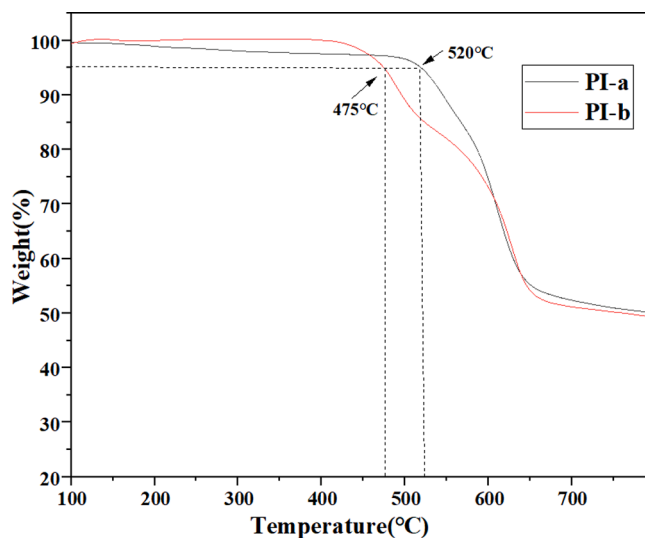
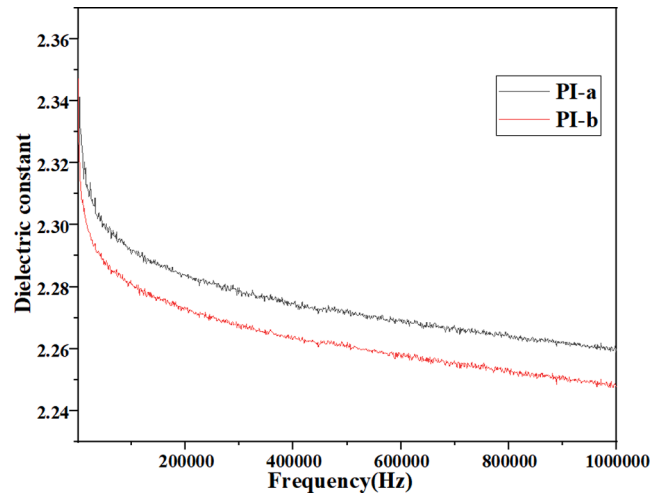
**Table 1**

The solubility of the PI-a and PI-b.

Samples	DMF	DMAc	NMP	DMSO	EA	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	Acetone
PI-a	++	++	++	++	++	++	++	+
PI-b	++	++	++	++	+	++	+	++

N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), ethyl acetate (EA).

++ = soluble at 20 °C; += partial soluble at 20 °C.

**Fig. 3.** X-ray diffraction of PI-a and PI-b.**Fig. 5.** DSC curves of the two PIs under a nitrogen atmosphere.**Fig. 4.** TGA curves of the two PIs under a nitrogen atmosphere.**Fig. 6.** The dielectric constant of two PI films at 1 kHz-1 MHz.

dianhydride 6FDA and alicyclic dianhydride CBDA through a two-step method. The two PIs had excellent solubility: PI-a was soluble in low boiling point solvents such as ethyl acetate, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> at room temperature. PI-b was soluble in low boiling point solvents acetone and CHCl<sub>3</sub> at room temperature. Good high temperature resistance: the decomposition temperature (T<sub>5%</sub>) of two PIs were 520 °C and 475 °C respectively, and the residual rate at 790 °C was 50% and 49%, respectively. The T<sub>g</sub> of two PIs were 338 °C and 336 °C, respectively. Both of PI-a and PI-b also had good mechanical properties; PI-a and PI-b tensile strengths were 59.8 and 48.4 MPa respectively, and both PIs had smaller modulus. And two PI films had a very low dielectric constant

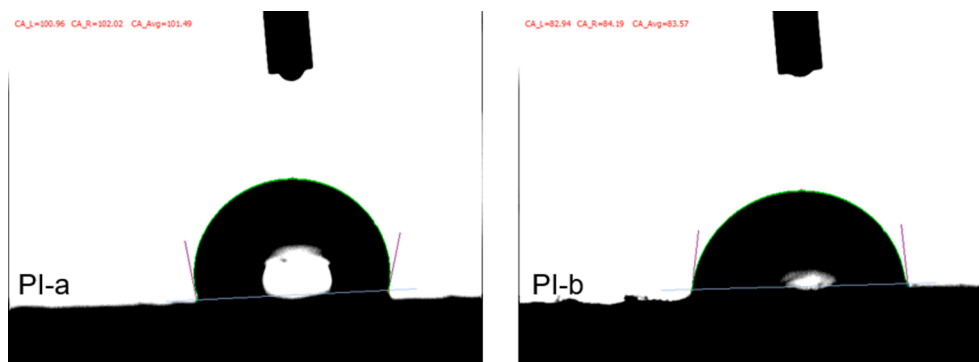
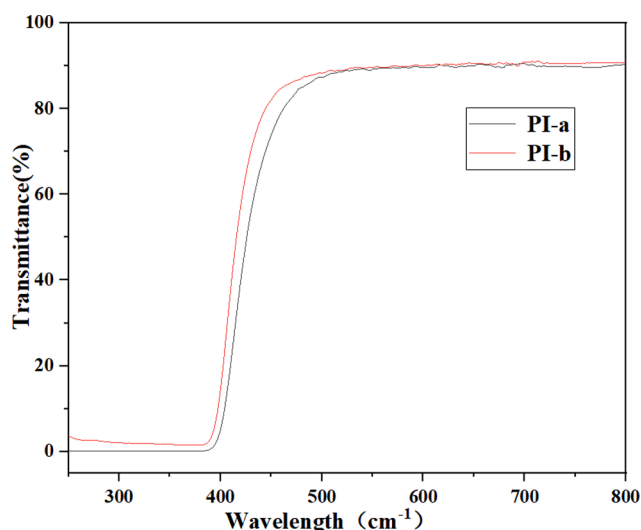
2.26 and 2.24, respectively, which were attributed to the alicyclic fragments and strong electron-withdrawing fluorine-containing groups. PI-a and PI-b had low water absorption; 0.66% and 0.72%, respectively. The contact angles were 101.49° and 83.57°, respectively. The light transmittance of two PIs high transparent films at 450 nm was 74% and 82%, respectively. The significant optical modification was mainly due to the weak electron-accepting alicyclic unit and the large tri-fluoromethyl electron withdrawing group. This work provided an effective strategy for synthesizing PIs with high transmittance, excellent solubility, low water absorption, high heat resistance and low dielectric constant. PIs films with good performance are expected to be used as flexible transparent substrates or dielectric layer insulating materials for integrated devices.

**Table 2**

Mechanical properties of two PI films.

Samples	T <sub>S</sub> (MPa)	T <sub>M</sub> (GPa)	E <sub>B</sub> (%)	T <sub>5%</sub> ( °C)	R <sub>790</sub> (%)	CA( °)	W <sub>A</sub> (%)
PI-a	59.8	1.05	7.2	520	50	101.49	0.66
PI-b	48.4	1.15	4.2	475	49	83.57	0.72

T<sub>S</sub>: tensile strength, T<sub>M</sub>: modulus, E<sub>B</sub>: elongation at break, T<sub>5%</sub>: 5% weight loss decomposition temperatures, R<sub>790</sub>: residual weight retention at 790 °C in nitrogen, CA: water contact angle, W<sub>A</sub>: water absorption rate at 25°C for 24 h.

**Fig. 7.** Contact angle of two PI films.**Fig. 8.** UV spectra of two PI films.**Author statement**

#Kaitai Hu had made the greatest contribution to this work. This project was funded by Jiangsu Provincial Higher Education (PAPD) key discipline development projects and industrial companies. Due to legal or ethical reasons, it is currently impossible to share the original/processed data needed to reproduce these findings.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Data availability**

Due to legal or ethical reasons, it is currently impossible to share the original/processed data needed to reproduce these findings.

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