

# Synthesis and properties of novel colorless and thermostable polyimides containing cross-linkable bulky tetrafluorostyrol pendant group and organosoluble triphenylmethane backbone structure

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## Abstract

A colorless and high temperature resistant fluorinated polyimide (PI) film based on a novel cross-linkable diamine monomer 4,4'-diamino-4''-(2,3,5,6-tetrafluoro-4-ethylenephenoxy) triphenylmethane (DFPTM) was successfully prepared. The special triphenylmethane backbone and the bulky tetrafluorostyrol pendant group in DFPTM gave the PI material eximious solubility in organic solvents, high tensile properties, good thermal stability, and excellent optical transparency (cutoff wavelength for 331 nm and light transmittance above 94% at 450 nm). Furthermore, the styryl could initiate self-crosslinking reaction to form a dense three-dimensional network structure by thermal curing. Hence, the cross-linked PI film showed superior combination property (including excellent resistance to solvents). Its  $T_g$  increased by 57.1–306.0°C, the 5% thermal weight-loss temperature improved by 10.2% to 500.0°C, and the tensile strength enhanced by 17.5% to 39.7 MPa. Moreover, after thermal curing, the cross-linked PI attained a lower elongation at break from 8.1 to 3.9%, and the thermal expansion coefficient reduced from 82.2 to 68.8 ppm/°C without obvious loss of optical transparency (cutoff wavelength for 347 nm and light transmittance remained 93.0% at 450 nm).

## KEYWORDS

colorless, cross-linking, fluorinated polyimide, high temperature stability, organosoluble

## 1 | INTRODUCTION

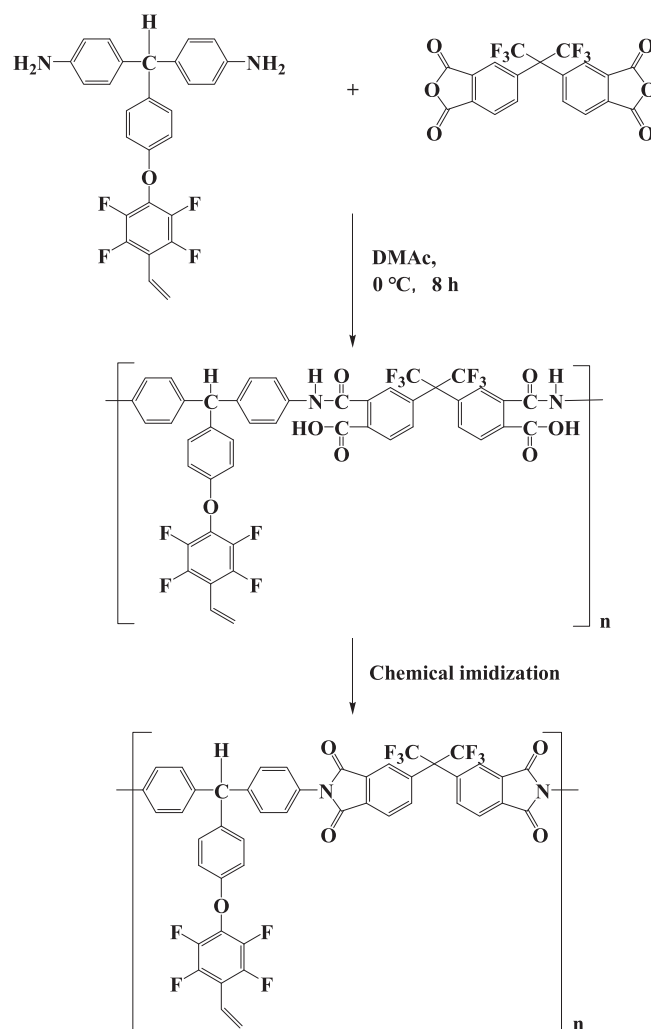
Over the past decade, with a rapid development of high-performance flexible wearable display technologies such as liquid crystal alignment layers, optical films, organic photovoltaic solar panels, flexible printed circuit boards and touch panels, colorless and high temperature resistant polyimide (PI) films have become one of the most attractive research directions.<sup>1–7</sup> The traditional PI film

called “gold film” has strong absorption from ultraviolet light to visible light due to the formation of inter-molecular and intramolecular charge transfer complex (CTC), thus showing a deep brown color, which limits its application in the optoelectronic field.<sup>8,9</sup> To this end, researchers have made great efforts to improve the optical transparency of PIs from the perspective of molecular structure design. Common methods include the introduction of alicyclic structures, fluorine atoms, bulky

substituents, twisted asymmetric structures and flexible links, and so forth, which could depress the close packing of polymer chains and disrupt the conjugation between the molecular chains to reduce the formation of CTC, and thereby increasing the light transmittance of the film.<sup>10–23</sup> However, the molecular structure designs that are in favor of optical transparency usually impair the thermal performance of the materials to some extent. For example, Zhou et al. synthesized a novel monomer *trans*-1,4-bis(2,3-dicarboxyphenoxy) cyclohexane dianhydride with alicyclic structure, which reacted with a variety of diamines to prepare a series of PIs. These PI films were highly transparent and had a maximum transmittance of 83% at 400 nm, but their  $T_g$ s were only 206–255°C.<sup>22</sup> Nevertheless, structural factors that increase thermal performance such as rigid aromatic rings and highly conjugated structures, will bring about the CTC effect, which can damage the optical transparency and solubility of materials. The case in point is the experiment conducted by Liu et al., where the rigid fluorenyl cardo structure introduced into the polymer backbones gave the PIs excellent heat resistance with  $T_g$ s as high as 337–378°C, whereas the best light transmittance of the films was only about 50% at 400 nm and for 83.7% at 450 nm.<sup>24</sup> In consequence, exploring a reasonable molecular design to achieve the balance of optical transparency and heat resistance has become the key to the preparation of colorless and high temperature resistant PI materials.

In addition, during the fabricated process of multi-layer optoelectronic devices, the polymeric materials must have good resistance to organic solvents. In another word, the initial materials could be dissolved in organic solvents, but insoluble after being films. In many cases, attaching cross-linkable pendant group is an efficient and simple strategy to realize the balance between processability and solvent resistance, and which could also be capable of effectively enhancing numerous properties of polymers involving a higher  $T_g$ , thermal stability, dimensional stability, mechanical property, chemical solvent resistance, and so forth. Benzocyclobutene, trifluorovinylether, terminal phenylethynyl, poly(maleic anhydride), and styryl groups are both frequently used cross-linking groups,<sup>25–32</sup> and in which the styryl-based thermal cross-linking reaction is readily accomplished by heating at a relative low temperature in the presence of any initiator.<sup>33–35</sup> Moreover, triphenylmethane and its derivative PIs have excellent solubility in high polar aprotic solvents, such as N-methyl pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF), due to their special twisted pyramid configuration, and have become worthy of attention in recent years. The research hotspots of the new soluble PIs have also given us available inspirations for molecular structure design.<sup>36–39</sup>

Based on the above viewpoints, we introduced a tetrafluorostyrol structure into the triphenylmethane type backbone to synthesize a novel fluorine-containing and heat cross-linkable diamine monomer 4,4'-diamino-4''-(2,3,5,6-tetra-fluoro-4-ethylenephenoxy) triphenylmethane (DFPTM) with high temperature resistance and high light transmittance. Figure S1 illustrates the preparation of DFPTM, first, 4-hydroxy benzaldehyde and aniline were catalyzed by protonic acid to obtain the intermediate 4,4'-diamino-4''-hydroxy triphenylmethane (DHTM), which was then combined with 2,3,4,5,6-pentafluorostyrol to produce the target monomer via a nucleophilic substitution. The PI material was prepared using DFPTM and commercial dianhydride 6FDA as raw materials (Scheme 1). Besides, in order to investigate the effect of introduction of bulky pendant group and cross-linkable structure on the comprehensive performance of the as-



**SCHEME 1** Synthesis of polyimide derived from 4,4'-diamino-4''-(2,3,5,6-tetrafluoro-4-ethylenephenoxy) triphenylmethane. DMAc, N,N-dimethylacetamide

synthesized PI, we conducted a series of measurements of the solubility, thermal stability, optical, and mechanical properties of polymers. These works are expected to provide more data and experience support for balance adjustment of the optical transparency and heat resistance of PI films, and are also worthy efforts for the preparation of high-performance PI materials suitable for flexible wearable display technology.

## 2 | EXPERIMENTAL

### 2.1 | Materials

Aniline, 4-hydroxybenzaldehyde, and aniline hydrochloride were purchased from the Adamas-beta, and used as received. 2,3,4,5,6-Pentafluorostyrol was obtained from the Hebei Bailingwei Super Fine Materials Co., and also used as received. 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was purchased from the Shanghai Dibai Chemical Technology Co., and was heated at 130°C under vacuum for 12 hr prior to use. Anhydrous triethylamine purchased from the Energy Chemical Co. was stored over 4 Å molecular sieves for use. The DMAc and acetic anhydride reagents used in the condensation reaction were analytical grade from the Tianjin Li'anlong New Material Co. and used without further purification.

### 2.2 | Measurements

Fourier transform infrared (FTIR) spectra of the monomers were measured on a Nicolet Impact 380 FTIR spectrometer by KBr pressed disc method, while FTIR spectra of the polymers were measured on a FTIR-650 liquid FTIR spectrometer of Tianjin Gangdong Technology Development Co. Nuclear magnetic resonance (NMR) spectra were performed on a Bruker 400 AVANCE III spectrometer operating at 400 MHz for  $^1\text{H}$  NMR, 376 MHz for  $^{19}\text{F}$  NMR and 101 MHz for  $^{13}\text{C}$  NMR using dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) as solvent. The chemical shifts relative to tetramethylsilane for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, and  $\text{CFCl}_3$  for  $^{19}\text{F}$  NMR as internal reference are reported on the ppm scale. MALDI-TOF-MS spectrometry adopted a Brook Dalton Autoflex tof/tofIII type matrix-assisted laser desorption-tandem time-of-flight mass spectrometer. The purities of the synthesized monomers were measured on an Agilent 1100 series high-performance liquid chromatograph (HPLC) with acetonitrile used as the mobile phase, the column temperature for 35.0°C, the flow rate for 1.00 ml/min and the ultraviolet (UV) detector wavelength for 249 nm. Besides, the melting range (m.r.) of the monomers was tested by a X-4 digital

microscope melting point analyzer of Gongyi Yuhua Instrument Co. The high-speed centrifuge used in the preparation of PI films is a TC16B centrifuge manufactured by Yancheng Kate Experimental Instrument Co. Gel permeation chromatograms (GPC) were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1 ml/min using polystyrol as a standard. Thermogravimetric analysis (TGA) on a TA TGA-Q500 instruments was used to assess the thermal stability of the PIs. The samples were evaluated over a temperature range of 25–800°C at a heating rate of 10°C/min under nitrogen.  $T_g$ s of the PI films were measured by differential scanning calorimetry (DSC) analysis with a TA DSC-Q20 instrument at a heating rate of 20°C/min from 100 to 400°C under nitrogen. The coefficient of thermal expansions (CTE) of the PI films were measured by a thermal mechanical analysis (TMA) using a TA-Q400 at a heating rate of 5°C/min. The CTE values were calculated as a mean coefficient of linear thermal expansion in the temperature range of 50–250°C after heating beyond  $T_g$  followed by cooling. Ultraviolet-visible (UV-vis) absorption and transmittance spectra were recorded on a GEN10S UV-vis spectrophotometer. Specifically, use a 50 mm × 50 mm × 0.8 mm quartz plate to sweep the background baseline, and then place the PI film-coated quartz plate in the UV-vis spectrophotometer for testing. The mechanical tests in tension were performed using a CMT6103 electronic universal testing machine of MTS Meters Industrial System at a constant crosshead speed of 10°C/min. The thicknesses of the films were measured on a AlphaStep D-100 step film thickness gauge manufactured by American KLA-Tencor company. According to ASTM D2765-16, gel content is an indicator reflecting the degree of cross-linking of the sample. The simplified test method is as follows, immerse the accurately weighed cross-linked PI in DMAc solvent for 24 hr, the residue after fully dry in a 120°C vacuum oven for 48 hr was taken as the gel component, and finally calculate the gel content (G%) according to the gel content formula Equation (1).

$$G\% = \frac{W_2}{W_1} \times 100\% \quad (1)$$

where  $W_1$  and  $W_2$  are the weights of the samples before immersing and after drying, respectively.

### 2.3 | Synthesis of monomers

#### 2.3.1 | Synthesis of DHTM

Intermediate DHTM was prepared according to the previous literature.<sup>40</sup> Concretely, a mixture of p-hydroxybenzaldehyde

(12.20 g, 0.10 mol), aniline hydrochloride (1.31 g, 0.01 mol), and aniline (27.90 g, 0.30 mol) were charged in a 100 ml three-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet, thermometer, Dean-Stark water separator, and a reflux condenser. The apparatus was purged with nitrogen. The reaction mixture was refluxed at 120°C for 3 hr to ensure complete dehydration. Then, 20 ml of ethanol was added into the cooled mixture, which was heated to 80°C for another 3 hr to dissolve the lumpy material afterwards. A pink powder product was filtered out from the entire mixture after cooling and washed with small amount of ethanol and water to remove the aniline residue and salts. Finally, purple needle crystal was obtained after recrystallization from *n*-propanol three times. Yield: 49.3%. M.r.: 215.3–216.7°C. Purity: 99.99% (HPLC).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 9.14 (s, 1H), 6.83 (d,  $J$  = 8.5 Hz, 2H), 6.69 (d,  $J$  = 8.4 Hz, 4H), 6.63 (d,  $J$  = 8.5 Hz, 2H), 6.45 (d,  $J$  = 8.4 Hz, 4H), 5.05 (s, 1H), 4.85 (s, 4H). FTIR (KBr,  $\text{cm}^{-1}$ ): 3,382 (O—H), 3,318, 3,192, 3,030 (N—H), 2,856 (C—H), 1,618, 1,508 (Ph, C—C), 1,244 (C—O). Mass spectrum:  $m/z$  288.4.

### 2.3.2 | Synthesis of DFPTM

DHTM (3.36 g, 11.60 mmol), calcium hydride (0.98 g, 23.20 mmol), cesium fluoride (0.18 g, 1.16 mmol), and 2,3,4,5,6-pentafluorostyrol (2.72 g, 14.00 mmol) were added into a 100 ml three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and outlet, and a reflux condenser. Then, DMAc (52 ml) was added into the flask under the nitrogen atmosphere. The mixture was heated to 80°C with stirring under nitrogen in the dark for 18 hr. After cooled to room temperature, it was filtered through a G6 sand core funnel to remove inorganic solids, and excess DMAc solvent was distilled off under vacuum. The residue was then purified by silica gel column chromatography (*n*-hexane/ethyl acetate, gradient elution) to afford the pure product, which was finally recrystallized three times with ethyl acetate/*n*-hexane mixed solvent to obtain light golden fine needle crystal DFPTM. Yield: 51.7%. M.r.: 158.2–160.1°C. Purity: 99.89% (HPLC).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 7.12–6.97 (m, 4H), 6.84–6.64 (m, 5H), 6.47 (d,  $J$  = 8.4 Hz, 4H), 6.06 (d,  $J$  = 18.0 Hz, 1H), 5.82 (d,  $J$  = 11.8 Hz, 1H), 5.16 (d,  $J$  = 11.7 Hz, 1H), 4.97 (s, 4H). <sup>13</sup>CNMR (101 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 155.21, 147.11, 143.91, 141.90, 140.41, 132.12, 130.77, 129.76, 124.62, 122.18, 115.25, 114.24, 113.19, and 54.21. <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): –143.66 ~ –144.62 (m, 2F) and –155.38 ~ –157.03 (m, 2F). FTIR (KBr,  $\text{cm}^{-1}$ ): 3,425, 3,330, 3,210 (N—H),

2,867 (C—H), 1,214, 1,072 (C—O—C), 968 (=C—H). Mass spectrum:  $m/z$  463.2.

## 2.4 | Synthesis of PIs

### 2.4.1 | Synthesis of polymers

The PI was prepared by a two-step chemical imidization method. Specifically, a 100 ml Schlenk reaction flask was charged with diamine DFPTM (1.39 g, 3.00 mmol) and 19.4 ml DMAc in an ice water bath. The solution was stirred under nitrogen atmosphere until diamine dissolved completely, and then equimolar amount of 6FDA (1.33 g, 3.00 mmol) was added into the flask. The reaction mixture was stirred at 0°C for 8 hr under a nitrogen atmosphere to form polyamic acid (PAA) solution with 15 wt% solid content. Chemical imidization was performed via the addition of 1.2 g of anhydrous triethylamine as a catalyst and 1.2 g of acetic anhydride as a dehydrating agent into the PAA solution. The mixture was stirred at 60°C for another 6 hr to yield a viscous PI solution. Then the solution was poured into a mixed solution of anhydrous methanol/deionized water (volume ratio 1/1) to give a precipitate and washed thoroughly. After that, the obtained polymer was soaked in the boiling anhydrous methanol for 12 hr to remove the impurities wrapped inside of that. Finally, the milk-white PI product was dried in a 100°C vacuum oven for 24 hr. Yield: 98.4%.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.13 (t,  $J$  = 18.5 Hz, 2H), 7.94 (d,  $J$  = 7.2 Hz, 2H), 7.75 (s, 2H), 7.42 (d,  $J$  = 8.1 Hz, 4H), 7.38–7.25 (m, 4H), 7.20 (t,  $J$  = 11.5 Hz, 2H), 7.11 (d,  $J$  = 8.2 Hz, 2H), 6.77–6.61 (m, 1H), 6.05 (t,  $J$  = 14.4 Hz, 1H), 5.90–5.68 (m, 2H). <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): –62.29 ~ –63.43 (m), –143.74 ~ –144.28 (m), –155.68 ~ –156.15 (m). FTIR ( $\text{cm}^{-1}$ ): 1,784, 1,726 (C=O), 1,377 (C—N).

### 2.4.2 | Preparation of PI films and thermally cross-linked PIs

The synthesized PI (0.8 g) was dissolved in DMAc (8.0 ml) overnight. Afterwards, the solution was then filtered through G3 sand core funnel, and centrifuged at 1,500 r/min for 10 min to eliminate air bubbles. The pure polymer solution was then cast directly on a 50 mm × 50 mm × 0.8 mm quartz plate (for optical performance test) and a 10 cm × 10 cm glass plate (for mechanical performance test after stripped off the plates by immersing into water) with a programmed procedure (60°C, 6 hr; 80°C, 6 hr; 100°C, 6 hr; 120°C, 6 hr) in a vacuum oven to remove the solvents. After dried thoroughly,



tough and flexible films of PIs were accomplished. The thicknesses of the films were in the range of 30–70 nm.

To measure the properties of cross-linked films (recorded as C-L PI), the PI films were put into a vacuum oven and cured at 260°C for 2 hr.

### 3 | RESULTS AND DISCUSSION

#### 3.1 | Synthesis and characterization of monomers

The structure of the monomers was characterized by FTIR, NMR, and MALDI-TOF-MS spectroscopy. Figure 1 shows the FTIR spectra of the intermediate DHTM and the novel diamine DFPTM. As shown, the C—O bond of DHTM gave characteristic peak at  $1,244\text{ cm}^{-1}$ , while the hydroxyl exhibited characteristic absorption at  $3,382\text{ cm}^{-1}$  (O—H stretch), which proved the successful introduction of phenolic hydroxyl group. In addition, the three strong stretching bands at about  $3,318$ ,  $3,192$  and  $3,030\text{ cm}^{-1}$  corresponded to the stretch of amino group. After the nucleophilic substitution reaction, the characteristic absorptions of the phenolic hydroxyl group disappeared, and the vinyl moiety of DFPTM gave absorption band at  $968\text{ cm}^{-1}$  (C=C—H out of plane vibrations). Meanwhile, ether bond C—O—C exhibited the anti-symmetric and symmetric stretching vibration absorption peaks at  $1,214$  and  $1,072\text{ cm}^{-1}$ , respectively. Both of them were compelling evidences

that the cross-linkable tetrafluorostyrol group had been successfully introduced into the molecular structure of diamine DFPTM.

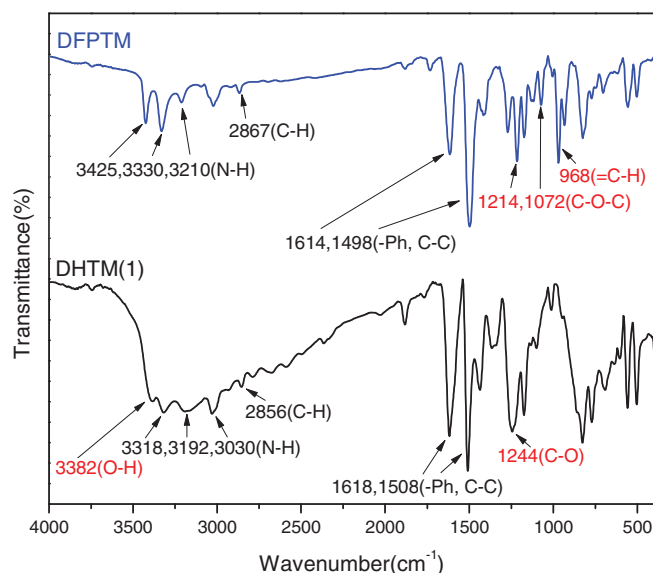
To confirm the structure of DFPTM further, the  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR, and  $^{13}\text{C}$  NMR spectra were also performed. As depicted in Figure 2(a), the single peak at 4.97 ppm was ascribed to the amino proton signal. The two characteristic resonances at 5.82 and 6.06 ppm were attributed to the protons H7 and H8 on the vinyl moiety of the tetrafluorostyrol units, while proton H6 appeared at 6.84–6.64 ppm due to its similar chemical shift to benzene ring proton H5. Besides, the signals at  $-155.99$  and  $-144.10$  ppm corresponded to the aromatic fluorine atoms F1 and F2 of tetrafluorostyrol structure in Figure 2(b). Besides, the absorption peaks at different 14 chemical shifts in the carbon spectrum were 155.21, 147.11, 143.91, 141.90, 140.41, 132.12, 130.77, 129.76, 124.62, 122.18, 115.25, 114.24, 113.19, and 54.21 ppm, respectively, corresponding to the carbon atoms at 14 different positions in the molecular structure of DFPTM. These results indicated the successful synthesis of the novel diamine monomer DFPTM.

In addition, the theoretical molecular molar mass of DFPTM was 464.0, and the molecular ion peak was 463.2 (M<sup>+</sup>) determined by the MALDI-TOF-MS spectrometry in Figure S2, which proved that the obtained diamine was consistent with the designed structure as well.

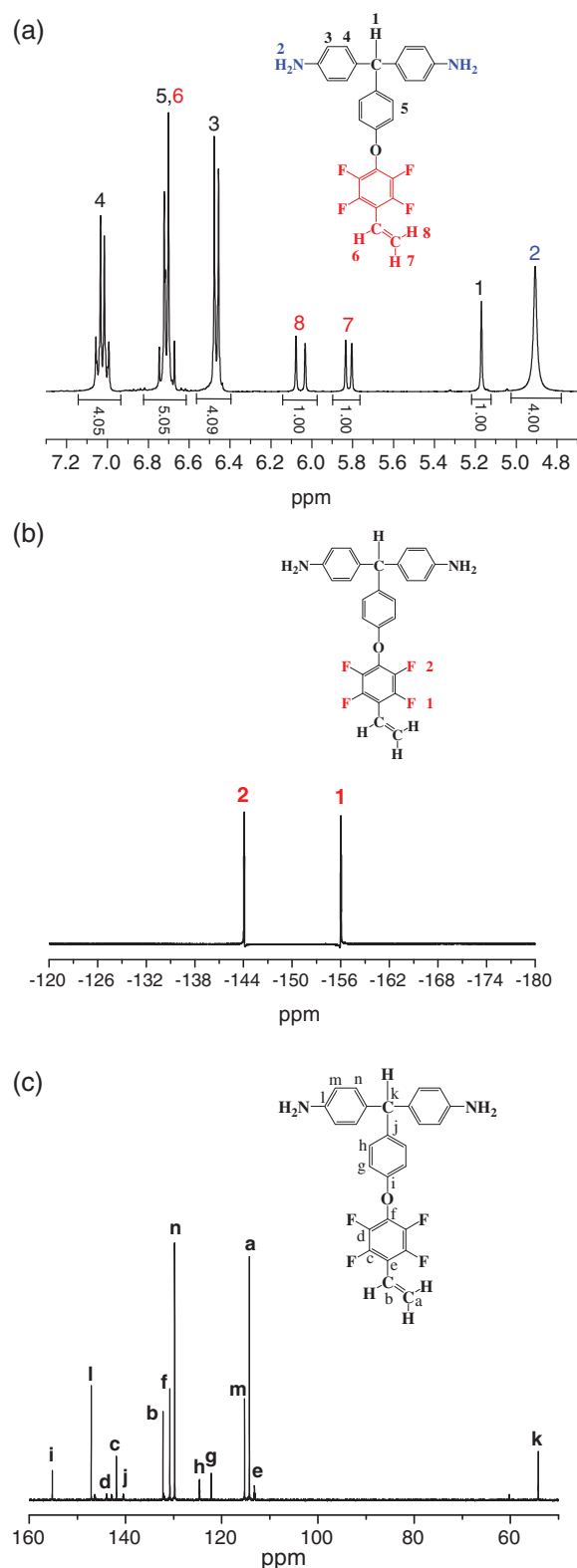
#### 3.2 | Synthesis and characterization of polymers

The novel fluorine-containing and heat cross-linkable PI was prepared in a conventional two-step procedure by the reaction of equal molar amounts of diamine DFPTM with commercially available aromatic dianhydride 6FDA in DMAc to form a precursor PAA, followed by chemical imidization, as shown in Scheme 1. The reduced viscosity  $\eta_{\text{sp}}/c$  of the PAA solution was 0.93 dL/g, which was measured using a Ubbelohde viscometer with a concentration of 0.5 g/dL in a constant temperature water bath at 30.0°C. The molecular weights of PIs were determined by GPC, and the results are all summarized in Figure S3. The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of polymers were  $6.01 \times 10^4$  and  $11.66 \times 10^4$ , respectively, with the polydispersity index value for 1.94, indicating that the synthesized PI possessed a high molecular weight.

The chemical structures of polymers derived from DFPTM and 6FDA were confirmed by FTIR and NMR spectroscopy. The typical FTIR spectra of the PAA and PI are shown in Figure 3. A series of characteristic signals of amic acid could be clearly observed. The wide absorption band around  $3,500\text{ cm}^{-1}$  was attributed to the stretching

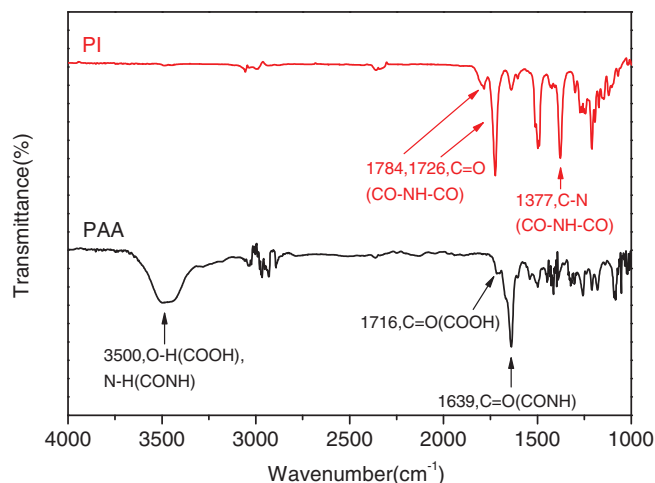


**FIGURE 1** Fourier transform infrared spectra of diamine monomers 4,4'-diamino-4''-hydroxy triphenylmethane (DHTM) and 4,4'-diamino-4''-(2,3,5,6-tetrafluoro-4-ethylenephenoxy) triphenylmethane (DFPTM) [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 2** (a) <sup>1</sup>H NMR, (b) <sup>19</sup>F NMR and (c) <sup>13</sup>C NMR spectra of 4,4'-diamino-4''-(2,3,5,6-tetrafluoro-4-ethylenephenoxy)triphenylmethane (DFPTM) in dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) [Color figure can be viewed at [wileyonlinelibrary.com](#)]

vibration absorption peaks of O—H (COOH) and N—H (CONH) bonds, while the C=O (COOH) and C=O



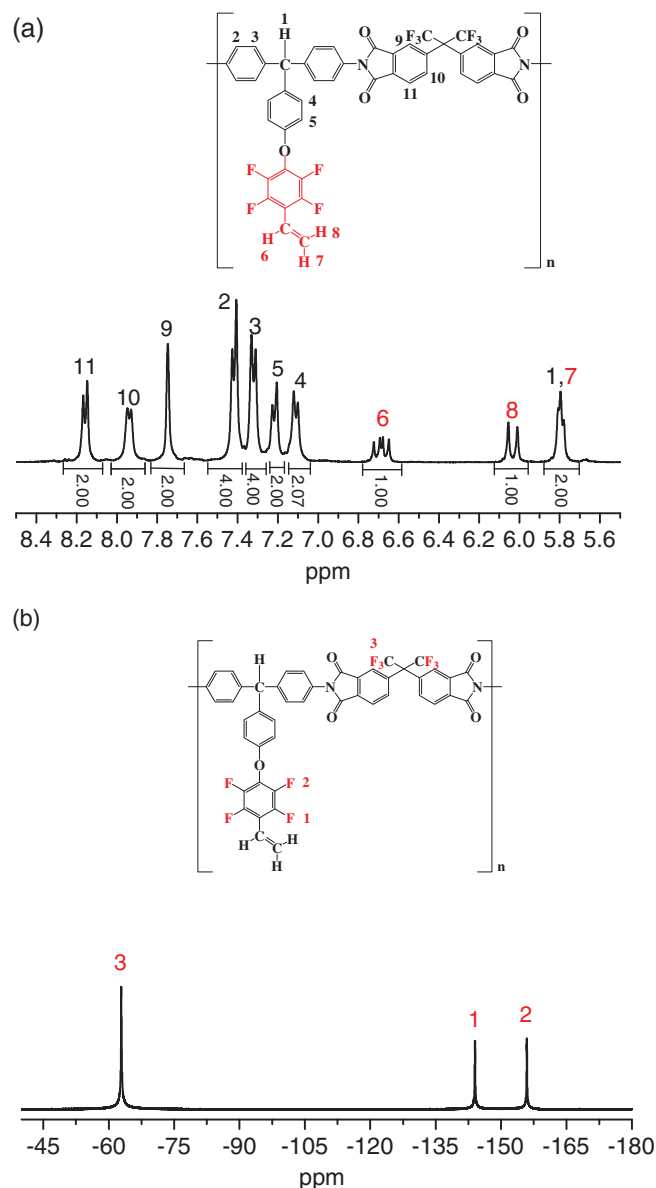
**FIGURE 3** Fourier transform infrared spectra of polyamic acid (PAA) and polyimide (PI) [Color figure can be viewed at [wileyonlinelibrary.com](#)]

(CONH) of precursor PAA gave characteristic absorption bands at 1,716 and 1,639 cm<sup>-1</sup>, respectively. In contrast, the characteristic signals of amic acid disappeared in the spectra of PI, meanwhile the characteristic absorption peaks of the imide ring near 1,784 and 1,726 cm<sup>-1</sup> due to C=O asymmetric and symmetric stretching, and 1,377 cm<sup>-1</sup> ascribing to C—N stretching appeared, indicating the complete imidization during cyclodehydration reaction.

Furthermore, it could be discovered that the structure of the obtained polymer was extremely in agreement with the designed molecular structure from <sup>1</sup>H NMR and <sup>19</sup>F NMR (as shown in Figure 4). In the <sup>1</sup>H NMR spectrum, three absorption peaks at 5.80, 6.03, and 6.70 ppm were observed and attributed to the protons on the vinyl moiety of tetrafluorostyrol group. No other aliphatic resonances exhibited, indicating that the tetrafluorostyrol units were introduced successfully into the PI and were stable to the polymerization and imidization conditions used. Moreover, the characteristic resonances at 7.75, 7.94, and 8.13 ppm corresponded to the aromatic protons H9–H11 in the dianhydride 6FDA unit, respectively. On detailed examination of the <sup>19</sup>F NMR spectrum, it was observed that two little peaks around at –144.02 and –155.92 ppm belonged to the F1 and F2 of the tetrafluorostyrol units, respectively. The absorption peak at –62.90 ppm was assigned to the fluorine atoms of –CF<sub>3</sub> in the anhydride unit. All the characterizations demonstrated that the desired PI was synthesized successfully.

### 3.3 | Solubility of PIs

The solubility of PI was tested in various organic solvents and the results are given in Table 1. It could be observed



**FIGURE 4** (a) <sup>1</sup>H NMR and (b) <sup>19</sup>F NMR spectra of polyimide in dimethyl sulfoxide-*d*<sub>6</sub> [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

that the as-synthesized PI in this work possessed excellent solubility in polar solvents such as DMSO, DMAc, and DMF, even in less polar solvents such as DCM, EtOAc, acetone, and THF, whereas the commercial aromatic PI (Kapton) as reference was insoluble in all the test solvents even on heating. This enhanced solubility is mainly attributed to the highly twisted non-planar structure of the triphenylmethane backbone, which has pyramid spatial configuration, and the three aromatic rings connected to the central carbon atom with lower rotation barrier can be highly rotated around the single bond. Such structure can increase the steric hindrance, and thus reduce the interactions between the molecular chains.<sup>35</sup> Coupled with the introduction of bulky tetrafluorostyrene units resulting in the increased free volume of polymer chains may further facilitate the diffusion and the solvation of solvents. In addition, the strongly electronegative F atoms and —CF<sub>3</sub> groups contained in the diamine and dianhydride units are also beneficial to increase solubility.<sup>41</sup>

Compared with the uncross-linked PI, the PI film after cross-linking exhibited excellent solvent resistance, which was insoluble in all the tested solvents even when heated, only showing slight swelling. This phenomenon can be attributed to the formation of a three dimensional network structure in polymer resulting from the self-crosslinking of the tetrafluorostyrene units at high temperatures. What is noticeable is that, this characteristic of being soluble before cross-linking and insoluble after that makes our PI materials as potential candidate for practical application in optoelectronic devices with higher processing requirements.

### 3.4 | Thermal cross-linking and thermal properties of PIs

The thermal properties of obtained PIs were monitored by DSC, TGA, and TMA. The results are listed in Table 2. As aforementioned, the unsaturated vinyl moiety in the

**TABLE 1** Solubility of PIs in organic solvent

Polymers	Solvent									
	DCM	EtOAc	Acetone	DMSO	DMF	DMAc	THF	CH <sub>3</sub> CN	Ethanol	Methanol
PI	++	++	++	++	++	++	++	—	—	—
C-L PI	—	—	—	—	—	—	—	—	—	—
Kapton	—	—	—	—	—	—	—	—	—	—

**Notes:** Qualitative solubility was determined with as 10 mg of polymer in 1 ml of solvent. “++” represents soluble at room temperature and “—” represents insoluble on heating to boiling point.

**Abbreviations:** CH<sub>3</sub>CN, acetonitrile; DCM, dichloromethane; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide; EtOAc, ethyl acetate; THF, tetrahydrofuran.

**TABLE 2** Mechanical properties, thermal properties, and gel content of PIs

Polymer	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (MPa)	$T_g^a$ (°C)	$T_{5\%}^b$ (°C)	$T_{10\%}^b$ (°C)	CTE <sup>c</sup> (ppm/°C)	Gel content <sup>d</sup> (%)
PI	33.8	8.1	944.1	248.9	453.9	491.6	82.2	0
C-L PI	39.7	3.9	1,015.9	306.0	500.0	532.8	68.8	99.7

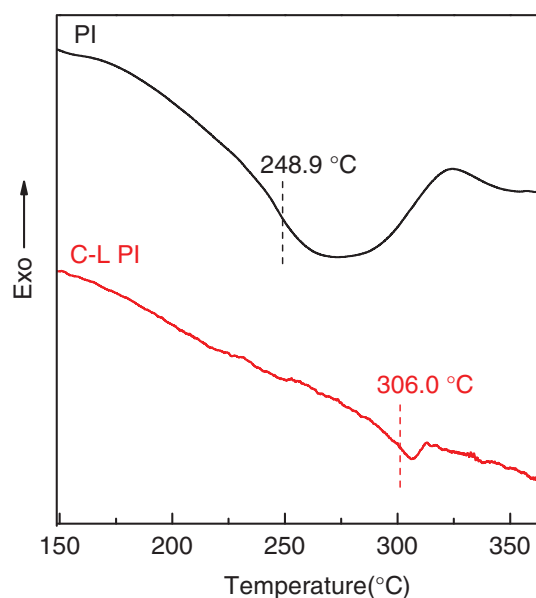
Abbreviations: CTE, coefficient of thermal expansion; DSC, differential scanning calorimetry; PI, polyimide; TGA, thermogravimetric analysis; TMA, thermal mechanical analysis.

<sup>a</sup> $T_g$ s were measured by DSC with a heating rate of 20°C/min in N<sub>2</sub>.

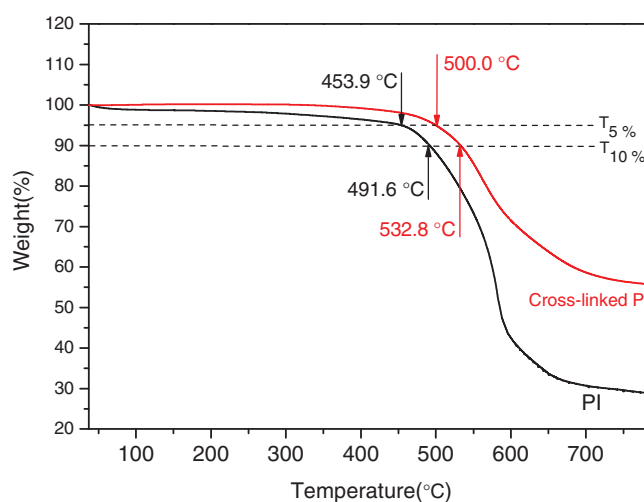
<sup>b</sup>Temperature at 5 and 10% weight-loss were recorded by TGA at a heating at 10°C/min in N<sub>2</sub>.

<sup>c</sup>CTE values of PI films were measured by TMA at a heating rate of 5°C/min in N<sub>2</sub>, which were calculated as a mean coefficient of linear thermal expansion in the temperature range of 50–250°C after heating beyond  $T_g$  followed by cooling.

<sup>d</sup>Gel content for cured samples.

**FIGURE 5** Differential scanning calorimetry curves of polyimide (PI) and C-L PI [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/terms-and-conditions)]

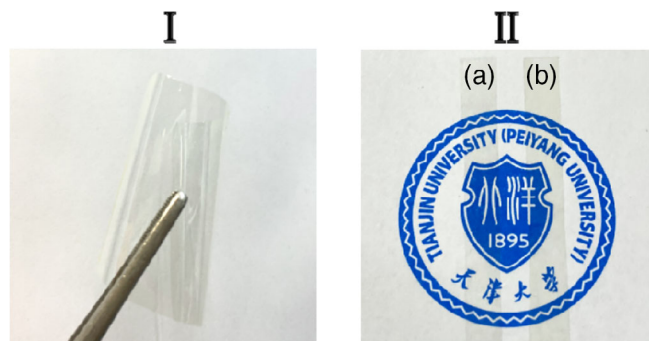
fluorinated polymers can initiate a cross-linking reaction by heating in the absence of any initiator. For this reason, DSC experiments were conducted at a heating rate of 20°C/min in nitrogen to investigate the thermal cross-linking and thermal properties of PIs. As shown in Figure 5, the  $T_g$  of the PI before cross-linking was 248.9°C, and the intense exothermic peak after 275°C was ascribed to the reaction of the vinyl moiety for the uncross-linked polymer. After curing at 260°C for 2 hr under vacuum, the  $T_g$  of the C-L PI increased by 22.9% to 306.0°C, and the cross-linking exothermic peak disappeared as well. Besides, according to Equation (1), the gel content of the cross-linked PI was calculated to be 99.7%, indicating that there had been a dense cross-linked network in the C-L PI with good solvent resistance after thermal curing adequately.

**FIGURE 6** Thermogravimetric analysis curves of polyimide (PI) and C-L PI [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/terms-and-conditions)]

The thermal stability of PIs was revealed by TGA at a heating rate of 10°C/min under nitrogen. As shown in Figure 6, the 5 and 10% weight-loss temperatures of the uncross-linked PI were 453.9 and 491.6°C, respectively. By contrast, the thermal stability of the C-L PI improved approximately 10%,  $T_{5\%}$  and  $T_{10\%}$  of which increased to 500.0 and 532.8°C, respectively, resulting from the highly cross-linked network.

The CTE of the C-L PI films decreased from 82.2 to 68.8 ppm/°C measured with TMA. The CTE value is dependent on both backbone chemistry and the morphology and strongly influenced by molecular orientation. In general, polymers consisting of rigid backbone structures and causing a higher degree of in-plane chain orientation have shown relatively low CTE value.<sup>42–44</sup> The superior dimensional stability of the cured PI film may be that the cross-linking restricts the segment movement of the polymer macromolecules, and hence



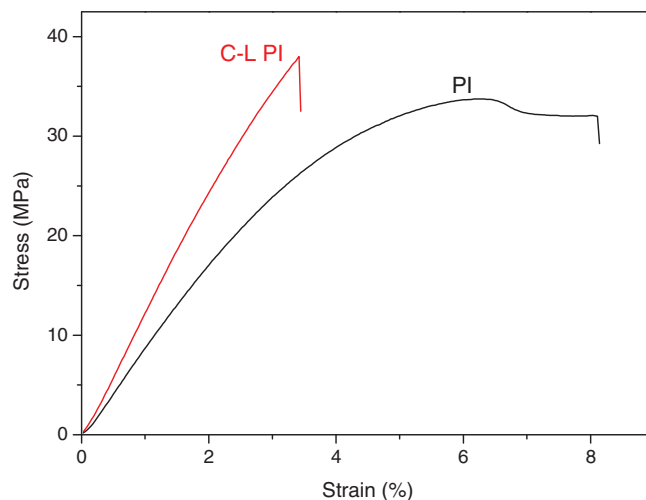


**FIGURE 7** (I) Photograph of the C-L polyimide (PI) film; (II) Comparison photograph of the (a) PI film and (b) C-L PI film [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

effectively enhancing the molecular rigidity and chain orientation of polymers.

### 3.5 | Optical properties of PIs

The photographs of PI films are shown in Figure 7, and it can be observed that both of the two films exhibited excellent optical transparency. The optical properties of the PI films were investigated by UV–vis spectroscopy as shown in Figure S4. The UV–vis spectra of the uncross-linked PI film presenting colorless observed in the visible region showed the  $\lambda_0$  value was 331 nm, and its corresponding transmittance ranges at the range from 400 to 450 nm exhibited from 75.8 to 94.4%. We know that most traditional PIs have highly conjugated aromatic structures, which facilitate formation of CTC, resulting in strong absorption in the ultraviolet and visible regions, and hence endowing the films with dark color. Nevertheless, our PI material was introduced a highly twisted triphenylmethane backbone and a bulky tetrafluorostyrol pendent group in their diamine moieties, which on the one hand increased the distance between polymer chains and reduced the chain packing density, on the other hand hindered the flow of electron clouds and destroyed the conjugation between molecular chains. This would decline the formation probability of CTC, so that the light transmittance and solubility of PI films were significantly improved.<sup>11,12</sup> In addition, the promotion of  $-\text{CF}_3$  groups to the film transparency was the weakening intermolecular dispersion forces due to low polarizability of its C–F bond.<sup>41</sup> In contrast, the optical performance of the C-L PI film was slightly lower than that of uncross-linked PI film with transmittance values at 400 and 450 nm for 62.1 and 93.0%, and the  $\lambda_0$  for 347 nm. The reason for the decrease maybe that the dense cross-linked network structure could strengthen the interaction between the molecular chains and facilitate the flow of



**FIGURE 8** The stress–strain curves of polyimide (PI) and C-L PI films [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

the electron clouds, which are conducive to the formation of CTC.

### 3.6 | Mechanical properties of PIs

The organosoluble PIs obtained in this work could afford flexible and tough films via solution casting, and the films before and after curing were subjected to tensile testing, yielding the mechanical properties values as shown in Table 2, and the stress–strain curves are shown in Figure 8. The uncross-linked PI film was in possession of tensile strength of 33.8 MPa, elastic modulus of 944.1 MPa, and elongation at break of 8.1%. After thermal cured at 260°C for 2 hr, the mechanical characterizations of the C-L film was 39.7 MPa, 1,015.9 MPa, and 3.9%, respectively, by comparison. As mentioned in the introduction, bulky pendent groups and twisted noncoplanar structures decreasing the symmetry and effectiveness of polymer chain stacking are favorable structures to improve light transmittance and solubility, but also unfavorable for mechanical properties. As a consequence, the obtained organosoluble PI film was relatively brittle than the conventional films. But it can be determined that cross-linking can effectively improve the mechanical properties of the PIs.

## 4 | CONCLUSIONS

The rapid development of optoelectronics fields has intensified the demand for PI flexible substrates with high temperature resistance and high transparency, while what the crucially important is the exploitation of high-performance

PI monomers. In this article, a novel cross-linkable diamine DFPTM was synthesized for the first time, which reacted with a commercial dianhydride 6FDA to produce a high molecular weight organosoluble PI film material. After cross-linking, the dense network structure gave the C-L PI excellent solvent resistance and superior thermodynamic properties with  $T_g$  increasing from 248.9 to 306.0°C,  $T_{5\%}$  improving from 453.9 to 500.0°C, and the tensile strength enhancing from 33.8 to 39.7 MPa, meanwhile the CTE of which reducing from 82.2 to 68.8 ppm/°C, and the elongation at break decreasing from 8.1 to 3.9% without significant loss of optical transparency. In a word, what is worthy is that, our cross-linkable PI materials with balanced high temperature resistance and high transparency prove to be a potential flexible optical film for practical application in optoelectronic devices.

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