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# High heat-resistant polyimide films containing quinoxaline moiety for flexible substrate applications

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Keywords: Quinoxaline Polyimide Thermostable	The development of thermostable polyimides (PIs) is urgently required for application in traditional aerospace and newly designing flexible-display substrates. The root to obtain intrinsic heat-resistant PIs is to seek novel monomers. Based on the high bond energy of quinoxaline, several quinoxaline diamines, including 3/2-(4- aminophenyl)-2/3-quinoxalin-6-amine ( <b>QHDA</b> ), 3/2-(4-aminophenyl)-2/3-phenyl quinoxalin-6-amine ( <b>QBDA</b> ), and 3/2-(4-aminophenyl)-2/3-methylquinoxalin-6-amine ( <b>QMDA</b> ) were synthesized, and the corresponding PI films were prepared with four aromatic dianhydrides. The introduction of a quinoxaline moiety provided the PI films with excellent thermal properties and an advanced mechanical performance. The <b>QHDA</b> -PIs possessed a high thermal stability with a 5% mass-loss temperature ( $T_d^{5\%}$ ) of 528–560 °C, a glass-transition temperature ( $T_g$ ) of 413–444 °C and a low coefficient of thermal expansion (CTE) of 1 ppm/K for <b>QHDA-m</b> because of its better linearity and closer packing. This study established design rules to tune the properties of quinoxaline PIs by side-

## 1. Introduction

Aromatic polyimides (PIs) have attracted extensive attention owing to their excellent performances, such as their outstanding heat endurance, superior chemical resistance and good mechanical and dielectric properties [1,2]. Among the various polyimides, thermostable PIs are important because of their significant applications, including traditional aerospace [3,4] and newly developing flexible active-matrix organic light-emitting-diode [5]. PI films play a key role as flexible substrates instead of hard glass substrates to produce flexible displays. The greatest challenge towards implementation of this technology is in the design and preparation of PI films with a higher heat resistance to withstand extremely high processing temperatures (450 °C) during the fabrication of low temperature polysilicon thin film transistors (LTPS TFTs) [6]. Glass transition temperature (Tg) indicates the ultimate-use temperature of polymer materials, it is believed to be a fundamental characteristic of the heat tolerance, and high-Tg polymers are in great demand for high-performance applications [7].

Extensive research has aimed to enhance the Tg of polyimides, including the use of nanocomposite [8-10], chemical crosslinking [11, 12] and novel monomer types [3,13,14]. However, the use of extra additives can only improve the Tg to a limited extent, and the key to fabricating high-T $_{\rm g}$  polyimide films is in the design and synthesis of novel monomers to obtain intrinsic thermostable PIs. It is generally accepted that a heterocyclic skeleton can improve the thermal properties of polymers by resonance with benzene rings. Many heterocyclic monomers have been synthesized [15-19], and their corresponding PIs were proven to have good heat resistance intrinsically. Quinoxaline is an important heterocyclic structure that exhibits a high bond energy and lone pair electrons of nitrogen atoms [20]. Hergenrother et al. have reported quinoxaline dianhydride and corresponding PIs with a high T<sub>g</sub> [21]. Diamines with a quinoxaline bulky pendent group have been applied to improve the PI solubility without harming the thermal properties [22,23]. However, quinoxaline diamines, which is easier to synthesize than its dianhydride, as polymer chains to improve the PI heat resistance has rarely been investigated. Therefore, the development

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in molecular design of quinoxaline monomers remains urgent to prepare high performance polyimides or other heterocyclic polymers.

Because steric hindrance effects can increase the  $T_g$  of polymers by restricting molecular-segment rotation, in this study, a series of quinoxaline diamines with various pendant groups, including 3/2-(4-aminophenyl)-2/3-quinoxalin-6-amine (QHDA), 3/2-(4-aminophenyl)-2/3phenyl quinoxalin-6-amine (QBDA), and 3/2-(4-aminophenyl)-2/3methylquinoxalin-6-amine (QMDA), were synthesized and polycondensated with four conventional dianhydrides, which was expected to provide PIs with enhanced thermal properties. The relationship between monomer structures and polymer properties was also discussed to design and manufacture intrinsic thermostable PI films.

# 2. Experimental section

## 2.1. Materials

All commercial materials were used as received from Energy Chemical or Adamas-beta, Alfa Aesar, TCI, and Acros unless otherwise noted. The 1,2,4,5-Benzenetetracarboxylic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzo-phenonetetracarboxylic dianhydride (BTDA), and 3,3',4,4'-oxy-diphthalic dianhydride (ODPA) were from ChinaTech (Tianjin) Chemical Co., Ltd, and were used without further purification. H<sub>2</sub> was from Wetry (99.999% purity).

#### 2.2. Synthesis of QHDA

Scheme 1 shows the synthesis route of the QHDA diamine monomer. A solution of 4-nitrobenzene-1,2-diamine (7.66 g, 50 mmol) and 2bromo-1-(4-nitrophenyl)ethanone (12.20 g, 50 mmol) in anhydrous dimethyl sulfoxide (DMSO) (100 mL) was stirred vigorously at room temperature for 5 h. The reaction was guenched by water addition (100 mL), and then the mixture was poured into excess water (1 L). During vacuum suction filtration, excess DMSO was removed by water rinsing and the precipitate was filtered. The solid was dissolved in dichloromethane followed by washed with brine (200 mL  $\times$  3), and dried over MgSO<sub>4</sub>. The organic solvent was evaporated and the resulting residue was purified by flash-column chromatography to give the corresponding precursor **QHDN** (8.50 g, 57%). <sup>1</sup>H nuclear magnetic resonance (NMR) (DMSO-d<sub>6</sub>, 500 MHz): δ 9.92-9.91 (1H), 9.00-8.98 (1H), 8.70-8.67 (2H), 8.65–8.61 (1H), 8.50–8.48 (2H), 8.45–8.42 (1H) (Fig. S1). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz): δ 151.50, 149.33, 148.59, 147.68, 146.90, 141.47-141.46, 140.72-140.67, 144.26. 131.87-131.42. 129.80-129.62, 125.84-125.47, 124.67-124.40 (Fig. S2).

According to the literature [24,25], 5% Pd/C (0.90 g) was added to a solution of dinitro compound (**QHDN**) (8.50 g, 29 mmol) in anhydrous MeOH (200 mL). The reaction atmosphere was replaced with  $H_2$  for three times. The reaction mixture was stirred overnight and reduced by  $H_2$  at room temperature and atmospheric pressure to obtain dark yellow

product, then recrystallized with MeOH to provide the corresponding brighter yellow diamine QHDA (5.14 g, 75%, m. p. 206–207 °C). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz): δ 9.14–8.97 (1H), 8.02–7.94 (2H), 7.73-7.68 (1H), 7.24-7.11 (1H), 6.96-6.91 (1H), 6.73-6.71 (2H), 5.97–5.93 (2H), 5.67–5.56 (2H) (Fig. 1). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz): δ 151.35-151.27, 151.00-150.56, 149.79-147.06, 144.48-143.03, 142.74-137.51, 135.86-134.86, 129.68-127.92, 128.68. 124.57-124.25, 122.64-120.91, 114.37-114.26, 106.03-105.72 (Fig. S3). Fourier transform infrared spectroscopy (FTIR) (KBr,  $cm^{-1}$ ): 3326, 3208, 3024, 1615, 1525, 1504, 831, 669. High resolution mass spectrometer (HRMS) (ESI) m/z calculated for  $C_{14}H_{12}N_4$  [M + H<sup>+</sup>] 237.1140, found 237.1135.

#### 2.3. Synthesis of QBDA

Scheme 2 shows the synthetic route of the **QBDA** diamine monomer. According to a modified literature procedure [26–30], a solution of 1-iodo-4-nitrobenzene (12.50 g, 50 mmol), ethynylbenzene (6.50 mL, 60 mmol), Pd (OAc)<sub>2</sub> (112.3 mg, 0.5 mmol), CuI (95.3 mg, 0.5 mmol), Xantphos (289.3 mg, 0.5 mmol CAS: 161265-03-8), and Cs<sub>2</sub>CO<sub>3</sub> (32.60 g, 100 mmol) in anhydrous DMF (200 mL) was heated to 60 °C for 16 h. After cooling to room temperature, water (200 mL × 2). The combined organic layer was washed with brine (200 mL × 2) and dried over MgSO<sub>4</sub>. The organic solvent was evaporated, the resulting residue was purified by flash column chromatography to give the 1-nitro-4- (phenylethynyl)benzene (**a**) (10.47 g, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.23–8.21 (m, 2H), 7.68–7.66 (m, 2H), 7.57–7.55 (m, 2H), 7.40–7.39 (m, 3H) (Fig. S4). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  146.98, 132.28, 131.85, 130.27, 129.29, 128.55, 123.65, 122.11, 94.72, 87.56 (Fig. S5).

PdCl<sub>2</sub> was added to a solution of **a** (8.90 g, 40 mmol) in anhydrous DMSO (250 mL) (709.3 mg, 4 mmol). The mixture was heated to 145 °C for 4 h and cooled to ambient temperature. Water (250 mL) was added to the reaction mixture, and the mixture was extracted with ethyl acetate (150 mL × 2). The combined organic phase was washed with brine (100 mL × 2) and dried over MgSO<sub>4</sub>. The organic solvent was removed under reduced pressure. The crude products were purified by column chromatography to afford the 1-(4-nitrophenyl)-2-phenylethane-1,2-dione (**b**) (8.78 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.37–8.34 (m, 2H), 8.18–8.16 (m, 2H), 8.00–7.98 (m, 2H), 7.73–7.69 (m, 1H), 7.57–7.54 (m, 2H) (Fig. S6). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  192.86, 192.08, 151.16, 137.30, 135.48, 130.97, 130.07, 129.24, 124.14 (Fig. S7).

The mixture of **b** (6.70 g, 26 mmol), 4-nitrobenzene-1,2-diamine (4.00 g, 26 mmol), and saccharin (241.0 mg, 1.3 mmol) in acetic acid (250 mL) was stirred at room temperature for 1 h. The reaction was monitored by TLC and quenched by water addition (250 mL). The precipitate was filtered, washed with brine three times, and dried in a vacuum oven to deliver the corresponding precursor **QBDN** (9.49 g, 98%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz):  $\delta$  8.99–8.96 (1H), 8.63–8.58 (1H), 8.43–8.38 (1H), 8.27–8.24 (2H), 7.81–7.79 (2H), 7.55–7.53 (2H),



Scheme 1. Synthetic route of QHDA.



Scheme 2. Synthetic route of QBDA.

7.49–7.40 (3H) (Fig. S8).  $^{13}$ C NMR (DMSO- $d_6$ , 125 MHz):  $\delta$  156.37–155.70, 154.77–154.14, 148.56–148.55, 148.25–144.91, 148.20–148.16, 143.73–143.19, 140.10–139.51, 137.80–137.76, 131.76–131.69, 131.42–131.31, 130.48–130.40, 130.28–130.14, 128.82, 125.45–125.33, 124.69–124.29, 123.75–123.73 (Fig. S9).

During the same hydrogen reduction of QHDN, the dinitro compound (QBDN) was transformed into bright yellow diamine monomer (**QBDA**) (m.p. 134–135 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 7.74–7.71 (1H), 7.46–7.41 (2H), 7.37–7.33 (3H), 7.23–7.16 (1H), 7.12–7.06 (2H), 6.94-6.92 (1H), 6.47-6.44 (2H), 6.02-5.98 (2H), 5.36-5.27 (2H) (Fig. 2). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz): δ 152.95–152.57, 151.03-150.47, 149.67–149.13, 148.25–147.57, 143.52-142.78, 140.83-140.79, 135.21-134.42, 131.24-130.94, 129.85-129.47, 129.77-129.69, 128.52-128.08, 128.37, 126.81-126.67, 122.80-122.05, 113.56-113.47, 105.41-105.15 (Fig. S10). FTIR (KBr, cm<sup>-1</sup>): 3352, 3220, 3028, 1621, 1520, 1489, 1352, 829, 700. HRMS (ESI) m/z calculated for C<sub>20</sub>H<sub>16</sub>N<sub>4</sub> [M + H<sup>+</sup>] 313.1453, found 313.1447.

2.4. Synthesis of QMDA

The synthesis and characterization of **QMDA** and the corresponding polyimide films are provided in the literature [20]. (m.p. 188-189 °C).

# 2.5. Synthesis of poly(amic acid) (PAA)

The monomer and PI structures are shown in Scheme 3. Precursors of the polyimides, poly (amic acid)s (PAAs), were synthesized from the reaction of diamine QHDA or QBDA with various aromatic dianhydrides (PMDA-m, BPDA-b, BTDA-t, ODPA-o) in DMAc. The synthesis of PAA-QHDA-m as a representative is as follows. QHDA (11.81 g, 50 mmol) was charged into a 250-mL three-neck round-bottom flask, equipped with a stirrer and a nitrogen inlet, which contained 50 mL of dimethylacetamide (DMAc). After the diamine had dissolved, 10.91 g (50 mmol) of PMDA was added slowly to the solution, and the mixture was stirred for ~12 h at room temperature to yield a viscous PAA solution.



Fig. 2. <sup>1</sup>H NMR spectrum of QBDA in DMSO-d<sub>6</sub>.



Scheme 3. Monomer structures and synthetic route of the PI films.

# 2.6. Preparation of polyimide (PI) films

Bubbles that were produced by stirring and that remained in the PAA solution were removed with a centrifugal defoaming machine. The PAA solution was cast slowly onto flat glass substrates with a 250- $\mu$ m-depth blade at room temperature. The PAA films were vacuumed to remove bubbles for 1 h and cured by using an annealing procedure (115 °C/15 min, 140 °C/15 min, 200 °C/30 min, 250 °C/5 min, 380 °C/90 min).

After cooling to ambient temperature, the corresponding PI films were immersed in hot water, peeled from the glass substrates, and dried at 80  $^\circ C$  for 2 h.

## 2.7. Characterization

Thin-layer chromatography (TLC) was performed on silica gel F254 precoated glass plates (HSGF254, Huanghai) and visualized by

irradiation under a 254 nm UV lamp. Flash chromatography was carried out on 200-300 mesh silica gel, eluting with a mixture of petroleum ether (b.p. 60-90 °C) and ethyl acetate. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured at 500 MHz and 125 MHz on a Bruker 500 AVANCE III HD spectrometer. Fourier transform infrared spectra (FTIR) were obtained with a Nicolet 6700 FTIR spectrometer (PerkinElmer, Inc., USA), where the samples were prepared with KBr pellets. High-resolution mass spectra (HRMS) were obtained on an ACQUITYTM UPLC & Q-TOF MS Premier (Waters, USA). The FTIR of the PI films was monitored by applying the attenuated total-reflectance (ATR) mode of a Nicolet 6700 FTIR spectrometer. The number-average  $(M_n)$  and weight-average  $(M_w)$ molecular weights were estimated by GPC LC-20AD (Shimadzu, Japan) using DMF solution containing 0.03 mol/L LiBr and 0.03 mol/L H<sub>3</sub>PO<sub>4</sub>. Optical transmittances spectra were recorded by using a UV-1800 spectrophotometer (SHIMADZU, Japan) from 200 to 800 nm. X-ray diffraction (XRD) spectra were measured by using a D8 ADVANCE Da Vinci (Bruker, Germany). Thermogravimetric analysis (TGA) was investigated by a Discovery 550 TGA (TA Instruments, USA) under nitrogen at 10 °C min<sup>-1</sup>. The glass transition temperature ( $T_o$ ) was detected by using a Q800 dynamic thermomechanical analysis (DMA, TA Instruments, USA) at a heating rate of 5  $^{\circ}$ C min<sup>-1</sup>. The coefficient of thermal expansion (CTE) was characterized by a Q400 thermomechanical analysis (TMA, TA Instruments, USA) at a heating rate of 5 °C min<sup>-1</sup>. The mechanical properties of the films were assessed on a CMT1104 universal electromechanical tester (SUST, China) using the average of 5 samples. The dielectric constant and dielectric loss were tested on a Concept 40 dielectric/impedance spectrometer (Novocontrol Company, Germany).

The geometry optimization of the chain structures of PIs was performed on BIOVIA material studio 2016 software by means of the density functional theory, with a large basis-set function. The fractional free volume (FFV) and the end-to-end distance (EED) were obtained using same methods described previously [31].

#### 3. Results and discussion

## 3.1. Monomer synthesis

Quinoxaline diamines with different side groups were designed and prepared. **QHDN** was synthesized readily from 4-nitrobenzene-1,2diamine and 2-bromo-1-(4-nitrophenyl)ethanone by Kornblum oxidation, where DMSO played the role of oxidant and solvent at room temperature. **QBDN** was produced by Sonogashira coupling, catalytic oxidation and cyclocondensation catalyzed by saccharin with a high yield. Precursors of the diamines, dinitrocompounds **QHDN** and **QBDN** were reduced by hydrogen in a clean and efficient way. The products of each step were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR. The structures and molecular masses of the target diamines **QHDA** and **QBDA** were confirmed by NMR, FTIR and HRMS. Similarly, the molecular structure of QMDA has been confirmed by various characterization methods in previous papers [20].

#### 3.2. Polymer synthesis

The PIs were prepared by the reaction between diamine **QHDA**/ **QBDA**/**QMDA** and equal molar dianhydride PMDA/BPDA/BTDA/ODPA in DMAc. Air-bubble elimination from the PAAs was important to fabricate PI films without cracks. The number-average ( $M_n$ ) and weightaverage ( $M_w$ ) molecular weights as well as the polydispersity indexes (PDIs) of the PAAs are listed in Table 1, which were high enough to form flexible and tough PI films.

All films were cured below 380 °C as a final annealing temperature and characterized by ATR-FTIR. As shown in Fig. 3, the introduction of quinoxaline structure was evidenced by the absorption band of quinoxaline rings at 1604/1601 cm<sup>-1</sup> (stretching vibration of C=N). The absorption peaks of the amide group at 1550 and 1660 cm<sup>-1</sup> were

Table 1Molecular weights and PDIs of the PAAs.

PAAs	$M_{ m n}$ ( $ imes$ 10 $^3$ )	$M_{w}$ ( $ imes$ $10^{3}$ )	PDI
QHDA-m	20	53	2.7
QHDA -b	15	38	2.5
QHDA -t	22	60	2.7
QHDA -o	11	28	2.5
QBDA-m	23	47	2.0
QBDA -b	21	43	2.0
QBDA -t	33	68	2.1
QBDA -o	16	31	1.9
QMDA-m	8	32	3.9
QMDA -b	15	43	2.8
QMDA -t	8	28	3.6
QMDA -o	8	28	3.5

undetectable, whereas characteristic absorption peaks at 1776/1778 cm<sup>-1</sup> (asymmetric stretching vibration of C=O), 1708/1713 cm<sup>-1</sup> (symmetric stretching vibration of C=O), 1357/1356 cm<sup>-1</sup> (stretching vibration of C–N–C) and 725 cm<sup>-1</sup> (bending vibration of C=O) that originated from imide rings were observed, which confirmed the complete thermal imidization [18,19,32].

#### 3.3. Optical properties

The PI film colors were analyzed with optical photographs as presented in Fig. 4. QHDA-PIs and QBDA-PIs are brown/orange and bright yellow, respectively, and the QMDA-PIs shifted gradually from orange to yellow. The formation of charge-transfer complexes (CTCs) between electron donating diamines and electron accepting dianhydrides is regarded as the main cause for the PI film colors. For the same dianhydride, the QBDA-PIs had a lighter color because of the substantial steric hindrance from the large pendant phenyl structure of the QBDA, which reduced the intermolecular and intramolecular CTC formation. The methyl pendant of QMDA had a weaker steric hindrance, which resulted in a darker QMDA-PIs compared with QBDA-PIs. QHDA-PIs show the darkest color due to the maximum conjugation formed within and between molecular chains. As for the same diamine, the formation of CTC was determined mainly by the electron accepting ability of the dianhydrides as indicated by the electron affinity (Ea). PMDA and BTDA had an Ea of 1.90 and 1.55, respectively, which was higher than BPDA (1.38) and ODPA (1.30) and lead to the deeper colors. However, the intramolecular interaction has a greater effect on the color of QBDA and QMDA than their intermolecular CTC.

# 3.4. Thermal properties

The most critical thermal properties of the PI films, including their thermal stability, glass-transition temperature and thermal dimensional stability, were determined by TGA, DMA and thermomechanical analysis (TMA), respectively. The TGA curves of all PI films in a nitrogen atmosphere are illustrated in Fig. S11 and the temperatures at which 5% mass was lost  $(T_d^{5\%})$  were used to indicate the thermal stability. As shown in Fig. 5, QHDA-PIs and QBDA-PIs demonstrated outstanding thermal decomposition behaviors with  $T_d^{5\%}$  values in the ranges of 528–560  $^\circ\text{C}$ and 537-556 °C, in contrast with QMDA-PIs (453-494 °C). It is commonly accepted that the thermal decomposition temperature depends on the chemical bond energy and the condensed state of the main polymer chains. The C=N bonds in quinoxaline structures were provided with a high bond energy. In addition, the absent side group on QHDA allowed for the tight packing of the main chains, which facilitated the effective heat diffusion between polymer chains, and promoted the decomposition temperature of the polyimides. The phenyl side group of the QBDA interrupted the tight packing somewhat and reduced the interchain interaction; however, the benzene ring had a good heat resistance and the conjugation effect between the benzene ring and



Fig. 3. ATR-FTIR spectra of (a) QHDA-PIs and (b) QBDA-PIs.



Fig. 4. Optical photographs of PIs.



Fig. 5. Td<sup>5%</sup> of the PIs.

quinoxaline ring helped to disperse the heat energy and prevent molecular decomposition. Methyl side groups on the **QMDA** with a low bond energy were weak points in terms of thermostability; as a consequence, the thermal decomposition temperature of the **QMDA**-PIs decreased sharply.

The glass-transition temperature  $(T_g)$  was evaluated by the peak value of tan delta in the DMA curves as shown in Fig. S12 and presented in Fig. 6. Tg is regarded as the highest usage temperature for polymer materials, over which polymeric segmental motions would acquire sufficient energy to overcome the intermolecular attraction. The  $T_{\sigma}$  for all quinoxaline-type PI films exceeded 350 °C because of the improved rigidity. The QHDA-PIs possessed the strongest intermolecular interaction because of close packing that leads to the highest rotational energy barrier and the highest Tg from 413 to 444 °C. The close packing of QHDA-PIs molecular chains also caused the formation of crystalline structure, which can be proved from the XRD pattern of their films as shown in Fig. 6b and c. PMDA is the most rigid dianhydride in favor of T<sub>g</sub> enhancement by restricting the chain-segment movement. Generally, the introduction of a flexible structure would damage the Tg of polymers; however, carbonyl bonds in BTDA and ether bonds in ODPA could generate radicals and cross-linking during high temperature treatment [33], reduce the free volume and enhance the thermal performance of corresponding QHDA-PIs and QMDA-PIs. The phenyl groups of QBDA-PIs increased the intermolecular distance, which hindered the radical reaction and avoided cross-linking formation. As such, the Tg values of QBDA-PIs decreased with the introduction of flexible units in dianhydrides. For comparison, Kapton H is used as a central, with Tg data from Ref. [34].

The thermal dimensional stability of the PI films was characterized by the in-plane coefficient of thermal expansion (CTE) that was evaluated by the second heating of TMA to eliminate the residual stress effect, as shown in Fig. S13. The in-plane CTE values for 50–300/350 °C are summarized in Table 2. Compared with CTE vales of most common polyimides greater than 30 ppm/K [35,36], quinoxaline polyimides have good dimensional stability. It is believed that the thermal



Fig. 6. T<sub>g</sub> (a) and XRD patterns (b and c) of the PIs.

#### Table 2

In-plane CTE (ppm/K) values of PIs.

	PMDA(m)		BPDA(p)		BTDA(t)		ODPA(o)	
	300 °C	350 °C						
QHDA	1	1	9	10	19	21	30	33
QBDA	13	14	30	37	40	n.d.	47	n.d.
QMDA	12	13	22	26	36	41	39	45

dimensional stability should be attributed to the linearity and rigidity of the molecular structure. A larger side group makes the chain easier to bend. Therefore, **QBDA**-PIs that contained phenyl had the highest in-plane CTE values and corresponded to the worst dimensional stability. The absent side group of the **QHDA** yielded the best linearity and lowest in-plane CTE values for the **QHDA**-PIs. Fig. 7 shows that the in-plane CTE values depended on the linearity of the main chain structures, in the order of **QHDA** < **QMDA** < **QBDA** for diamines and PMDA < BPDA < BTDA < ODPA for dianhydrides. Therefore, the most outstanding thermal dimensional stability belonged to the combination of QHDA and PMDA. QHDA-m exhibited the in-plane CTE as low as 1 ppm/K in the range of 50 °C-350 °C.

#### 3.5. Mechanical properties

The mechanical properties of the PI films that contained a tensile strength ( $\sigma$ ), initial modulus (E), and elongation at break ( $\varepsilon$ ) are summarized in Table 3. QHDA-m had the highest initial modulus over 6 GPa because QHDA incorporated the most rigid dianhydride PMDA, whereas the highest tensile strength that exceeded 200 MPa belonged to QHDA-t. This result may be ascribed to the fact that the tight packing of polyimide chains derived from QHDA and the formation of crystalline structures was conducive to enhance the mechanical properties. However, excessive rigidity originated from PMDA and QHDA blocked the rotation and movement of chain segments and gave rise to fracture-mechanism transition from ductile to brittle fracture [37,38]. A certain rotation space is necessary to ensure ductile fracture. Hence the combination of QBDA with the largest free volume and dianhydrides with freely rotating linkage structure corresponded to the highest elongation at rupture of 12.8% for QBDA-b and 11.8% for QBDA-o.

## 3.6. Dielectric properties

Polyimide is excellent electrical insulators with high resistances and high dielectric strength. However, like all polymers, the electronic, atomic polarization and orientation polarization of dipole moments in polyimide chains can be caused under an external electric field, showing



Fig. 7. In-plane CTE of PIs in the range of 50–300 °C.

Table 3	
Mechanical	properties of PIs.

PIs	$\sigma_{max}$ (MPa)	ε <sub>b</sub> (%)	E (GPa)
QHDA - PMDA	$57\pm3$	$1.1\pm0.2$	$\textbf{6.2}\pm\textbf{0.4}$
QHDA - BPDA	$195\pm7$	$8.2\pm0.7$	$3.9\pm0.4$
QHDA - BTDA	$209\pm4$	$8.3\pm0.5$	$4.1\pm0.4$
QHDA - ODPA	$172\pm4$	$7.4\pm0.3$	$3.4\pm0.2$
QBDA- PMDA	$127\pm4$	$4.5\pm0.5$	$3.7\pm0.5$
QBDA - BPDA	$138\pm5$	$12.8\pm0.6$	$2.3\pm0.1$
QBDA - BTDA	$109\pm4$	$5.2\pm0.5$	$2.6\pm0.2$
QBDA - ODPA	$145\pm4$	$11.8 \pm 1.8$	$\textbf{2.6} \pm \textbf{0.2}$
QMDA - PMDA	$95\pm4$	$\textbf{2.4} \pm \textbf{0.6}$	$5.2\pm0.3$
QMDA - BPDA	$141\pm4$	$5.7\pm0.1$	$3.5\pm0.1$
QMDA - BTDA	$157\pm9$	$\textbf{8.8} \pm \textbf{0.4}$	$\textbf{3.2}\pm\textbf{0.4}$
QMDA - ODPA	$174\pm11$	$\textbf{9.7}\pm\textbf{0.3}$	$3.5\pm0.3$

the storage of electrostatic energy, which is generally expressed by dielectric constant ( $\varepsilon$ ). It is the ratio of the permittivity of the dielectric to the permittivity of a vacuum.

If an alternating electric current is applied, all modes of polarization will oscillate with the changing electric field. Thus, dielectric constant is dependent on the frequency of the oscillating electric field. Dielectric loss (tan  $\delta$ ) results from the inability of polarization process in a material to follow the rate of change of the oscillating applied electric field, resulting in the energy absorption and dissipated as heat. The dielectric properties of the quinoxaline-type PI films were recorded in a frequency range of 100 Hz to 100 kHz at room temperature (Fig. S14). In current PI system, we found that the **QBDA**-PIs containing phenyl pendant group exhibited a significantly lower dielectric constant and dielectric loss as shown in Table 4, indicating that the size of the pendant group plays the major role to vary the dielectric properties.

The relation between dielectric constant and polymer structure can be expressed by the Clausius-Mossotti equation [39].

$$\varepsilon = \frac{1 + 2(P/FFV)}{1 - (P/FFV)}$$
(1)

where P and FFV are the molar polarizability and the molar fractional free volume of the polymer, respectively. Guided by the experimental results, the effect of polarity and free volume on dielectric properties were further investigated on these PIs by molecular dynamics simulations (Fig. 8). As the polarity of a macromolecular chain largely depends on the chain conformation, the net dipole of the chain can be considered to be equivalent, within a multiplicative constant, to the end-to-end vector of the chain [40–42]. From the simulation results, the dielectric constants could not build a linear correlation with neither polarity, which is proportional to the end-to-end distance (EED) of PIs, nor 1/FFV

Table 4
Dielectric properties of the PIs.

	PMDA		BPDA		BTDA		ODPA	
	ε <sup>a</sup>	$tan \ \delta^b$	$\epsilon^{a}$	$tan \ \delta^b$	ea	$tan \; \delta^b$	$\epsilon^{a}$	$tan \ \delta^b$
QHDA QBDA QMDA	3.8 3.3 3.8	7.8 E-3 2.8 E-3 9.5 E-3	3.7 3.6 4.0	6.8 E–3 2.1 E–3 6.1 E–3	3.8 3.7 3.9	6.5 E–3 3.8 E–3 4.7 E–3	3.9 3.7 3.8	4.7 E-3 3.2 E-3 4.5 E-3

<sup>a</sup> Dielectric constant at 1 kHz.

<sup>b</sup> Dielectric loss.



Fig. 8. Relationships between EED, FFV with the dielectric constants ( $\epsilon$ , a) and the dielectric loss (tan  $\delta$ , b) based on molecular dynamic simulation results.

(Fig. S15), but was found to be positively correlated with EED to FFV (Fig. 8a), suggesting that the polarity and free volume have the synergism action on dielectric constant in our PIs. In addition, the dielectric losses were positively correlated with 1/FFV (Fig. 8b and Fig. S16), which means that the greater the fractional free volume of the polyimide, the lower its dielectric loss.

## 4. Conclusions

A series of quinoxaline diamines was designed and synthesized through improved synthetic routes. The corresponding novel polyimide films were prepared by incorporating four typical dianhydrides. All quinoxaline-type PI films displayed a good thermostability, dimensional stability, mechanical property, and dielectric property, which suggested that quinoxaline has a promising application in high temperatureresistant polymer materials. The QHDA-PIs had the best thermal properties, including a mass-loss temperatures ( $T_d^{5\%}$ ) from 528 to 560 °C, a high Tg from 413 to 444  $^{\circ}$ C, a CTE of as low as 1 ppm/K, and a superior tensile strength (209 MPa) and initial modulus (6.2 GPa). This behavior could be attributed to the rigidity, linearity, strong intermolecular interaction, and close packing of the polymer-chain segments. Steric hindrance began to take effect with the appearance of large side groups. As a result, QBDA-PIs was pale-yellow because of the decreased intermolecular interaction, strong ductility with a breaking elongation up to 12.8% and a significantly lower dielectric constant and dielectric loss because of the increased free-volume size. These intensive structureproperty relationships are significant for guiding future monomer design to obtain high performance polyimides in a rational way.

# 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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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2020.122963.

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