



Synthesis and properties of the novel polyimides containing cyano and biphenyl moieties

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Abstract

A series of cyano-functionalized polyimides (CN-PIs) were prepared and derived from a novel diamine monomer having cyano and biphenyl groups. Meanwhile, another series of PIs without cyano groups (H-PIs) were prepared as counterparts for comparison purposes. Both series of PIs exhibited good solvent resistance, good thermal stability, remarkable film-forming ability, and excellent tensile properties. The T_g values of CN-PIs were 260–330°C, which were 10–17°C higher than the corresponding –CN free H-PIs. The CN-PIs exhibited no obvious decomposition below 470°C, and their 5% weight loss temperatures were above 568°C under nitrogen atmosphere. All the CN-PI films had high tensile strength and Young's moduli, which were related to their rigid backbones and strong interactions between molecular chains. Due to their higher molar polarization, CN-PIs expressed the higher dielectric constants (3.29–3.69 at 1 MHz) in comparison with the corresponding H-PIs. CN-PIs exhibited the improved transparency, and both CN-PIs and H-PIs had better transparency than commercial Kapton[®] film. Introducing –CN groups could have an effect on the coefficient of thermal expansion and peel strength of the PIs. The peel strength of the PI, which was derived from cyano-functionalized diamine monomer and 4,4'-oxydiphthalic anhydride, could even reach 1.10 N mm⁻¹, suggesting its strong interaction to copper matrix and potential use in flexible circuit board.

Keywords

Polyimides, dielectric constant, peel strength, thermal stability, film

Introduction

Due to their unique chemical structure and outstanding properties, polyimides (PIs) have attracted much attention and been widely used as high-strength structural materials, high-temperature resistant films, high-efficiency separation membranes, low- k insulators, and flexible copper clad laminates.^{1–9} Recently, many efforts have been focused on the modifications of the PIs with the improvement of their specific properties without deterioration of their excellent thermal and mechanical properties. Some functional moieties, such as trifluoromethyl (–CF₃), sulfonic acid (–SO₃H), hydroxyl (–OH), and ethynyl groups, were introduced into the PI backbones to enhance the performance of gas permeability, dielectric property, transparency, proton conducting ability, and thermo-mechanical integrity.^{3,10–13}

It is well known that polar cyano groups (–CN) have large dipole moment and polarizability; thus, they can form stable complex through hydrogen bonds and strong intermolecular forces.^{14–17} In addition, the cyano-containing

polymers usually have strong interaction with the matrix, when they work as coating materials.¹⁸ It is of interest to introduce the –CN groups into high-performance polymers to enhance their adhesive strength and other properties,

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especially when they used as functional coatings and multi-layer films. However, only several cyano-functionalized PIs (CN-PIs) have been successfully synthesized, and a systematic investigation on the effects of $-\text{CN}$ groups on polymer properties is necessary.

Lin and Xu believed that the existence of $-\text{CN}$ groups on the PI backbones would lead to an increase in dielectric constant.¹⁹ Kang et al. reported the successful conversion of $-\text{CN}$ groups into carboxylic groups ($-\text{COOH}$), and the obtained PIs could have improved solubility in some polar aprotic solvents.¹⁵ Recently, a new family of sulfonated PIs containing multiple $-\text{CN}$ groups was prepared for study as proton exchange membranes, and they exhibited improved dimensional stability under hot and humid circumstances.³

In the present study, as an attempt to find a new way to prepare low coefficient of thermal expansion (low-CTE) and high peel strength materials, a series of novel PIs having polar $-\text{CN}$ groups and rigid biphenyl units were synthesized and derived from a newly designed diamine monomer. For the sake of the investigation of the effects of the pendent $-\text{CN}$ groups on the PIs, corresponding PIs having similar structure but without $-\text{CN}$ groups were also prepared as counterparts. Some properties including solubility, thermal and mechanical properties, dielectric constant, transparency, thermal expansion, and adhesion to copper were carefully investigated, and the structure-property relationships were illustrated.

Experimental

Materials

4,4'-Dihydroxybiphenyl (J&K Scientific Ltd, Beijing, China), 1-chloro-4-nitrobenzene (Aladdin Chemistry Co. Ltd), 2-chloro-5-nitrobenzonitrile (Shanghai Darui Fine Chemical Co. Ltd, Shanghai, China), potassium carbonate (Beijing Chemical Reagent, Beijing, China), and 4,4'-dihydroxybiphenyl (Aladdin Chemistry Co. Ltd, Shanghai, China) were used as received without further purification. Pyromellitic dianhydride (PMDA), 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd (Changzhou, China) and dried at 120°C for 12 h prior to use. *N,N*-Dimethylacetamide (DMAc; Tianjin Chemical Reagent, Tianjin, China), 80% hydrazine monohydrate (Acros), ethanol (Beijing Chemical Reagent, China), *N,N*-dimethylformamide (DMF; Tianjin Chemical Reagent, China), dimethyl sulfoxide (DMSO; Tianjin Chemical Reagent, China), *N*-methyl pyrrolidone (NMP; Tianjin Chemical Reagent, China), tetrahydrofuran (THF; Tianjin Chemical Reagent, China), trichloromethane (CHCl_3 ; Beijing Chemical Reagent, China), and toluene (Beijing

Chemical Reagent, China) were used as solvents and azeotropic reagents.

Synthesis of the 4,4'-bis(4-amino-2-cyanophenoxy)-biphenyl (CN-BP-DA)

2-Chloro-5-nitrobenzonitrile (0.105 mol; 19.1692 g), 4,4'-dihydroxybiphenyl (0.050 mol; 9.3104 g), and potassium carbonate (0.060 mol; 8.2924 g) were put into a 500-mL three-necked round-bottomed flask equipped with a nitro inlet, a Dean-Stark trap (Tianjin Glass Instrument Factory, Tianjin, China) with a condenser, and a magnetic stirrer. DMF (71 mL) and toluene (15 mL) were added as solvent and azeotropic reagent, respectively. The mixture was refluxed at 130–135°C for 3 h, and then toluene/water mixture was removed. The system was refluxed at 155°C for another 6 h and poured into 200 mL of cold ethanol to obtain yellow solid. Crude product of the 4,4'-bis(4-amino-2-cyanophenoxy)-biphenyl (CN-BP-NT) was washed several times in deionized water and recrystallized by DMSO. After drying at 80°C in an oven for 12 h, a yellow product was obtained (yield: 80%).

Fourier-transform infrared spectroscopy (FTIR; potassium bromide (KBr), cm^{-1}): 1510 ($-\text{NO}_2$) and 2245 ($-\text{CN}$).

Proton nuclear magnetic resonance (^1H NMR; DMSO- d_6 , ppm): 8.90 (d, $J = 2.7$ Hz, 2H); 8.48, 8.49 (dd, $J_1 = 9.3$ Hz and $J_2 = 2.7$ Hz, 2H); 7.91 (d, $J = 8.7$ Hz, 4H); 8.90 (d, $J = 2.7$ Hz, 2H); 7.45 (d, $J = 8.7$ Hz, 4H); 7.11 (d, $J = 2.7$ Hz, 2H).

CN-BP-NT (10 g), 0.4 g of 10% palladium on carbon, and 10 mL of hydrazine hydrate were added into a 500 mL three-necked round-bottomed flask equipped with a nitrogen (N_2) inlet with a dropping funnel, a condenser, and a magnetic stirrer. Ethanol (150 mL) and dioxane (150 mL) were added as solvents. Then, the mixture was refluxed with stirring for 8 h. After hot filtration, the yellow filtrate was poured into 300 g of ice and white precipitation was gained by filtration. The crude product was then recrystallized by acetone/ethanol and dried under vacuum at 80°C for 12 h. Off-white product was obtained (yield: 70%). The synthesis routine of the diamine monomer is shown in Figure 1.

FTIR (KBr, cm^{-1}): 3450 ($-\text{NH}_2$) and 2245 ($-\text{CN}$).

^1H NMR (DMSO- d_6 , ppm): 7.62 (d, $J = 8.7$ Hz, 4H), 7.02–6.97 (m, 6H), and 6.93–6.88 (m, 4H).

Synthesis of the 4,4'-bis(4-aminophenoxy)-biphenyl (H-BP-DA)

H-BP-DA monomer without $-\text{CN}$ groups was synthesized using a procedure similar to CN-BP-DA as shown in Figure 1. The yields of the dinitro compound and diamine monomers were 80% and 75%, respectively.

H-BP-DA. FTIR (KBr, cm^{-1}): 3450 ($-\text{NH}_2$) and 1260 ($\text{C}-\text{O}$).

^1H NMR (DMSO- d_6 , ppm): 7.53 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), and 6.60 (d, $J = 8.7$ Hz, 2H).

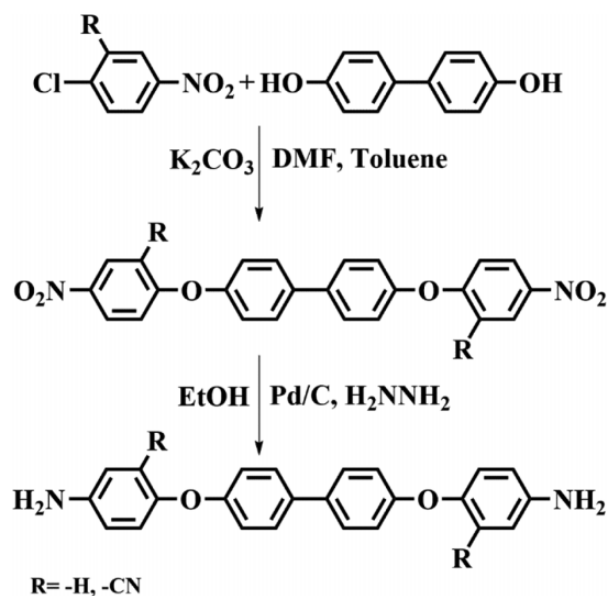


Figure 1. Synthesis of the cyano-containing diamine monomer (CN-BP-DA) and its corresponding diamine monomer without –CN groups (H-BP-DA).

Synthesis of the polymers

Both two series of PIs were synthesized via a two-step reaction procedure including a formation of poly(amic acid)s (PAAs) and, then, thermal imidization of PAAs.²⁰ As a typical procedure for the preparation of PIs, the synthesis of CN-6FDA was given as follows: CN-BP-DA diamine (0.8369 g; 2 mmol) and DMAc (6.7 mL) were placed into a 25 mL three-necked round-bottomed flask equipped with a N₂ inlet and a magnetic stirrer under N₂ atmosphere. After the diamine was entirely dissolved, 6FDA (0.8885 g; 2 mmol) was added to the solution. The mixture was stirred at room temperature for 24 h to yield PAA solution. The solution was cast onto a glass plate and then heated by the following procedure: 80°C/3 h, 110°C/1 h, 150°C/1 h, 180°C/1 h, 210°C/1 h, 240°C/1 h, 270°C/1 h, and 300°C/1 h. The PI film (CN-6FDA) was removed by immersing the glass plate in boiling water. All the other PIs were synthesized by using a similar procedure (Figure 2), and the thickness of the films was about 60 μm.

CN-6FDA. FTIR (KBr, cm⁻¹): 2250 (–CN), 1730 (imide C=O), 1373 (imide C–N), and 1170 (–CF₃).

CN-ODPA. FTIR (KBr, cm⁻¹): 2250 (–CN), 1743 (imide C=O), 1374 (imide C–N), and 1280 (Ar–O–Ar).

CN-BPDA. FTIR (KBr, cm⁻¹): 2249 (–CN), 1747 (imide C=O), and 1373 (imide C–N).

CN-BTDA. FTIR (KBr, cm⁻¹): 2250 (–CN), 1733 (imide C=O), and 1375 (imide C–N).

CN-PMDA. FTIR (KBr, cm⁻¹): 2251 (–CN), 1744 (imide C=O), and 1374 (imide C–N).

H-6FDA. FTIR (KBr, cm⁻¹): 1731 (imide C=O), 1373 (imide C–N), and 1170 (–CF₃).

H-ODPA. FTIR (KBr, cm⁻¹): 1743 (imide C=O), 1374 (imide C–N), and 1280 (Ar–O–Ar).

H-BPDA. FTIR (KBr, cm⁻¹): 1747 (imide C=O) and 1373 (imide C–N).

H-BTDA. FTIR (KBr, cm⁻¹): 1733 (imide C=O) and 1375 (imide C–N).

H-PMDA. FTIR (KBr, cm⁻¹): 1744 (imide C=O) and 1374 (imide C–N).

Characterization

¹H NMR spectra were recorded on a Bruker 510 spectrometer (Billerica, Massachusetts, USA; 300 MHz) using DMSO-*d*₆ as solvents. FTIR spectra were obtained on a Bruker Vector-22 spectrometer. Thin films for polymer samples and powder for monomers and precursors were used. Viscosities of PAAs were measured using a thermostatically controlled Ubbelohde viscometer (Shanghai Sunny Hengping Scientific Instrument Co. Ltd, Shanghai, China) with polymer concentrations of 0.5 g dL⁻¹ in DMAc at 25 ± 0.1°C. The mechanical properties of the films were measured at room temperature on Shimadzu AG-I 1KN (Shimadzu, Japan) at a strain rate of 2 mm min⁻¹. The size of the samples was 50 × 5 mm². Each film was measured three times, and the final results were the average value of the three data. Differential scanning calorimetry (DSC) was performed on a TA Q20 instrument (TA, New Castle, Delaware, USA) from 100°C to 350°C at a heating rate of 10°C min⁻¹ under N₂ atmosphere at a constant flow of 50 mL min⁻¹. The thermal properties of materials were performed via the experiments of thermal gravimetric analyses (TGAs) using a heating rate of 10°C min⁻¹ in N₂ or air atmosphere on a PerkinElmer Pyris 1 TGA analyzer (Waltham, Massachusetts, USA). The CTE was measured by TOLEDO 84le TMA (Mettler Toledo, Swiss) in expansion mode over the range of 50–400°C at the heating rate of 10°C min⁻¹ in N₂ atmosphere. In order to eliminate internal stress, the strip samples (10 mm long and 6 mm wide) were first heated to 400°C at the heating rate of 15°C min⁻¹ and then fast cooled to room temperature, followed by CTE measurement. For ease of comparison among all samples, we calculated the CTE values in the range of 100–200°C. The CTE value of the films was calculated as follows^{21,22}:

$$\text{CTE} = (L_2 - L_1)/L_0 \times (T_2 - T_1)$$

where L_2 is the length of film at 200°C, L_1 is the length of film at 100°C, $L_0 = 10$ mm, $T_2 = 200^\circ\text{C}$, and $T_1 = 100^\circ\text{C}$.

The solubility of the PI films was measured by immersing the films into different solvents, and then, the solubility of the films was observed at the temperature before and after heating. The dielectric properties of the PI films were measured by an Agilent 4294A precision impedance analyzer (Santa Clara, California, USA) from 1 MHz to 10 MHz at 25°C. Liquid silver was spread through the films to cover a

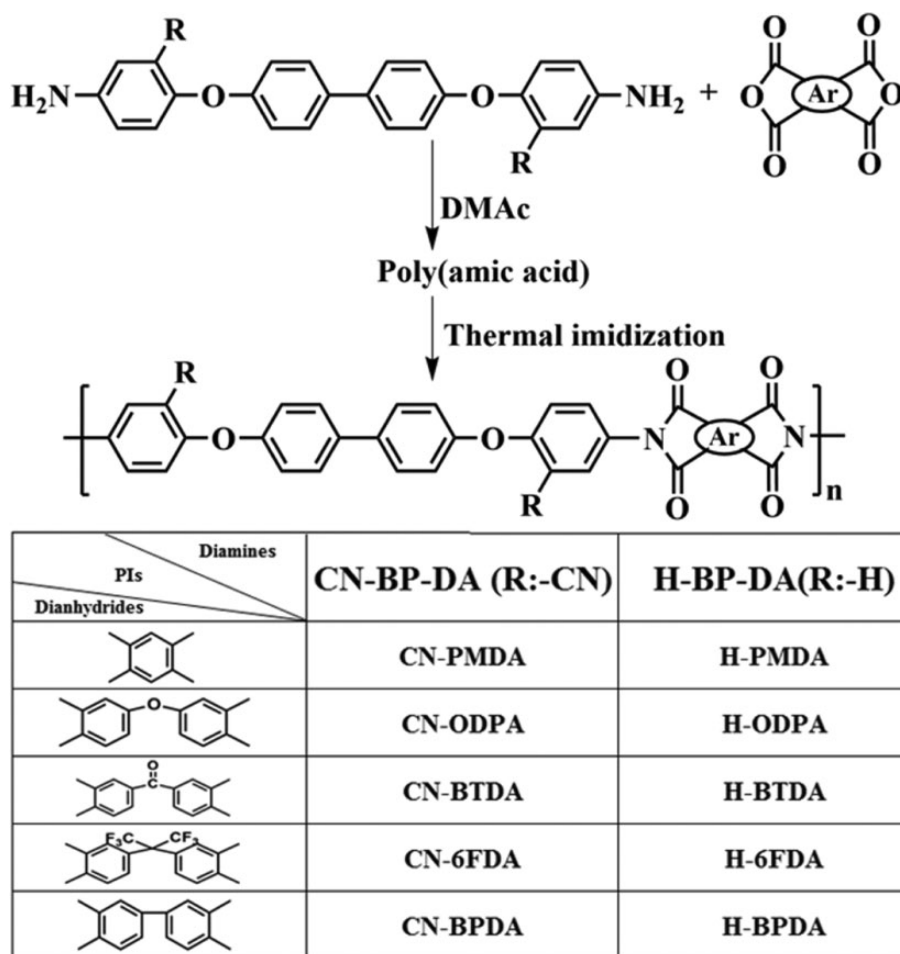


Figure 2. Synthesis of cyano-containing PIs (CN-PIs) and the counterpart without cyano groups (H-PIs). PI: polyimide.

double-sized circle of 10 mm diameter and dried under vacuum at 150°C for 5 h to dry off the liquid silver layer. Eventually, the sample films were put in the electrode, and the dielectric constants were measured. The transparency of the PI films was performed on a Lambda 950 UV-Vis-near-infrared spectrophotometer (PerkinElmer, USA). Peel strength of the materials was measured on Shimadzu AG-I 1KN (Shimadzu, Japan) at room temperature at a strain rate of 2 mm min⁻¹. The size of samples was 50 × 5 mm². Before measurement, the PAA solution was cast on the copper foil. And then the samples were heated by the following procedure: 80°C/3 h, 110°C/1 h, 150°C/1 h, 180°C/1 h, 210°C/1 h, 240°C/1 h, 270°C/1 h, and 300°C/1 h. After heat treatment, the sample was measured by the tensile machine to measure the peel strength values. During measurement, the sample was stripped off at the beginning of the sample at 90° direction, and then, the membrane and copper were separated gradually. The films were vacuum-dried at 100°C for 24 h before testing the water absorption, for which they were weighed and immersed in deionized water at room temperature for 24 h. The samples were wiped to remove water from the sample surface and quickly weighed again.

The water absorption of the films was calculated in weight percent as follows

$$\text{Water absorption} = [(W_2 - W_1)/W_1] \times 100\%$$

where W_2 represents the weight of the film after absorption water and W_1 represents the weight of dry film.

Results and discussion

Synthesis and characterization of the monomers and polymers

The diamine monomer, CN-BP-DA, was prepared by a traditional two-step reaction starting from an aromatic nucleophilic substitution, followed by a reduction reaction. The structure of the monomer was confirmed by FTIR and ¹H NMR spectroscopies. The FTIR spectra of CN-BP-DA and CN-BP-NT are shown in Figure 3. In FTIR spectrum of CN-BP-NT, the absorption bands at 1523 and 1355 cm⁻¹ were assigned to the stretching vibrations and bending vibrations of nitro groups (-NO₂). For comparison, the absorption bands at 3466 and 3373 cm⁻¹ assigned to the

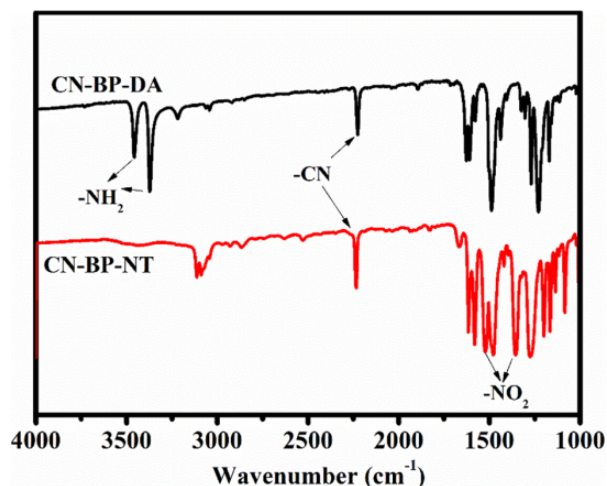


Figure 3. FTIR spectra of CN-BP-DA and CN-BP-NT. FTIR: Fourier-transform infrared spectroscopy.

stretching vibrations and bending vibrations of amino groups ($-\text{NH}_2$) were observed in the FTIR spectrum of diamine monomer (CN-BP-DA). The absorption bands at 2250 cm^{-1} due to the stretching vibrations of $-\text{CN}$ groups in both CN-BP-NT and CN-BP-DA were observed. It was clear to see the disappearance of the absorptions belonging to $-\text{NO}_2$ groups in CN-BP-NT and the appearance of the absorptions belonging to $-\text{NH}_2$ groups in CN-BP-DA after the reduction reaction.

^1H NMR spectra of CN-BP-DA and H-BP-DA monomers are shown in Figure 4. All protons with expected multiples and integrations are consistent with the proposed chemical structures of the monomers. It was observed that the $-\text{CN}$ groups could significantly affect the chemical shifts and peak splits of the protons on the benzene rings attached $-\text{CN}$ pendants. The signals of $-\text{NH}_2$ around $5.56\text{--}5.48\text{ ppm}$ were also found.

PIs were prepared according to a typical two-step polymerization method, including the formation of a PAA intermediate and the completion of the thermal imidization to yield the high-molecular-weight polymers (Figure 2). The polymerizations of two diamine monomers with stoichiometric amounts of five different commercially available dianhydride monomers, PMDA, ODPA, 6FDA, BTDA, and BPDA, were carried out in DMAc at a solid content of about 20%. The thermal conversion to PIs carried out by successive heating of the PAA films to 300°C .

The formation of PIs was confirmed by FTIR spectroscopy. The FTIR spectra of 6FDA-based PIs are shown in Figure 5. FTIR spectra of the PAA showed the absorption bands at $3300\text{--}3100\text{ cm}^{-1}$ corresponding to amide ($-\text{NH}-$) and acid ($-\text{OH}$) stretching, 1718 cm^{-1} to $\text{C}=\text{O}$ stretching of carboxylic acid, 1730 cm^{-1} to $\text{C}=\text{O}$ stretching of amide, and 1373 cm^{-1} $\text{C}-\text{N}$ stretching of amide. The characteristic absorption bands of the imide ring appear near 1785 cm^{-1} corresponding to asymmetric $\text{C}=\text{O}$ stretching, 1730 cm^{-1} to symmetric $\text{C}=\text{O}$ stretching, 1373 cm^{-1} to $\text{C}-\text{N}$ stretching,

and 721 cm^{-1} to $\text{C}-\text{N}$ bending. The characteristic $\text{C}\equiv\text{N}$ absorption appeared at 2250 cm^{-1} . As for other samples of the series of CN-PIs, it was also pretty clear to find the characteristic $\text{C}\equiv\text{N}$ absorption at around 2250 cm^{-1} . Besides, all the polymers showed standard characteristic peaks of PIs. The observation of these absorption bands clearly indicated the existence of imide groups and cyano groups and confirmed the successful synthesis of cyano-containing PIs.

Inherent viscosity and solubility

Due to the poor solubility of the obtained PIs, the intrinsic viscosities of the PAA intermediates were used to indirectly express the molecular weights of the PIs. As shown in Table 1, their inherent viscosities were in the range of $0.94\text{--}1.17\text{ dL g}^{-1}$, which suggested their high molecular weights.

The solubility of the PI films was investigated in various solvents, including DMAc, DMF, NMP, DMSO, CHCl_3 , and THF (Table 1). Except that CN-6FDA, CN-ODPA, and H-6FDA, all the other PIs had good solvent resistance and could not be dissolved in above solvents even on heating. This could be explained by their rigid biphenyl-containing backbones and strong chain-chain interactions caused by $-\text{CN}$ and some other polar groups.

Thermal properties and CTE of the PI films

The thermal properties of the PI films were characterized by TGA, DSC, and TMA, and the results are listed in Table 2. DSC and TMA results showed that the T_g values of all polymers were in the range of $245\text{--}330^\circ\text{C}$. The rigid biphenyl element increases the rigidity of the polymer chain which, in turn, gives high glass-transition temperatures of PIs. The T_g 's order of CN-PI polymers was as follows: CN-ODPA < CN-BTDA < CN-BPDA < CN-6FDA < CN-PMDA, and the T_g 's order of H-PIs was the same. Due to the strong polarity and chain-chain interaction caused by $-\text{CN}$ groups, CN-PIs showed higher T_g values (Table 2). It was found that the T_g values of CN-PIs were $10\text{--}17^\circ\text{C}$ higher than the corresponding H-PIs, and a direct comparison of T_g values is shown in Figure 6.

As listed in Table 2, all the obtained PIs showed excellent thermal stability both in air and in N_2 . Their 5% weight loss temperatures (TD_5) and 10% weight loss temperatures (TD_{10}) in N_2 were $543\text{--}587^\circ\text{C}$ and $566\text{--}612^\circ\text{C}$, respectively. And, the TGA test in air also showed the competitive values. It was noticed that the incorporation of $-\text{CN}$ groups could affect the thermal stability of the PIs (Figure 7). In most cases, CN-PIs had better thermal stability and exhibited higher TD_5 and TD_{10} in N_2 . As for the residue weights at 800°C , the CN-PIs were also higher than their responding H-PIs, and the CN-BPDA polymer had the maximum residue weight of 65% at 800°C . This may be associated with the formation of the possible crosslinking networks through the triple bonds in $-\text{C}\equiv\text{N}$ moieties.

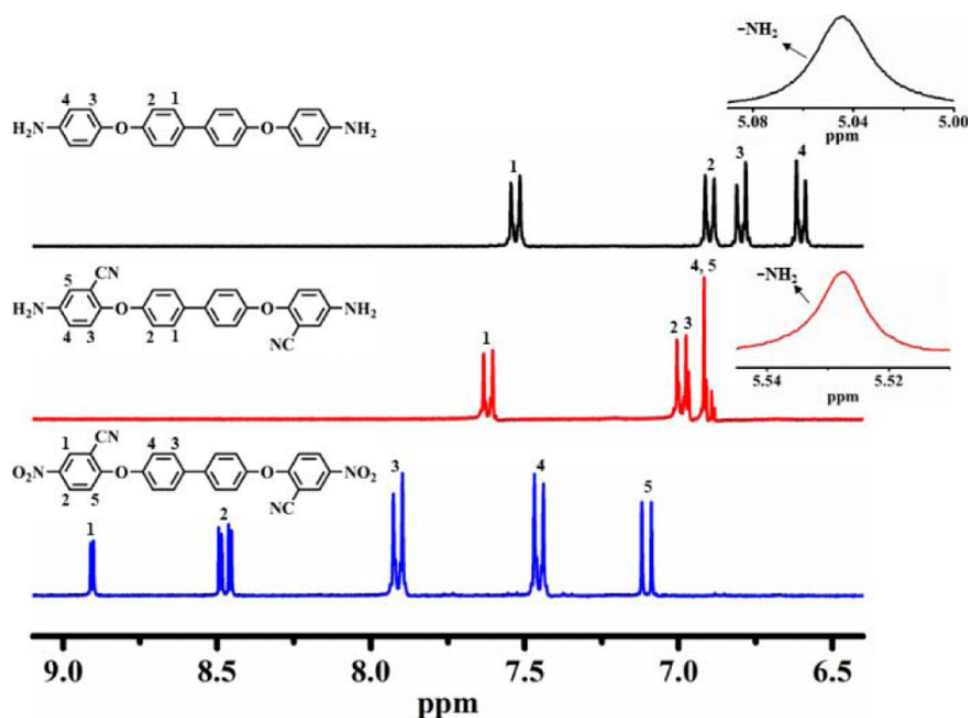


Figure 4. ^1H NMR spectra of H-BP-DA, CN-BP-DA, and CN-BP-NT. ^1H NMR: proton nuclear magnetic resonance.

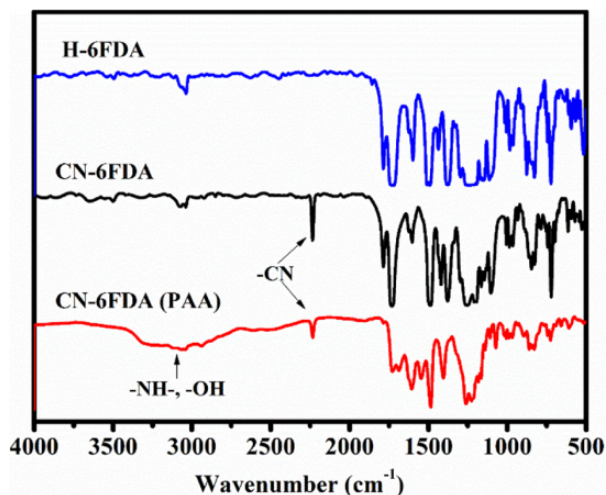


Figure 5. FTIR spectra of H-6FDA, CN-6FDA, and CN-6FDA (PAA). PAA: poly(amic acid); FTIR: Fourier-transform infrared spectroscopy; 6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride.

The preparation of low-CTE polymeric materials is crucial for their applications as coatings on metal surface to avoid dimensional mismatch of polymers and metals especially at high temperature, since CTE values of metals are often much lower than those of polymers.^{22,23} A few studies have been involved to look for the ways to decrease the CTE values of PIs.^{24–26} In this work, we found that CTE was influenced by the chain rigidity and the existence of $-\text{CN}$ groups. For each series, the PMDA-based PI had the lowest

Table 1. Intrinsic viscosities of PAAs and solubility of PIs.

Samples	η (dL g ⁻¹)	DMAc	DMF	NMP	DMSO	CHCl ₃	THF
H-6FDA	1.08	+-	+-	+-	+-	-	-
H-ODPA	1.02	-	-	-	-	-	-
H-BPDA	0.97	-	-	-	-	-	-
H-BTDA	0.94	-	-	-	-	-	-
H-PMDA	0.94	-	-	-	-	-	-
CN-6FDA	1.17	+-	+-	+-	+-	-	-
CN-ODPA	1.09	+-	+-	+-	+-	-	-
CN-BPDA	1.03	-	-	-	-	-	-
CN-BTDA	1.01	-	-	-	-	-	-
CN-PMDA	0.99	-	-	-	-	-	-

PAA: poly(amic acid); PI: polyimide; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methyl pyrrolidone; DMSO: dimethyl sulfoxide; CHCl₃: trichloromethane; THF: tetrahydrofuran; 6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride; ODPA: 4,4'-oxydiphthalic anhydride; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride; BTDA: 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PMDA: pyromellitic dianhydride; +-: partially soluble or swelling on heating; -: insoluble even on heating.

CTE value, and the one from 6FDA had highest CTE. Cyano-functionalized CN-PMDA had the lowest CTE value of 38.0 ppm K⁻¹, and as comparison, the CTE value of H-6FDA was up to 61.7 ppm K⁻¹. That meant the synthetic strategies could be applied to obtain low-CTE PI films.

Mechanical properties

Good mechanical properties are necessary for the PIs to use as thin films in many fields. In this study, the mechanical

Table 2. Thermal properties of the PI films.

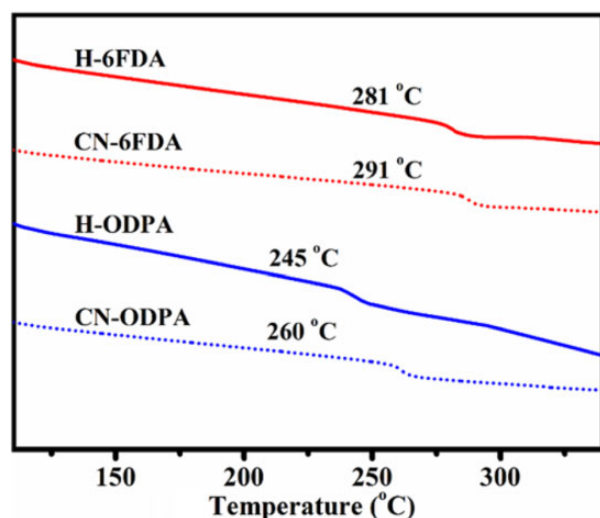
Samples ^a	T_g (°C)	CTE (ppm K ⁻¹)	TD (°C) in N ₂		TD (°C) in air	
			5%	10%	5%	10%
H-6FDA	281	61.7	543	566	569	590
H-ODPA	245	61.3	558	583	542	590
H-BPDA	274	53.2	566	589	570	605
H-BTDA	265	46.8	564	586	578	605
H-PMDA	313	42.0	570	592	587	611
CN-6FDA	291	61.2	584	612	553	581
CN-ODPA	260	60.1	587	608	541	588
CN-BPDA	286	53.3	570	601	575	611
CN-BTDA	276	45.3	568	598	564	610
CN-PMDA	330 ^c	38.0	571	592	567	610

PI: polyimide; CTE: coefficient of thermal expansion; DMAc: *N,N*-dimethylacetamide; DSC: differential scanning calorimetry; N₂: nitrogen; 6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride; ODPA: 4,4'-oxydiphthalic anhydride; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride; BTDA: 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PMDA: pyromellitic dianhydride; TD: decomposition temperature.

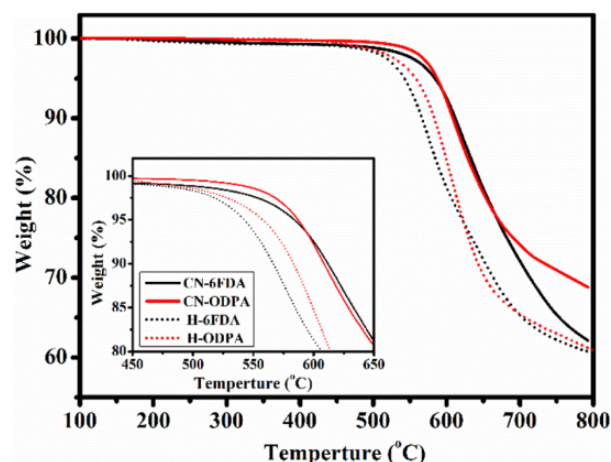
^aFilms casted by the polymer solution in DMAc.

^bFrom the second heating trace of DSC measurements conducted at a heating rate of 10 °C min⁻¹.

^cThe T_g value of CN-PMDA was measured by TMA, since the backbone of CN-PMDA was too rigid to exhibit discernible T_g value by DSC.

**Figure 6.** DSC curves of the PIs. PI: polyimide. DSC: differential scanning calorimetry.

properties of novel films were tested and the results are listed in Table 3. The samples of H-PI films had tensile stress at a maximum load of 112–157 MPa, Young's moduli of 1.9–3.1 GPa, and elongation at break of 17–25%. As for CN-PI films, the samples showed even more excellent mechanical properties with tensile stress of 126–163 MPa, Young's modulus of 2.0–3.4 GPa, and elongations at break of 19–30%. A direct comparison between CN-PIs and H-PIs is shown in Figure 8, and a higher mechanical strength may be associated with the strong interactions caused by the –CN groups on the CN-PI

**Figure 7.** TGA curves of the PIs under N₂ atmosphere. PI: polyimide; TGA: thermal gravimetric analysis; N₂: nitrogen.**Table 3.** Mechanical properties of the PI films.

Samples	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
H-6FDA	112	1.9	25
H-ODPA	127	2.4	21
H-BPDA	139	2.4	24
H-BTDA	144	2.9	17
H-PMDA	157	3.1	17
CN-6FDA	126	2.0	30
CN-ODPA	136	2.4	24
CN-BPDA	144	2.6	24
CN-BTDA	154	3.2	19
CN-PMDA	163	3.4	19

PI: polyimide; 6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride; ODPA: 4,4'-oxydiphthalic anhydride; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride; BTDA: 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PMDA: pyromellitic dianhydride.

backbones. These tensile results undoubtedly showed that CN-PIs were strong and flexible membrane materials.

Transparency measurements and peel strength of PI/copper

Transparency is one of the important parameters for optical films,²⁷ and cutoff wavelength and transmittance at 800 nm are listed in Table 4. It was observed that the presence of –CN groups would affect cutoff wavelength, and CN-PIs usually had lower cutoff wavelength in comparison with corresponding H-PI ones. As for transmittance, CN-PIs usually exhibited a better transparency than H-PIs. Fluorine-containing H-6FDA showed the best transparency and its transmittance at 800 nm reached as high as 91%. This was because the presence of the –CF₃ groups in the monomers significantly reduces the formation of the charge-transfer complex as well as the intermolecular interactions.²⁸ As illustrated in Figure 9, all the films showed

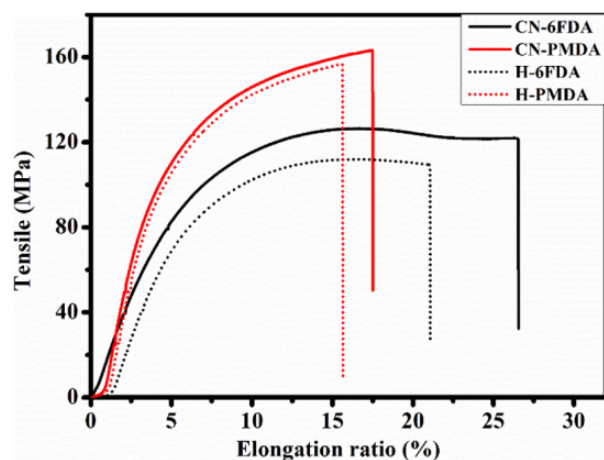


Figure 8. Comparisons of tensile properties between CN-PIs and H-PIs. PI: polyimide.

Table 4. Cutoff wavelength, transparency, and peel strength of the polymers.

Samples	Water absorption (%)	Cutoff wavelength (nm)	T_{\max}^a (%)	Peel strength (N mm^{-1})
H-6FDA	0.07	395	91	—
H-ODPA	0.41	413	90	0.71
H-BPDA	0.39	436	87	0.64
H-BTDA	0.39	461	86	—
H-PMDA	0.37	477	86	—
CN-6FDA	0.26	380	90	—
CN-ODPA	0.97	384	90	1.10
CN-BPDA	0.88	411	88	0.95
CN-BTDA	0.84	432	89	—
CN-PMDA	0.83	447	87	—

6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride; ODPA: 4,4'-oxydiphthalic anhydride; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride; BTDA: 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PMDA: pyromellitic dianhydride.

^aThe transmittance of samples at 800 nm.

improved transmittance compared with commercial used Kapton[®] film (produced by DuPont de Nemours) at the similar thickness.

To reveal the difference of peel strength between the two series of PIs, we tested several samples by our own method. The results between copper foils and PIs are listed in Table 4. It was clear that the CN-PIs showed improved peel strength compared with the H-PI PIs, and CN-ODPA showed the largest peel strength of 1.10 N mm^{-1} , suggesting its strong interaction to copper matrix and the potential use in flexibility circuit board.

Dielectric constants of the PIs

Dielectric constant (k) is the ability of a dielectric material to store electric potential energy under the influence of an

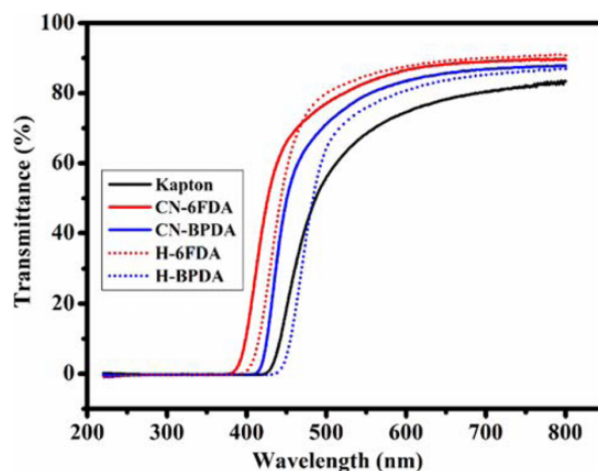


Figure 9. UV-vis spectra of the PIs and commercial Kapton. PI: polyimide; UV-vis: ultraviolet and visible.

Table 5. Dielectric properties of the polymers.

Samples	Dielectric constant	Dielectric loss	Volume resistivity ($\Omega\cdot\text{cm}$)
H-6FDA	3.01	0.0017	2.06×10^{11}
H-ODPA	3.15	0.0011	1.15×10^{11}
H-BPDA	3.18	0.0013	8.49×10^{10}
H-BTDA	3.45	0.0022	2.24×10^{11}
H-PMDA	3.28	0.0027	2.57×10^{11}
CN-6FDA	3.29	0.0055	4.15×10^{10}
CN-ODPA	3.46	0.0044	2.35×10^{11}
CN-BPDA	3.64	0.0056	5.24×10^{10}
CN-BTDA	3.69	0.0047	6.50×10^{10}
CN-PMDA	3.67	0.0068	3.68×10^{10}

6FDA: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride; ODPA: 4,4'-oxydiphthalic anhydride; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride; BTDA: 3,3',4,4'-benzophenonetetracarboxylic dianhydride; PMDA: pyromellitic dianhydride.

electric field, and the PIs have been widely investigated for using as low- k materials.²⁹ One can see from Table 5 that the dielectric constants at 1 MHz of the PI films vary in the range of 3.01–3.69 depending on the chemical structure. Obviously, it could be seen that the dielectric constants of H-PIs ($k = 3.01$ – 3.45 at 1 MHz) were somewhat lower than the corresponding CN-PIs ($k = 3.29$ – 3.69 at 1 MHz) under the same measurement conditions. The introduction of the –CN group into the PI structure would make a contribution toward increasing dielectric constants. The increase in the dielectric constant was related to the high molar polarization ($PM = 11.0 \text{ cm}^3 \text{ mol}^{-1}$) and low molar-specific volume ($VM = 19.5 \text{ cm}^3 \text{ mol}^{-1}$) of the –CN groups.¹⁹ Besides, the H-6FDA and CN-6FDA had the minimum values of dielectric constants in their own series due to the existence of –CF₃ groups, which could make an increase in free volume and a decrease in the polarizability.^{30,31} Both H-PIs and CN-PIs have good performance in terms of the

dielectric loss (<0.01 at 1 MHz). As for the volume resistivity, H-PIs and CN-PIs are both more than $10^{10} \Omega\cdot\text{cm}$ at 1000 Hz and more than $10^6 \Omega\cdot\text{cm}$ at 10^6 Hz, which fully demonstrated their good insulation performance.

On the other hand, the dielectric constants of PI films were often dramatically affected by their water absorption.³² The test results showed that the water absorptions of the resulting PIs were below 1%, and this could be attributed to the strong hydrophobic properties of the PI main chains (Table 4). It is worth noting that the water absorption capacity of CN-PIs was little higher than those of the H-PIs. This was a result of the introducing of $-\text{CN}$ groups with higher polarity which showed higher hydrophilicity than phenyl groups. The fluorinated polymers, 6FDA-based PIs, possessed the lowest extent of water absorption in their own series. This is probably due to the presence of the highly hydrophobic $-\text{CF}_3$ groups incorporated in the main chains.³³

Conclusions

A novel cyano and biphenyl containing diamine (CN-BP-DA) was synthesized through a two-step reaction with high yield. To study the effects of the cyano substituents on PI backbones, two series of aromatic PIs derived from CN-BP-DA and another diamine without $-\text{CN}$ groups were successfully prepared. All the aromatic polymers exhibited high inherent viscosities and good film-forming ability. Due to the existence of rigid and regular biphenyl units, most of the PI films had good solvent resistance. It was worth noting that the existence of the $-\text{CN}$ groups endowed CN-PIs more excellent performance in the aspect of thermal properties, mechanical strength, and peel strength to copper. In addition, the comparative studies revealed that the $-\text{CN}$ groups could also have an influence on dielectric constants, transparency, and water absorption of the PIs.

Declaration of Conflicting Interests

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