



Synthesis and properties of cyano group-containing polyimides with high peel strength

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Abstract

In order to investigate the effect of cyano groups (–CN) on the properties of the polymers, two series of polyimides (PIs) based on a –CN-containing diamine monomer and a diamine monomer without –CN group were synthesized and characterized, respectively. After studying the structure–property relationships of these polymers, it was found that some properties could be greatly improved with the incorporation of –CN groups. Firstly, the tensile test showed that the –CN-containing polymeric films had higher tensile strength and Young's moduli. The tensile strength and the Young's modulus of 4,4'-(hexafluoroisopropylidene) diphthalic with –CN groups anhydride reached 154.1 MPa and 1.66 GPa, respectively. Secondly, thermogravimetric analysis results revealed that the –CN-containing polymers (CN-PI polymers) had good thermal stability and exhibited no decomposition below 470°C under nitrogen atmosphere. Thirdly, the dielectric constants of the CN-PI polymers were in the range of 3.67–3.84 at 10 MHz, which had an increase of 0.5 in comparison with the corresponding PIs without –CN groups. Fourthly, the CN-PI polymers had higher peel strength to copper foils. The peel strength of 4,4'-biphenyltetracarboxylic dianhydride-containing –CN groups could reach 1.28 N mm^{–1}, suggesting its strong interaction to copper matrix and the potential use in flexibility circuit board. Finally, all the films showed better optical transparency compared with DuPont's Kapton[®] film.

Keywords

Polyimide, synthesis, peel strength, property

Introduction

Aromatic polyimides (PIs) possessed marked thermal stability and excellent mechanical and dielectric properties, and they have been widely applied in the fields of aviation, aerospace, and microelectronics.^{1–5} Because of their outstanding performance as structural or functional materials, the studies on the synthesis and applications of aromatic PIs were widely conducted. With the rapid development of advanced information technology, the conventional PIs can't completely meet the requirements of flexible circuit board. In order to meet these requirements, raising the peel strength of PIs but without sacrificing thermal and mechanical properties is very necessary.⁶ A variety of experiments were conducted to prepare the PIs with specific pendant moieties, such as trifluoromethyl, sulfonic acid, and methyl groups to improve gas permeability, dielectric constant, solubility, or proton conductivity.^{7–13}

Cyano group (–C≡N; –CN) with a triple bond structure endows it to have strong interactions with some other atoms

and also permit the occurrence of some reactions.^{14–16} Yu et al. reported the cross-linking of CN-containing PI (CN-PI) polymer catalyzed by zinc chloride, and the cross-linked polymer exhibited excellent thermal properties.¹⁵ Li and coworkers reported the successful conversion from –CN groups to carboxylic groups (–COOH), which indicated the reactivity of the –CN groups on the polymer chains.¹⁶ Recently, our group even found that

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sulfonated PIs containing multiple $-\text{CN}$ groups could greatly improve the dimensional stability due to the existence of the $-\text{CN}$ groups, and these acid-functionalized PIs were promising for polymer electrolyte films.¹⁷

In current study, in order to investigate the effect of $-\text{CN}$ groups on the properties of the polymers, two series of PIs based on a $-\text{CN}$ -containing diamine monomer (CNDA) and a diamine monomer without $-\text{CN}$ group (HDA) were synthesized. Some important properties including mechanical and thermal properties, solubility, transparency, dielectric constant, and peel strength of these PIs were thoroughly investigated. The effects of the $-\text{CN}$ groups on the property improvements of the PIs were revealed for the first time after direct comparison of the polymers with $-\text{CN}$ groups and their counterparts without $-\text{CN}$ groups.

Experimental

Materials

1-Chloro-4-nitrobenzene (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), 2-chloro-5-nitrobenzonitrile (Shanghai Darui Fine Chemical Co. Ltd, Shanghai, China), and 2,2-bis(4-hydroxyphenyl)propane (Aladdin Chemistry Co. Ltd, Shanghai, China) were used as received. 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 Sinopharm Chemical Reagent Beijing Co. Ltd and dried at 120°C for 12 h before use. Potassium carbonate (Beijing Chemical Reagent, China) was ground into fine powder and kept at 120°C prior to use. *N,N*-dimethylacetamide (DMAc, Tianjin Chemical Reagent, China), 80% hydrazine monohydrate (Acros, Beijing), ethanol (Beijing Chemical Reagent, China), *N,N*-dimethylformamide (DMF, Tianjin Chemical Reagent, China), and toluene (Beijing Chemical Reagent, China) were used as solvents and azeotropic reagent, respectively.

Synthesis of the CNDN

2-Chloro-5-nitrobenzonitrile (5.751 g, 0.0315 mol), 3.424 g of 2,2-bis(4-hydroxyphenyl)propane (0.015 mol), and 2.3 g of potassium carbonate (0.017 mol) were put into a 250 mL three-necked flask equipped with a nitrogen inlet, a Dean-Stark trap with a condenser and a magnetic stirrer. DMAc (45 mL) and toluene (10 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 150°C for another 5 h and poured into 200 mL cold ethanol to obtain yellow solid. Crude product of dinitro compound was washed several times in deionized water and recrystallized by ethanol. After drying at 80°C in an oven for 12 h, a yellow

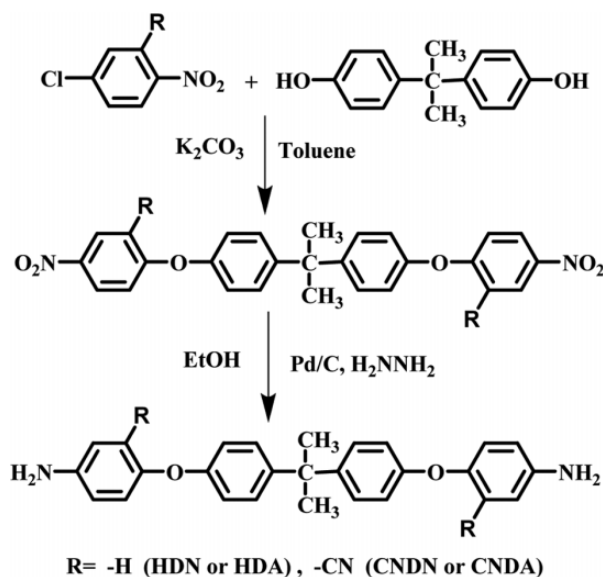


Figure 1. Synthesis of HDA and CNDA. HDA: cyano-free diamine monomer; CNDA: cyano-containing diamine monomer.

product was obtained (yield: 95%). The synthesis routine of a dinitro compound is shown in Figure 1.

Fourier transform infrared (FTIR; potassium bromide (KBr)): 1523, 1347 ($-\text{NO}_2$), and 2235 ($-\text{CN}$).

Proton nuclear magnetic resonance (^1H NMR; deuterated chloroform (CDCl_3), ppm): 8.56 (d, $J = 2.4$ Hz, 2 H), 8.42–8.38 (m, 3 H), 7.75 (d, $J = 8.7$ Hz, 2 H).

Synthesis of the CNDA

Dinitro compound with $-\text{CN}$ group (CNDN; 5.20 g, 0.01 mol), 0.4 g of 10% palladium on carbon, and 15 mL of hydrazine hydrate were added into a 250 mL three-necked flask equipped with a nitrogen (N_2) inlet with a dropping funnel, a condenser, and a magnetic stirrer. Ethanol (100 mL) was added as solvent. Then, the mixture was refluxed with stirring for 6 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 water/ethanol (50/50 v/v) and dried under vacuum at 80°C for 12 h. Off-white product was obtained (yield: 80%). The synthesis routine of the diamine monomer is shown in Figure 1.

FTIR (KBr): 3429, 3354 (amino group; $-\text{NH}_2$), and 2235 ($-\text{CN}$).

^1H NMR (CDCl_3 , ppm): 7.18 (d, $J = 8.7$ Hz, 2H), 6.90 (s, 2H), and 6.87–6.79 (m, 3H).

Synthesis of the (HDN)

$-\text{CN}$ -Free dinitro compound (HDN) compound was synthesized using a procedure similar to CNDN (yield: 93%). The synthesis routine is shown in Figure 1.

FTIR (KBr): 1523, 1347 ($-\text{NO}_2$).

^1H NMR (CDCl_3 , ppm): 8.20 (d, $J = 8.9$ Hz, 2H), 7.30 (d, $J = 8.9$ Hz, 2H), and 7.05–7.0 (m, 4H).

Synthesis of HDA

HDA monomer was synthesized using a procedure similar to CNDA (yield: 75%). The synthesis routine of diamine monomer with $-\text{CN}$ group is shown in Figure 1.

FTIR (KBr): 3429, 3354 ($-\text{NH}_2$).

^1H NMR (CDCl_3 , ppm): 7.12 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 6.66 (d, $J = 8.7$ Hz, 2H).

Synthesis of the polymers

As a typical procedure for the preparation of PIs, the synthesis of PI based on CNDA and 6FDA (CN-6FDA) (CN-6FDA) was given as follows: CNDA-diamine (0.4605 g, 1 mmol) and DMAc (4 mL) were placed into a 25-mL three-necked flask equipped with a magnetic stirrer and a N_2 inlet under N_2 atmosphere. After the diamine was entirely dissolved, 6FDA (0.4442 g, 1 mmol) was added to the solution. The mixture was stirred at room temperature for 24 h to yield polyamic acid solution. The solution was cast onto a glass plate and then heated by the following procedure: $80^\circ\text{C}/3$ h, $110^\circ\text{C}/0.5$ h, $150^\circ\text{C}/0.5$ h, $180^\circ\text{C}/0.5$ h, $210^\circ\text{C}/0.5$ h, $240^\circ\text{C}/0.5$ h, and $270^\circ\text{C}/0.5$ h. The PI film (CN-6FDA) was removed by immersing the glass plate in boiling water. The molecular weight of CN-6FDA was measured by gel permeation chromatography and the number-average molecular weight of CN-6FDA was $76,500 \text{ g mol}^{-1}$ and polydispersity index was 1.60.

All the other PIs were synthesized by a similar procedure, and the thickness of the films was about $60 \mu\text{m}$. The synthesis routine is shown in Figure 2.

PI based on HDA and ODPA (H-ODPA). FTIR: 1653 and 1755 ($\text{C}=\text{O}$ from imide ring).

^1H NMR (CDCl_3 , ppm): 8.02 (d, $J = 8.1$ Hz, 2 h), 7.57 (d, $J = 2.1$ Hz, 2 h), 7.49 (d, $J = 9.0$ Hz, 2 h), 7.39 (d, $J = 8.7$ Hz, 4 h), 7.26 (d, $J = 9.0$ Hz, 4 h), 7.13 (d, $J = 9.0$ Hz, 4 h), 7.01 (d, $J = 8.7$ Hz, 4 h).

PI based on HDA and 6FDA (H-6FDA). FTIR: 1655 and 1760 ($\text{C}=\text{O}$ from imide ring).

^1H NMR (deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$), ppm): 8.05 (d, $J = 8.1$ Hz, 2H), 7.94–7.88 (m, 4H), 7.37 (d, $J = 8.7$ Hz, 4H), 7.27 (d, $J = 8.7$ Hz, 4H), 7.13 (d, $J = 8.7$ Hz, 4H), 7.01 (d, $J = 8.7$ Hz, 4H).

PI based on CNDA and ODPA (CN-ODPA). FTIR: 1655 and 1755 ($\text{C}=\text{O}$ from imide ring), 2235 ($-\text{CN}$).

^1H NMR ($\text{DMSO}-d_6$, ppm): 8.08 (d, $J = 9.0$ Hz, 2H), 7.98 (s, 2H), 7.75 (d, $J = 9.0$ Hz, 2H), 7.72 (s, 4H), 7.37

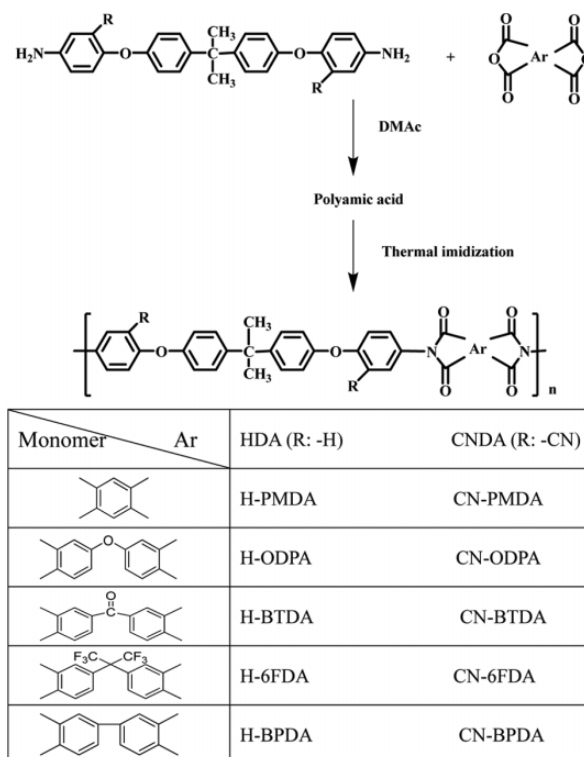


Figure 2. Synthesis of CN-PI and H-PI. CN-PI: cyano-containing polyimides; H-PI: polyimide without cyano groups.

(d, $J = 8.4$ Hz, 4H), 7.17 (d, $J = 8.4$ Hz, 4H), 7.10 (d, $J = 9.0$ Hz, 2H).

CN-6FDA. FTIR: 1652 and 1763 ($\text{C}=\text{O}$ from imide ring), 1350–1120 (CF_3), 2235 ($-\text{CN}$).

^1H NMR ($\text{DMSO}-d_6$, ppm): 8.01–8.04 (m, 2H), 7.93 (d, $J = 9.0$ Hz, 4H), 7.77 (d, $J = 2.4$ Hz, 2H), 7.60–7.55 (m, 2H), 7.11–7.00 (m, 6H).

Measurements

Characterization

^1H NMR experiments were carried out on a Bruker 510 spectrometer (Billerica, Massachusetts, United States; 300 MHz) using $\text{DMSO}-d_6$ or CDCl_3 as solvent. FTIR spectra were measured on a Nicolet impact 410 FTIR spectrometer at a resolution of 2 cm^{-1} in the range of 400–4000 cm^{-1} , and thin film samples were used and thin film samples were used.

Mechanical properties of the PIs

The mechanical properties of the films were measured at room temperature on Shimadzu AG-I 1KN (Kyoto, Japan) at a strain rate of 2 mm min^{-1} . The size of the samples was $50 \times 5 \text{ mm}^2$. Each membrane was measured three times, and the final results were the average value of the three data.

Thermal properties of the PIs

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 821e instrument (Columbus, Ohio, USA) from 30°C to 350°C at a heating rate of 20°C min⁻¹ under N₂ atmosphere at a constant flow of 200 mL min⁻¹. Thermogravimetric analysis (TGA) on a PerkinElmer Pyris-1 thermal analyzer system (Waltham, Massachusetts, USA) was employed to evaluate the thermal stability of the polymers. Before measurement, the samples were kept in the TGA furnace at 150°C for 15 min under N₂ atmosphere to remove water from the samples. Then, the samples were reheated from 50°C to 800°C at the rate of 10°C min⁻¹ under N₂ atmosphere and the temperature at 5% and 10% weight losses (TD₅ and TD₁₀, respectively) were recorded.

Solubility properties of the PIs

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.

Dielectric constants of the PIs

The dielectric properties of the PIs were measured by an Agilent 4294A precision impedance analyzer (Santa Clara, California, USA) from 1 to 10 MHz at 25°C. Before measurement, the sample films were dried under vacuum at 150°C for 5 h to remove moisture. Then liquid silver was spread through the films to cover a 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.

Transparency measurement of the PI films

Ultraviolet–visible (UV-Vis) spectra were acquired on a Shimadzu 3600 UV-Vis-near-infrared spectrophotometer. The membrane samples were fixed in quartz pool and empty quartz pool for comparison. The membrane samples were cut into 9 × 45 mm².

Peel strength of PI/copper

Peel strength of the materials was measured by Shimadzu AG-I 1kN at room temperature at a strain rate of 2 mm min⁻¹. The size of samples was 100 × 5 mm². Before measurement, the polyamic acid solution was cast on the copper foil. Then the samples were heated by the following procedure: 80°C/3 h, 110°C/0.5 h, 150°C/0.5 h, 180°C/0.5 h, 210°C/0.5 h, 240°C/0.5 h, and 270°C/0.5 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 180° direction and then the membrane and copper was separated gradually.

Results and discussion

Synthesis and characterization of the monomers and PIs

The diamine monomers, HDA and CNDA, were prepared by a two-step reaction starting from an aromatic nucleophilic substitution, followed by a reduction reaction (Figure 1). The structure of the monomers was confirmed by FTIR and ¹H NMR spectroscopies. In FTIR spectrum of CNDN, the absorption bands at 1523 and 1347 cm⁻¹ were assigned to the stretching vibrations and bending vibrations of nitro groups (–NO₂). The absorption bands at 2235 cm⁻¹ due to the stretching vibrations of –CN groups in CNDN and CNDA were observed. The absorption bands at 3354 and 3429 cm⁻¹ were assigned to the stretching vibrations and bending vibrations of –NH₂ groups in the diamine monomers (HDA and CNDA). It was clear to see the disappearance of the absorptions belonging to –NO₂ groups in CNDN and the appearance of the absorptions belonging to –NH₂ groups in CNDA after the reduction reaction (Figure 3).

¹H NMR spectra of HDA and CNDA 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 –CN groups could significantly affect the chemical shifts and peak splits of the protons on the benzene rings attached to –CN pendants. The signals of –NH₂ around 6.32–6.15 ppm were also found.

PIs were prepared according to a typical two-step polymerization method, including the formation of a polyamic acid 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 dianhydride monomers, PMDA, ODPA, 6FDA, BTDA, and BPDA, were carried out in DMAc at a solid content of about 10%.

A soluble CN-ODPA was used to analyze the chemical structure of the polymers. In its ¹H NMR spectrum, all spectral signals in the range of 8.2–7.0 ppm were well assigned to the protons of CN-ODPA, which suggested the successful preparation of the polymer. The peaks centered at 7.4 and 7.2 were assigned to H5 and H4, which were influenced by the ether and –C(CH₃)₂– linkages, leading to a relatively lower chemical shifts. The peaks centered at 7.6 were assigned to H6 and H8, and the peaks in the range of 7.8–7.7 were assigned to H2. The peaks in the range of 8.2–7.9 were assigned to H7 and H1 (Figure 5).

Mechanical properties

The mechanical properties of the PI films were evaluated, and the results are listed in Table 1. The polymer films had tensile strengths of 121.9–154.1 MPa, elongations at break of 6.2–15.8%, and Young's moduli of 1.09–1.66 GPa,

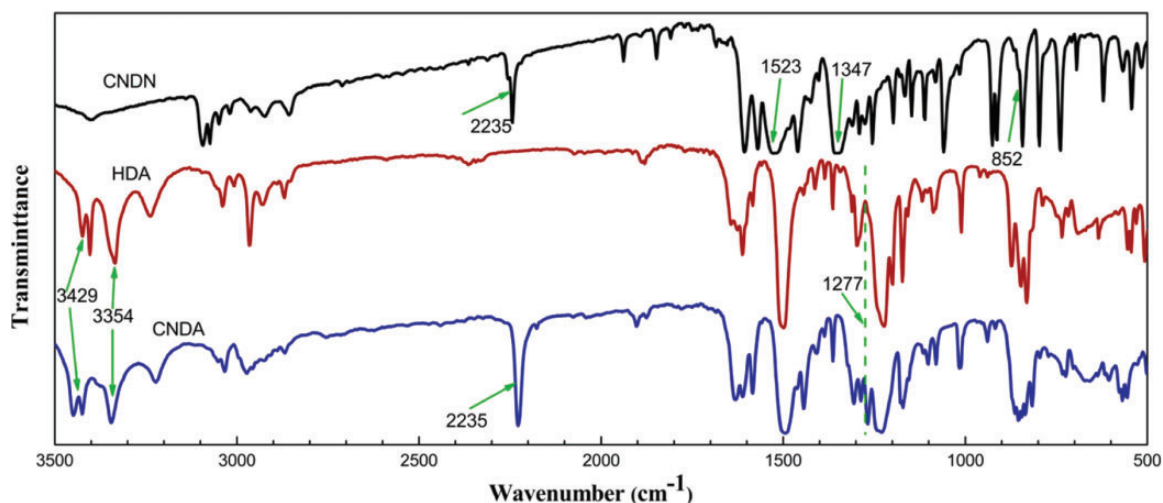


Figure 3. FTIR spectra of CNDN, HDA, and CNDA. FTIR: Fourier transform infrared; CNDN: dinitro compound with cyano groups; HDA: cyano-free diamine monomer; CNDA: cyano-containing diamine monomer.

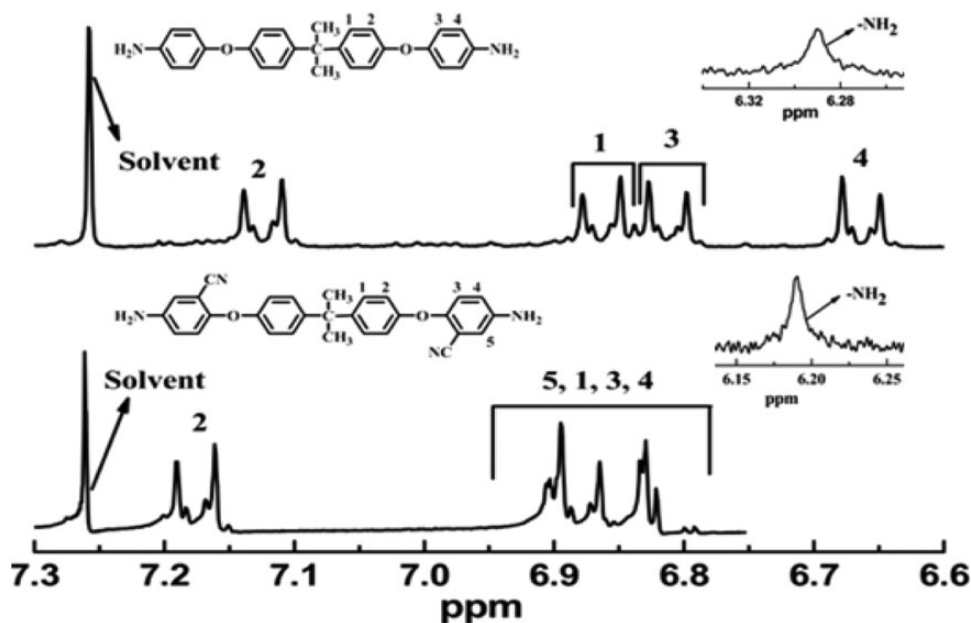


Figure 4. ^1H NMR spectra of HDA and CNDA. ^1H NMR: proton nuclear magnetic resonance; HDA: cyano-free diamine monomer; CNDA: cyano-containing diamine monomer.

indicating that they are strong polymeric materials. It was interesting to find that the CN-PI polymers showed improved tensile strength and Young's moduli. The existence of $-\text{CN}$ groups had an obvious influence on the values of tensile strength and Young's moduli, which may be explained by the strong interactions caused by polar $-\text{CN}$ groups.

Thermal properties

The thermal property of the films was characterized by TGA and DSC, and the results are shown in Table 2. The glass transition temperature (T_g) values of the polymers

were in the range of $239\text{--}308^\circ\text{C}$. The order of T_g s of PI without $-\text{CN}$ groups (H-PI) polymers was as follows: $\text{H-BTDA} < \text{H-ODPA} < \text{H-BPDA} < \text{H-6FDA} < \text{H-PMDA}$. However, the order of T_g s of PI polymers with $-\text{CN}$ groups was different, and the order was as follows: $\text{CN-ODPA} < \text{CN-BTDA} < \text{CN-6FDA} < \text{CN-BPDA} < \text{CN-PMDA}$. The T_g value was affected by multifactors, such as the rigidity of the polymer backbones, the polarity of the pendants, the interaction of the groups, and the molecular weight of the polymers. The different T_g orders between CN-PI and H-PI could be explained by the contradictory effects of $-\text{CN}$ groups on T_g values. The high polarity and strong

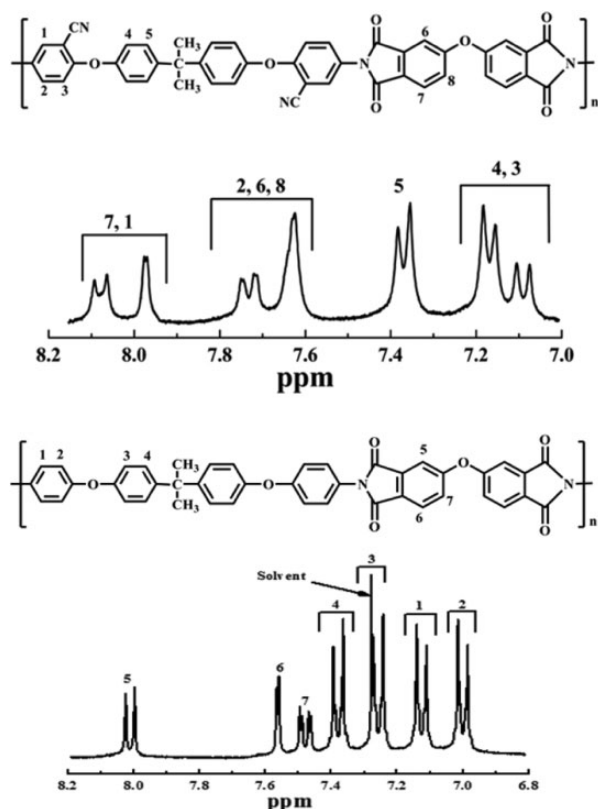


Figure 5. ^1H NMR spectra of CN-ODPA and H-ODPA. ^1H : proton nuclear magnetic resonance; CN-ODPA: 4,4'-oxydiphthalic anhydride with cyano group; H-ODPA: 4,4'-oxydiphthalic anhydride without cyano groups.

Table 1. Mechanical properties of the PI films.

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
H-PMDA	121.9	1.09	7.9
H-ODPA	126.7	1.12	15.8
H-BTDA	122.8	1.23	9.8
H-6FDA	124.9	1.30	6.9
H-BPDA	127.0	1.21	6.2
CN-PMDA	138.2	1.33	11.5
CN-ODPA	143.5	1.54	11.1
CN-BTDA	147.9	1.64	8.3
CN-6FDA	154.1	1.66	7.6
CN-BPDA	144.9	1.57	6.7

PI: polyimide; H-PMDA: PI based on pyromellitic dianhydride and a diamine without cyano groups; H-ODPA: PI based on 4,4'-oxydiphthalic anhydride and a diamine without cyano groups; H-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine without cyano groups; H-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine without cyano groups; H-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine without cyano groups; CN-PMDA: PI based on pyromellitic dianhydride and a diamine with cyano groups; CN-ODPA: PI based on 4,4'-oxydiphthalic anhydride and a diamine with cyano groups; CN-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine with cyano groups; CN-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine with cyano groups; CN-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine with cyano groups.

Table 2. Thermal properties of the PI films.

Polymer	Film quality ^a	T_g ($^{\circ}\text{C}$) ^b	TD_5 ($^{\circ}\text{C}$) ^c	TD_{10} ($^{\circ}\text{C}$) ^d
H-PMDA	Clear, flexible	308	541	557
H-ODPA	Clear, flexible	244	524	537
H-BTDA	Clear, flexible	239	542	560
H-6FDA	Clear, flexible	257	534	549
H-BPDA	Clear, flexible	247	546	558
CN-PMDA	Clear, flexible	295	514	532
CN-ODPA	Clear, flexible	239	505	524
CN-BTDA	Clear, flexible	254	519	542
CN-6FDA	Clear, flexible	260	524	543
CN-BPDA	Clear, flexible	267	530	550

PI: polyimide; H-PMDA: PI based on pyromellitic dianhydride and a diamine without cyano groups; H-ODPA: PI based on 4,4'-oxydiphthalic anhydride and a diamine without cyano groups; H-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine without cyano groups; H-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine without cyano groups; H-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine without cyano groups; CN-PMDA: PI based on pyromellitic dianhydride and a diamine with cyano groups; CN-ODPA: PI based on 4,4'-oxydiphthalic anhydride and a diamine with cyano groups; CN-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine with cyano groups; CN-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine with cyano groups; CN-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine with cyano groups; T_g : glass transition temperature; DMAc: *N,N*-dimethylacetamide; DSC: differential scanning calorimeter; TGA: thermogravimetric analysis; TD_5 : 5% weight loss temperature; TD_{10} : 10% weight loss temperature; N_2 : nitrogen.

^aFilms casted by the polymer solution in DMAc.

^bFrom the second heating trace of DSC measurements conducted at a heating rate of $20^{\circ}\text{C min}^{-1}$.

^c TD_5 measured by TGA at a heating rate of $10^{\circ}\text{C min}^{-1}$ under N_2 atmosphere.

^d TD_{10} measured by TGA at a heating rate of $10^{\circ}\text{C min}^{-1}$ under N_2 atmosphere.

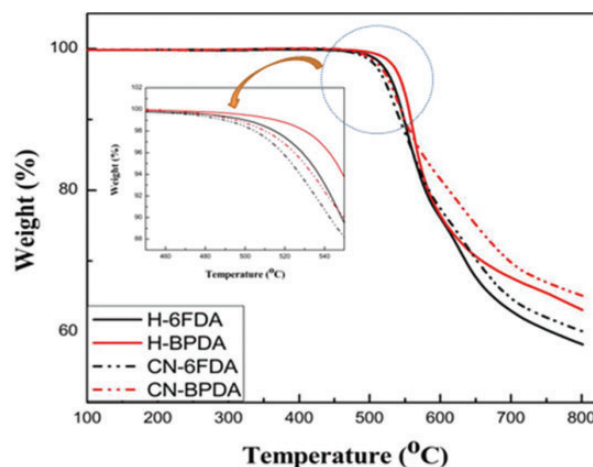


Figure 6. TGA curves of the PIs. TGA: thermogravimetric analysis; PI: polyimide.

interaction of the $-\text{CN}$ groups may lead to the increase in the T_g values. Meanwhile, the electron-withdrawing effects of $-\text{CN}$ groups may decrease the rigidity of the backbones and lead to lower T_g values.

Table 3. Solubility of the PIs.

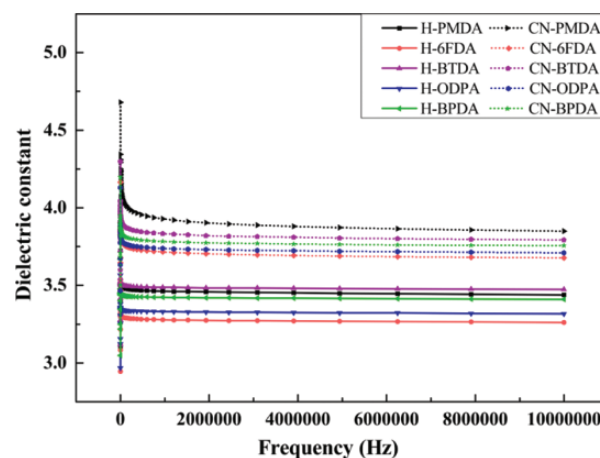
Polymer	Solvent					
	DMAc	DMF	NMP	DMSO	CHCl ₃	THF
H-PMDA	—	—	—	—	—	—
H-ODPA	+	+	+	+	+	+
H-BTDA	—	—	—	—	—	—
H-6FDA	+	+	+	—	+	+
H-BPDA	—	—	—	—	—	—
CN-PMDA	—	—	+	—	—	—
CN-ODPA	+	+	+	+	+	+
CN-BTDA	—	—	—	—	—	—
CN-6FDA	+	+	+	—	+	+
CN-BPDA	—	—	—	—	—	—

PI: polyimide; H-PMDA: PI based on pyromellitic dianhydride and a diamine without cyano groups; H-ODPA: PI based on 4,4'-oxydipthalic anhydride and a diamine without cyano groups; H-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine without cyano groups; H-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine without cyano groups; H-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine without cyano groups; CN-PMDA: PI based on pyromellitic dianhydride and a diamine with cyano groups; CN-ODPA: PI based on 4,4'-oxydipthalic anhydride and a diamine with cyano groups; CN-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine with cyano groups; CN-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine with cyano groups; CN-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine with cyano groups; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; CHCl₃: chloroform; THF: tetrahydrofuran; +: soluble at room temperature; -: soluble on heating; —: insoluble.

According to Figure 6, all of the obtained PIs showed very good thermal stability. The TD₅ of the polymers was over 505°C, and the TD₁₀ of the polymers was over 524°C. The –CN-containing polymers had good thermal stability and exhibited no decomposition below 470°C under N₂ atmosphere. It was seen that the residue weights at 800°C of the CN-PI polymers was higher than their responding H-PI polymers, and the BPDA with –CN groups (CN-BPDA) polymer had the maximum residue weight of 65% at 800°C. Also, the incorporation of –CN groups didn't obviously decrease the thermal stability of the polymers.

Solubility properties

The solubility of the PIs obtained by the thermal imidization method was investigated in various solvents including DMAc, DMF, *N*-methyl-2-pyrrolidone (NMP), DMSO, DMF, chloroform (CHCl₃), and tetrahydrofuran (THF), as shown in Table 3. H-ODPA, H-6FDA, CN-ODPA, and CN-6FDA could be dissolved in DMAc, DMF, NMP, DMAc, CHCl₃, and THF at room temperature or under heating, which suggested thin films could be prepared by typical solution casting method. Overall, the solubility of the –CN series was weaker than that of –CN-free series.

**Figure 7.** Dielectric constants of two series of polymers.**Table 4.** Peel strength, cut off wave number, transparency, and dielectric constants of polymers.

Polymer	Peel strength (N/mm)	Cut off wave number (nm)	T (%) ^a	Dielectric constant ^b
H-PMDA	1.08	455	84.60	3.43
H-ODPA	0.86	397	85.38	3.26
H-BTDA	0.84	457	79.56	3.47
H-6FDA	0.76	405	87.58	3.31
H-BPDA	1.17	425	84.03	3.40
CN-PMDA	1.19	432	82.24	3.84
CN-ODPA	0.89	407	86.54	3.67
CN-BTDA	0.85	435	69.17	3.79
CN-6FDA	0.83	375	87.79	3.70
CN-BPDA	1.28	410	83.18	3.75

PI: polyimide; H-PMDA: PI based on pyromellitic dianhydride and a diamine without cyano groups; H-ODPA: PI based on 4,4'-oxydipthalic anhydride and a diamine without cyano groups; H-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine without cyano groups; H-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine without cyano groups; H-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine without cyano groups; CN-PMDA: PI based on pyromellitic dianhydride and a diamine with cyano groups; CN-ODPA: PI based on 4,4'-oxydipthalic anhydride and a diamine with cyano groups; CN-BTDA: PI based on 4,4'-benzophenonetetracarboxylic dianhydride and a diamine with cyano groups; CN-6FDA: PI based on 4,4'-(hexafluoroisopropylidene) diphthalic anhydride and a diamine with cyano groups; CN-BPDA: PI based on 4,4'-biphenyltetracarboxylic dianhydride and a diamine with cyano groups.

^aTransmittance at 600 nm wave number (%).

^bDielectric constant value at the frequency of 10 MHz.

Dielectric constants of the PIs

Dielectric constant is the ability of a dielectric material to store electric potential energy under the influence of an electric field, and the fluorinated PIs have been widely investigated for use as low dielectric constant materials.^{18,19} In this study, dielectric constants of the PIs were measured from 1 to 10 MHz, as showed in Figure 7. The dielectric constant values of the PIs at

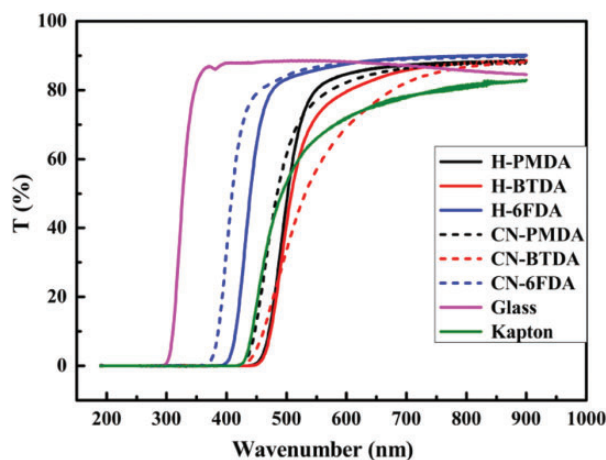


Figure 8. UV-Vis spectra of the PIs, glass, and commercial Kapton. UV-Vis: ultraviolet-visible; PI: polyimide.

10 MHz were ranged from 3.26 to 3.84 at 10 MHz, and the H-6FDA and CN-6FDA had the minimum values of dielectric constants in their own series due to the existence of $-\text{CF}_3$ groups (Table 4). It was found that the introduction of the nitrile group into the PI structure would make a large contribution toward increasing dielectric constant. The increase of the dielectric constant (about 0.5 at 10 MHz) was related to the high molar polarization ($\text{PM} = 11.0 \text{ cm}^3 \text{ mol}^{-1}$) and low molar-specific volume ($\text{VM} = 19.5 \text{ cm}^3 \text{ mol}^{-1}$) of the $-\text{CN}$ groups.²⁰

Transparency measurements of the PI films

The transparency is one of the important parameters for thin films to apply as optical materials.²¹ A direct comparison of the PIs (Thickness: approximately 60 μm), glass, and commercial Kapton® film (Thickness: approximately 50 μm) is shown in Figure 8. Cut off wave number and transmittance at the wave number of 600 nm are listed in Table 4. When the wavelength was lower than 300 nm, the transmittance of the glass and PI membrane was 0. CN-6FDA showed the best transparency, and its transparency at 600 nm reached 87.79%. All of the films showed improved transmittance compared with commercial used Kapton® membrane at the similar thickness. The presence of $-\text{CN}$ groups may affect both cut off wave number and transmittance, and CN-PI polymers had lower cut off wave number in comparison with corresponding H-PI ones.

Peel strength of PI/copper

Peel strength reflects the bond strength of the materials to the substrates,^{22,23} and the results between copper foils and PIs are listed in Table 4. It was clear that the CN-PI polyimides showed improved peel strength compared with the H-PI, and CN-BPDA showed the largest peel strength of

1.28 N mm^{-1} , suggesting its strong interaction to copper substrates and the potential use in flexibility circuit board.

Conclusions

We have successfully synthesized two series of polymers with and without $-\text{CN}$ groups and thoroughly studied the influences on the property caused by the introduction of $-\text{CN}$ groups. Some useful results were given as follows: (1) The CN-PI polymer films had higher tensile strength and Young's moduli; (2) the CN-PI polymers had higher residue weights at 800°C, and the incorporation of $-\text{CN}$ groups didn't obviously decrease the thermal stability of the PIs; (3) the incorporation of $-\text{CN}$ groups would make an increase of 0.5 on the dielectric constants of the polymers in comparison with the corresponding PIs without $-\text{CN}$ groups; and (4) The presence of $-\text{CN}$ groups may affect both cut off wave number and transparency; and (5) The CN-PI PIs possessed improved peel strength values to copper foils.

Declaration of Conflicting Interests

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