

Synthesis and Properties of Crosslinked Poly(arylene ether nitriles) Containing Pendant Phthalonitrile

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ABSTRACT: In this study, poly(arylene ether nitriles) containing pendant carboxyl groups (PEN-COOH) was first synthesized via nucleophilic aromatic substitution reaction from phenolphthalein, hydroquinone and 2,6-dichlorobenzonitrile. Then, poly(arylene ether nitriles) with pendant phthalonitrile groups (PEN-CN) was obtained via the Yamazaki-Higashi phosphorylation route from 4-(4-aminophenoxy)phthalonitrile (APN) with PEN-COOH in the presence of CaCl_2 , thus the phthalonitrile as pendant groups in PEN-CN were easily crosslinked by further thermal treatment. The effect of crosslinking density on the thermal stabilities, dielectric properties and water absorption of the PEN-CN was investigated. These results showed that the T_g of PEN-CN was improved from 182 to 213°C, dielectric constant (ϵ) was increased from 3.1 to 3.9, and dielectric loss ($\tan \delta$) was decreased from 0.090 to 0.013 at 1 kHz. The water absorption of PEN-CN after thermal crosslinking was <1.01 wt %, which showed excellent water resisting property. Therefore, this kind of poly(arylene ether nitriles) containing pendant phthalonitrile could be a good candidate as matrix resins for high-performance polymeric materials. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: synthesis; crosslinking; thermal stability; dielectric properties; thermoplastics

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INTRODUCTION

As a well-known class of engineering thermoplastics, poly(arylene ether)s are the most commonly used materials in transportation, aerospace, electrical, and electronic fields. For example, sulfone-containing poly(arylene ethers) such as Udel™ (Amoco) or ketone functional polymers such as PEEK™ (Victrex) have gained significant commercial importance. Among the categories of high performance thermoplastics, poly(arylene ether nitriles) (PEN) is well-known for a class of semicrystalline polymers with pendant nitrile groups. The first commercialized PEN product, developed by Idemitsu with trade name PEN ID300, has been identified as excellent matrix resins for carbon reinforcement. Moreover, the pendant nitrile groups (CN) also serve as potential sites for crosslinking reaction, which could improve the mechanical and thermal properties.^{1,2}

However, due to the premature crystallization from organic solvent mediums, the poor solubility of PEN hampers its synthesis, processing and widespread application. Compared with other commercially available polymers (PES, PEKEK), the glass transition temperature of PEN is lower (ID 300, $T_g = 148^\circ\text{C}$),

which results in the decrease of mechanical property and failure to use at elevated temperatures, especially in aerospace, industrial or other extreme conditions. Nevertheless, these problems have initiated several researches such as structural modification of polymer chain to improve solubility and thermal stability.^{3–6} Among them, many researches have been done through incorporating flexible linkages, noncoplanar units into the polymer backbones or attaching pendant groups to the main chain of polymer.^{7,8} On the other hand, enhancing the crosslinking density of polymer is also an effective way to improve the glass transition temperature and achieve good thermal stability of polymer resin. For instance, it was feasible to introduce nitriles into the polymer chain as pendant or terminal groups. As a result, high-temperature s-triazine or phthalocyanine resins can be formed via trimerization or tetramerization reaction of nitrile groups.^{9–11}

Recently, our laboratory has been investigating on the synthesis, modification, and composites of poly(arylene ether nitriles), especially in the synthesis of copolymers from different dihydric phenol with 2,6-dichlorobenzonitrile (DCBN). For example, functional fluorescence PEN has been obtained by

copolymerization from phenolphthalein and phenolphthalein with DCBN. This polymer contains pendant carboxyl group and can be further react with other active groups. Meanwhile, our laboratory prepared phthalonitrile monomer and studied the reaction mechanism of nitriles.^{12–15} These results showed the crosslinking of phthalonitrile is easier than that of pendant nitrile groups of PEN even without catalyst. For this reason, we synthesized 4-(4-aminophenoxy)phthalonitrile (APN) as a active monomer which contains amino-group ($-NH_2$) and phthalonitrile group. The amino-group of APN would react with $PEN-COOH$ via the Yamazaki–Higashi phosphorylation and thus poly(arylene ether nitriles) with pendant phthalonitriles ($PEN-CN$) was obtained. On the basis of this idea, we here introduced phthalonitrile groups into the main chains as pendant groups to increase the concentration of activated nitriles and then the crosslinking temperature is decreased under normal pressure. To obtain various crosslinking density samples, the $PEN-CN$ films underwent heat treatments with different temperatures. In addition, we also studied the effect of crosslinking reaction on the thermal properties, dielectric properties, water absorption capability, and crystallinity.

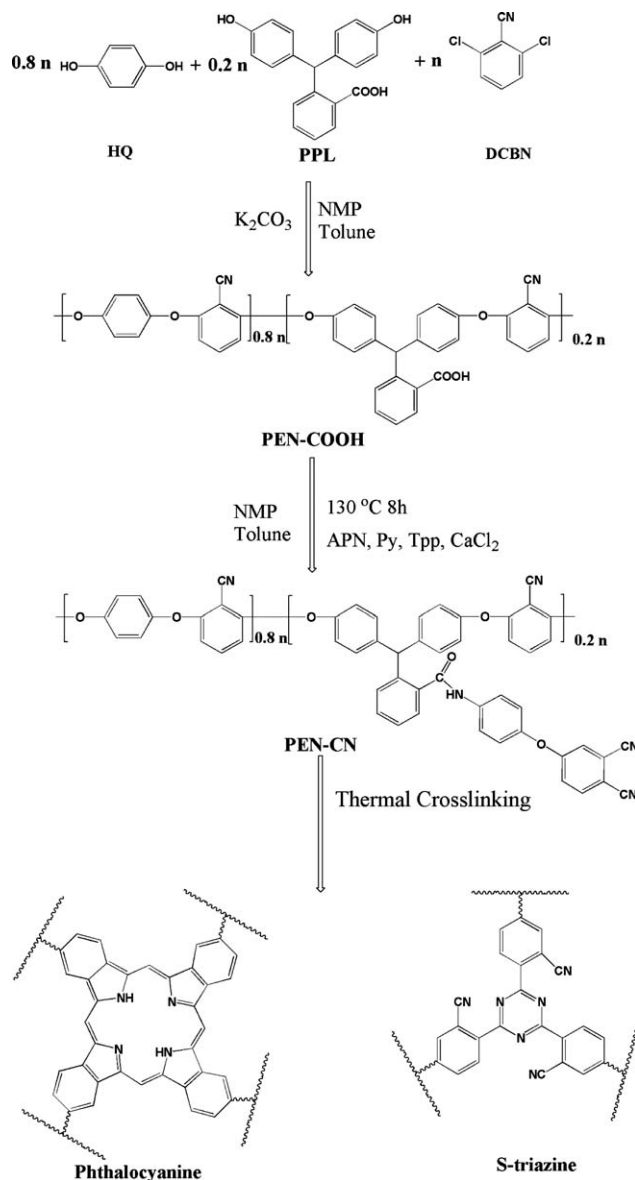
EXPERIMENTAL

Materials

N,N'-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), toluene, zinc powder, sodium hydroxide, potassium carbonate, pyridine (Py), triphenyl phosphite (TPP), and anhydrous calcium chloride ($CaCl_2$) were purchased from Tianjin BODI chemicals. The 2,6-dichlorobenzonitrile (DCBN) was obtained from Yangzhou Tianchen chemicals, Jiangsu, China. The 4-nitrophthalonitrile (99%) was supplied by Alpha chemicals (Dezhou). Phenolphthalein and hydroquinone (HQ) were gained from Chengdu Haihong chemicals. All the materials were used without further purification. Phenolphthalein (PPL) and 4-(4-aminophenoxy)phthalonitrile (APN) were synthesized according to the literatures.^{16,17}

Measurements

The FTIR spectra of samples were recorded on NICOLET MX-1E Fourier Transform Infrared spectrometer in KBr pellets between 4000 and 400 cm^{-1} in air. The 1H -NMR spectra was recorded on a Bruker DPX-300 nuclear magnetic resonance (NMR) spectrometer at a proton frequency of 300 MHz with dimethylsulfoxide- d_6 ($DMSO-d_6$) as the solvent. The thermal curing behavior of the polymers was measured by the TA Instruments Modulated DSC-Q100 at a heating rate of 10 $^{\circ}C\ min^{-1}$ with a nitrogen flow rate of 50 $mL\ min^{-1}$ from 100 to 370 $^{\circ}C$. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were used to determine the thermal decomposition of the polymers by TA Instruments Q50 with a heating rate of 20 $^{\circ}C\ min^{-1}$ in nitrogen. Dielectric properties were measured by using two-probe method with LCR digital meter in the frequency range of 20–200 kHz at room temperature. Mechanical properties of samples were tested with a SANS CMT6104 series desktop electromechanical universal testing machine (Shenzhen, China). The stretching direction of the sheets was the same as the tensile deformation direction. The moving speed of the crosshead



Scheme 1. Synthetic route of PEN-CNs and the crosslinking model after heat treatment.

was 5 $mm\ min^{-1}$, and the measurement temperature was about 20 $^{\circ}C$. All the reported values were calculated as averages of five specimens for each sample. Water absorption was measured by using TA Instruments Q50, with a heating rate of 10 $^{\circ}C\ min^{-1}$ from 25 to 100 $^{\circ}C$ and then isothermal for 20 min. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku D/max 2400 automatic X-ray diffractometer with Ni-filtered Cu K α radiation (40 kV, 100 mA).

Synthesis of Polymers

Synthesis of Acid-Contained Poly(arylene ether nitriles). Similar to the synthetic method we reported before,¹⁴ acid-contained poly(arylene ether nitriles) ($PEN-COOH$) was synthesized via nucleophilic aromatic substitution, as depicted in Scheme 1.

In a 500-mL three-necked round-bottom flask equipped with a mechanical stirrer and refluxing condenser, DCBN (0.4 mol, 68.8 g), HQ (0.32 mol, 35.2 g), PPL (0.08 mol, 25.6 g) and K_2CO_3 (0.048 mol, 66 g) were mixed in the flask with 180 mL NMP and 50 mL toluene. The mixture was stirred and heated to the reflux temperature about 150°C for 2 h to dehydrate the system. After the water-toluene azeotrope was distilled off, the reaction mixture was heated to the 190°C for about 2 h until the stirring became difficult to increase the viscosity. The product was poured into mixture of methanol and hydrochloric acid. The aqua solid polymer was washed thoroughly with hot water. After filtration, it was dried at 120°C under vacuum overnight. The yields were essentially quantitative for all the polymerization (>91% yield). The typical FTIR characteristic data: 2896 cm^{-1} (stretch, —CH), 2230 cm^{-1} (stretch, —CN), 1229 and 1269 cm^{-1} (stretch, Ar—O—Ar), 1680 cm^{-1} (stretch, C=O).

Synthesis of PEN Containing Pendant Phthalonitrile Groups.

The PEN containing pendant phthalonitrile group (PEN-CN) was obtained via the Yamazaki-Higashi phosphorylation route from APN with PEN-COOH in the presence of $CaCl_2$, which is shown in Scheme 1. In a 100-mL three-necked round-bottom flask equipped with a mechanical stirrer and refluxing condenser, PEN-COOH (12 g, about 10 mmol —COOH group), excess APN (4.7 g, 20 mmol), $CaCl_2$ (1.4 g, 13 mmol), TPP (5 mmol), and Py (6 mL) were mixed in the flask with 45 mL NMP and 20 mL toluene. The mixture was stirred and heated to the reflux temperature about 130°C for 8 h. Then the viscous solution was slowly poured into ethanol and stirred vigorously. The threadlike polymer was crushed into a powder after cooling. Next, the powder was washed with hot ethanol and water several times to remove the unreacted APN and dried at 110°C under vacuum for 24 h. Selected data of PEN-CN: 1H -NMR (300 MHz, $DMSO-d_6$) δ (ppm): 10.48 (N—H), 6.70–8.09 (Ar—H), 6.48 (C—H).

Crosslinking of the PEN-CN

To prepare the PEN-CN solution, PEN-CN (4 g) was dissolved into 40 mL NMP by heating and stirring for 2 h at 160°C. Afterward the solution was cast onto four clean glass plates and dried in an oven at 70, 100, 120, 160, and 200°C (2 h each) to remove the solvent. After slowly cooling to room temperature, the PEN-CN films were obtained (named PEN-CN-0). To prepare different crosslinked densities samples, three PEN-CN-0 films were heated at 250°C for 2 h, and fetch out the first sample (named PEN-CN-1); after that the rest of samples were heated to 270°C for 2 h, also fetch out a sample (named PEN-CN-2); the last sample was heated to 300°C for 2 h, named PEN-CN-3. Therefore, the different crosslinked densities of PEN-CN films were prepared for further study.

Long-Term Water Absorption Study

PEN-CN and crosslinked PEN-CN films were prepared and cut to dimensions of $\sim 10\text{ mm} \times 10\text{ mm} \times 0.05\text{ mm}$. The samples were immersed in distilled water at 25°C for 30 days. The films were removed from the water, sponged up, and weighed periodically to determine the amount of water absorption.

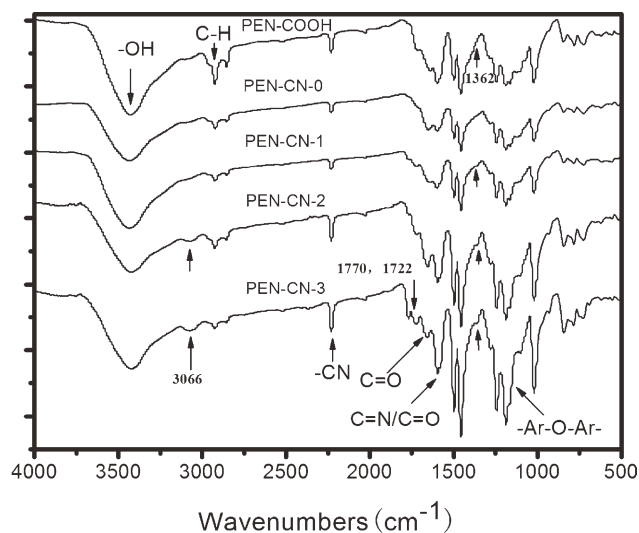


Figure 1. Fourier Transform Infrared Spectra (FTIR) of the PEN-COOH and PEN-CN.

RESULTS AND DISCUSSION

PEN-COOH and PEN-CN Synthesis

The PEN-COOH copolymer was successfully synthesized by the aromatic nucleophilic substitution polymerization of PPL and HQ with the equimolar DCBN (Scheme 1). The O—H of HQ and PPL, as acidic, had proved a good reactivity in the nucleophilic substitution reaction. The carboxyl group (—COOH) did not take the reaction with the DCBN, so the —COOH as a pendant activated group in the main chains. This —COOH group is ideal as a functional group, which can react with the —NH₂ group through the dehydration reaction. The PEN—COOH was obtained in essentially quantitative yields (92%) and the inherent viscosity (η_{inh}) is 0.58 $dL\ g^{-1}$ tested by Ubbelohde capillary viscometer at 30°C in the NMP solvent (0.5 $g\ dL^{-1}$). APN has an activity group (—NH₂), therefore it would react with —COOH group of PEN—COOH easily. In this study, APN was reacted with the —COOH group of PEN—COOH according to the phosphorylation method, which was first reported by Yamazaki.¹⁸ In addition, the η_{inh} of PEN-CN was 0.56 $dL\ g^{-1}$ also measured by Ubbelohde capillary viscometer at 30°C in the NMP solvent (0.5 $g\ dL^{-1}$).

Characterization of PEN-COOH and PEN-CN

The chemical structures of PEN-COOH and PEN-CN were characterized by FTIR, which is shown in Figure 1. The absorptions in the range of 3200–3500 cm^{-1} were assigned to the O—H from the pendant carboxyl and the terminal groups (—OH) of PEN-COOH. The characteristic stretching band of pendant nitrile groups appears at about 2229 cm^{-1} , indicating that nitrile group has been introduced into the main chain successfully during the reaction. The absorption band of carbonyl (C=O) in PPL appears at 1680 cm^{-1} and the band for Ph—O—Ph linkage appears at about 1244 cm^{-1} correlated well with the expected structure of the target polymer. In the FTIR spectra of PEN-CN, no absorption band of N—H were appeared, which may be covered by the absorption band of O—H.^{19,20} As shown in Figure 2, the 1H -NMR spectra data of

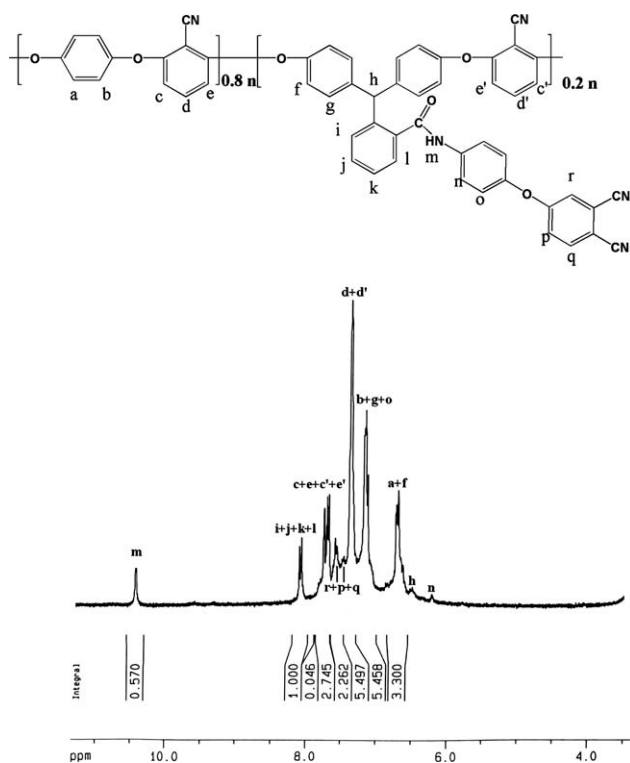


Figure 2. $^1\text{H-NMR}$ spectra of PEN-CN measured in DMSO-d_6 .

PEN-CN showed that the single peak splitting and shifting at 10.08 was attributed to the $-\text{NHCO}-$ groups, indicating the successful introduction of phthalonitrile to PEN chains as pendant groups. After thermal crosslinking, some other new characteristic peaks observed at 3066, 1722, 1770, and 1362 cm^{-1} indicated the formation of triazine rings and phthalocyanine rings. In short, all these FTIR data showed that the crosslinking reaction happened as the reaction model in Scheme 1.¹¹

Thermal Properties of PEN-CN Based on Crosslinking Between Nitriles

Poly(arylene ether nitriles) is well-known as a class of semicrystalline polymer with pendant nitrile groups since it was discovered. In the past years, many studies had focus on the crosslinking reaction among the nitrile or cyano groups to obtain thermal-stability structures, such as *s*-triazine and phthalocyanine. For instance, the cyano-terminated aromatic polyimide was crosslinked to *s*-triazine thermosets by heating with *p*-toluenesulfonic acid monohydrate at $200\text{--}300^\circ\text{C}$ under $30\text{--}60\text{ atm}$.^{21–23} However, this method also need some extremely conditions. Phthalonitrile has two nitrile groups in the paraposition and orthoposition, which has higher activity and can easily form the phthalocyanine or triazine structure than the nitriles of DCBN or DFBN. Considering the above factors, we introduced phthalonitrile into the pendant of polymer chains and studied the thermal activated crosslinking of PEN-CN without other catalyst.

The thermal crosslinked samples of PEN-CNs were prepared through the thermal activated crosslinking at different temperatures. DSC traces of all the PENs, including PEN-COOH, PEN-

CN-0, PEN-CN-1, PEN-CN-2, and PEN-CN-3 were illustrated in Figure 3. The sample of PEN-COOH has a glass transition temperature of 143.2°C . In the range of $215\text{--}300^\circ\text{C}$, the endothermic curve was due to the decomposition of carboxyl groups of PEN-COOH. The glass transition temperatures of PEN-CNs are recorded in the range of $182\text{--}213^\circ\text{C}$. It is apparent that all DSC heating scans reveal only single obvious T_g for each samples and the T_g values increase gradually with the increase of heat treatment temperature. For example, the T_g of PEN-CN-1 increased from 182.1 to 206.4°C after being thermal treated at 250°C for 2 h. This indicated that the pendant phthalonitrile groups experienced crosslinking reaction at 250°C and thus phthalocyanine or triazine structures was formed, which would hamper the movement of polymer chains. Similarly, the T_g of PEN-CN-2 increased to 211.4°C , and that of PEN-CN-3 was increased to 213.4°C . Owing to the low concentration of phthalonitrile groups, the T_g of PEN-CN-3 was slightly enhanced compared with that of PEN-CN-2. In addition, each sample of PEN-CNs showed a melting peak in Figure 3 and the melting points were in the range of $256.6\text{--}306.9^\circ\text{C}$, which also increased with the increase of heat treatment temperatures.

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) under nitrogen atmosphere were performed to study the thermal behavior of both PEN-COOH and PEN-CN samples. TGA and DTG curves of PEN-COOH and series of PEN-CN samples were shown in Figure 4 and 5, respectively. The 10% weight loss temperatures ($T_{10\%}$) of PEN-CN samples under nitrogen atmosphere determined by TGA were listed in Table I. Compared with the TGA curves of PEN-COOH and PEN-CN-0 in Figure 4, the $T_{10\%}$ of PEN-CN-0 was increased. This result was influenced by the nature of pendant groups: the carboxyl groups of PEN-COOH are easily dissociated from the Ph-COOH bonds when the temperature is up to $\sim 250^\circ\text{C}$. Besides, the phthalonitrile group of PEN-CN-0 has higher thermal stability than the carboxyl group of PEN-COOH. As shown in Figures 4 and 5, the thermal stability of PEN-CN became more stable with the increase of heat treatment temperature. Therefore, the crosslinking of the nitrile groups would improve the thermal stability.

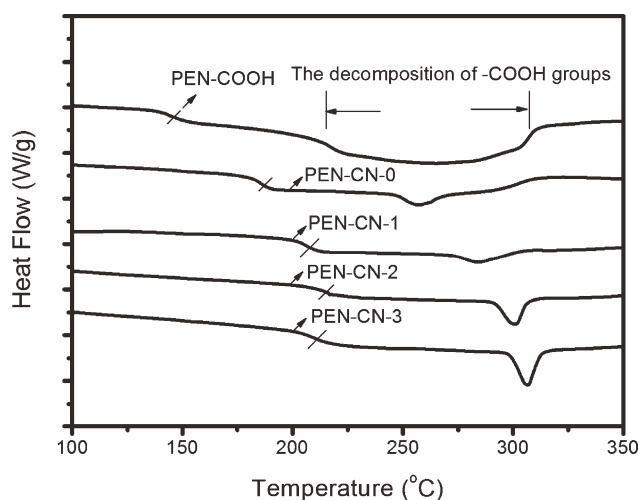


Figure 3. DSC curves of the PEN-COOH and PEN-CN samples.

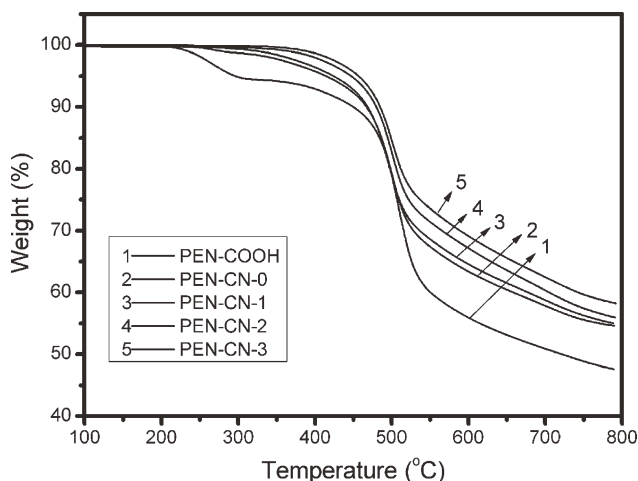


Figure 4. Thermogravimetric analysis (TGA) curves of the PEN-COOH and PEN-CN_s.

The Effect of Crosslinking on the Dielectric Properties

Polymers as dielectric materials have been applied to prepare capacitors due to their high dielectric breakdown strengths, low dissipation factors, and good dielectric stability over a wide range of frequencies and temperatures. For example, some kinds of thermoplastic polymer, such as engineering plastic PEEK, PPS, PEI, and PEN have excellent dielectric properties for preparing high energy density capacitors and would have extensive application in organic film capacitor.²⁴ The dielectric properties of polymer are determined by the chemical structure, process method and other factors. In our study, we measured the dielectric constant and the dielectric loss, expecting the values would reflect the internal changes of PEN-CN chemical structures. The dielectric constants (ϵ) were shown in the Figure 6. The ϵ of PEN-COOH is 3.5 at 1 kHz; in addition, there were no noticeable variation on the dielectric constant in the frequency range of 20 Hz–200 kHz. This result is similar to other kinds of PEN.²⁵ Meanwhile, the carboxyl group did not affect the dielectric constant conspicuously. After the APN monomers were reacted with the PEN-COOH, the dielectric constant of PEN-CN-0 decreased to 3.1 at 1 kHz. After being heat treatment at different temperatures, the ϵ of the PEN-CN_s increased with the increase of crosslinking density. Particularly, the ϵ of PEN-CN-3 increased to 3.9, higher than that of the PEN-COOH. Oligoph-

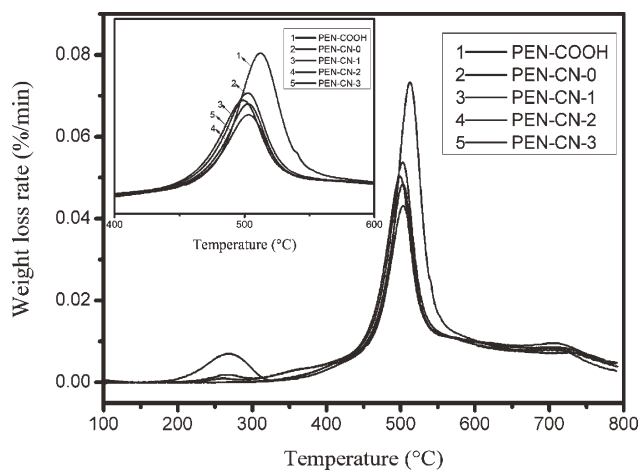


Figure 5. Derivative thermogravimetric analysis (DTG) curves of the PEN-COOH and PEN-CN_s.

thalocyanines like CuPc oligomers, where at least one benzene ring is shared by two phthalocyanines, have an extended π -conjugation and show high dielectric constants (ϵ) and intrinsic electric conductivity. Therefore, the formed phthalocyanine structure improved the dielectric properties through crosslinking reaction.^{26–28}

The dielectric losses ($\tan \delta$) of PEN-CN_s were shown in Figure 7. It was observed that the dielectric loss of PEN-COOH is about 0.01 in the frequency range of 20 Hz–200 kHz, which did not rely on the change of frequency. Owing to the pendant polar group —CN, the $\tan \delta$ of PEN is larger than that of PEEK or PPS. Because of the introduction of phthalonitrile groups, the nitrile's density of PEN-CN-0 was increased. Therefore, the $\tan \delta$ increased to 0.09 at 1 kHz and affected by the frequency obviously. With the increase of heat treatment, the $\tan \delta$ of PEN-CN_s changed and became lower. Surely, it was attributed to the decreasing of polar nitrile group. In summary, the crosslinking of nitrile groups would influence the dielectric properties of PEN-CN, so it is a very useful method to judge whether the nitrile groups were crosslinked through measuring the dielectric properties of PEN-CN.

Long-Term Water Absorption Capability of PEN-CN_s

The water absorption capability of polymer is also an important aspect for the crosslinked networks. To obtain the water

Table I. Thermal Properties and Long-Term Water Absorption of PEN-COOH and PEN-CN_s

	T_g^a (°C)	T_m^a (°C)	$T_{10\%}^b$ (°C)	T_{max}^c (°C)	C_y^d (%)	Water uptake (%)
PEN-COOH	143.2	-	450	265.2, 509.8	47.6	1.39
PEN-CN-0	182.1	256.6	467	258.7, 501.1	54.6	1.55
PEN-CN-1	206.4	284.7	469	497.6	55.0	1.18
PEN-CN-2	211.4	302.3	479	501.5	55.9	1.04
PEN-CN-3	213.4	306.9	485	501.8	58.3	1.01

^aGlass transition temperature (T_g) and melting temperature (T_m) tested by DSC in nitrogen, $10^\circ\text{C min}^{-1}$, ^bTemperature for 10% weight loss tested by TGA in nitrogen, $20^\circ\text{C min}^{-1}$, ^cTemperature for the maximum tested by DTG in nitrogen, $20^\circ\text{C min}^{-1}$, ^dChar yield calculated as the percentage of solid residue after heating from 100 to 800°C by TGA in nitrogen, $20^\circ\text{C min}^{-1}$.

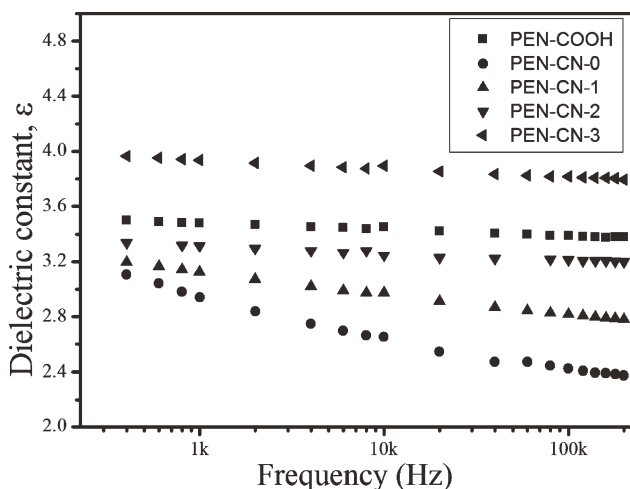


Figure 6. Effect of frequency on the dielectric constant of PEN-COOH and PEN-CN_s films at room temperature.

absorption capability of PEN-CN_s and study the effect of cross-linking density on the water absorption property, long-term water absorption experiments on film samples were carried out. The results were summarized in Table I, and the values were maximum amount of water absorption at the room temperature over the course of 30 days. Each of PEN film samples had different water absorption capabilities and ranged from 1.01 to 1.55 wt %. These values indicated that PEN-CN-0 had the highest water uptake value, which was attributed to the introduction of bulky phthalonitrile unit in the backbone of PEN as side chain. Dense packing of the polymer chains was probably disturbed by the bulky pendent groups, which led to increase of chain distances and weaken chain interactions. Consequently, the water molecules were able to penetrate more easily to the polymer chains. After the samples were crosslinked by thermal treatment, the dense packing of the polymer chains increased, which would prevent the penetration of water molecule. Thus the water absorb of PEN-CN_s decreased. Using the PEN-CN_s in a high humidity or aqueous environment, the tiny water

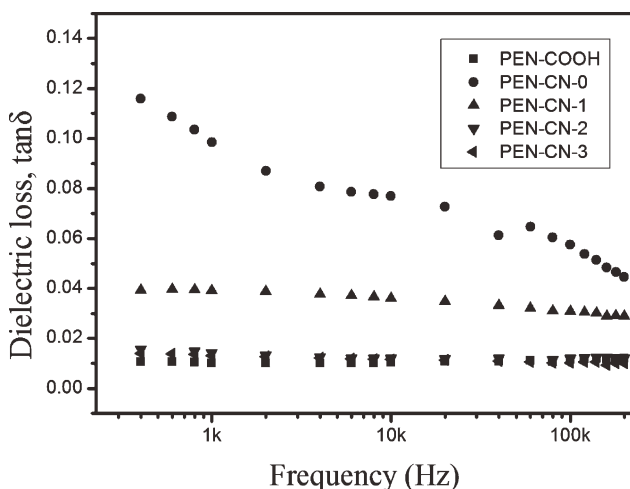


Figure 7. Effect of frequency on the dielectric loss of PEN-COOH and PEN-CN_s films at room temperature.

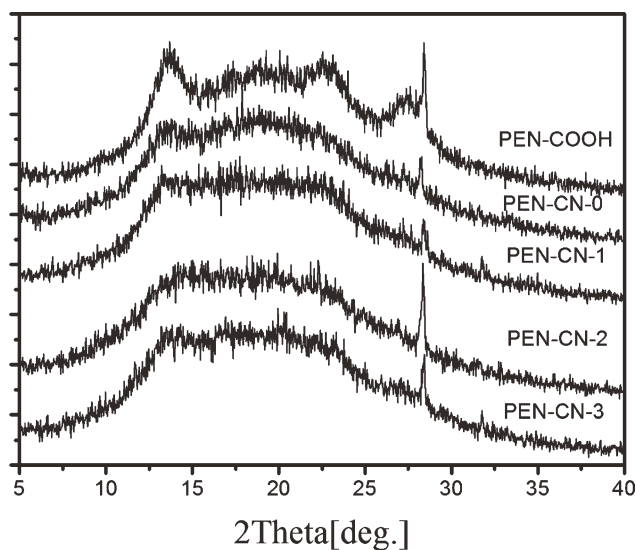


Figure 8. Wide-angle X-ray diffraction (WAXD) diffractograms of PEN-COOH and PEN-CN_s.

absorption is a significant advantage over other high performance polymers.¹⁰

Crystallinity of PEN-CN_s

Each film sample of PEN-CN_s had a melting peak in the DSC curve, which implied that the PEN-CN_s have crystallinity partly. We investigated the crystallinity of PEN-COOH and PEN-CN_s by means of wide-angle X-ray diffraction (WAXRD) on film samples at room temperature. Figure 8 illustrates WAXD diffractograms of the PEN-CN_s. All the samples had a sharp peak crystalline nature ($2\theta = 27^\circ$). Besides, there were also some other weak peaks. Thus these samples were crystallinity partly, which is consistent with the results of DSC.¹⁹

CONCLUSIONS

The poly(arylene ether nitriles) containing pendant carboxyl group was successfully synthesized via nucleophilic substitution polycondensation from phenolphthalein, hydroquinone with 2,6-dichlorobenzonitrile. The incorporation of phenolphthalein into the polymer chain would bring a functional group in the pendant. Poly(arylene ether nitriles) with pendant phthalonitrile was synthesized from 4-(4-aminophenoxy)phthalonitrile and PEN-COOH. The nitriles of phthalonitrile demonstrated much higher activated reactivity than the pendant nitriles of PEN and more easily crosslinking without other catalyst. After thermal crosslinking, the physical properties of PEN-CN_s were enhanced, including thermal properties, dielectric properties, and limited water absorption. This kind of PEN-CN may be considered as a potential high performance materials in a wide range of applications.

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