

Synthesis and Crosslinking Behavior of a Soluble, Crosslinkable, and High Young Modulus Poly(arylene ether nitriles) with Pendant Phthalonitriles

Jian Yang,^{1,2} Xulin Yang,^{1,2} Yanke Zou,^{1,2} Yingqing Zhan,^{1,2} Rui Zhao,^{1,2} Xiaobo Liu^{1,2}

¹Research Branch of Functional Materials, Institute of Microelectronic and Solid State Electronic, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China

²High-Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu 610054, P.R. China

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ABSTRACT: Poly(arylene ether nitriles) (PEN) with pendant phthalonitrile groups (PEN-CN) were obtained via the Yamazaki-Higashi phosphorylation route of 4-(4-aminophenoxy)phthalonitrile (APN) with acid-contained PEN (PEN-COOH) in the presence of CaCl₂. The chemical structure and molecular weight of PEN-CN were characterized by ¹H-NMR, Fourier transform infrared spectroscopy, and Gel permeation chromatography. The synthesized PEN-CN had superior solubility in polar organic solvent and can be easily processed into thin films from the solutions of *N*-methylpyrrolidone, dimethylsulfoxide, *N,N'*-dimethylformamide, dimethylacetamide, and tetrahydrofuran. Compared with PEN-COOH, PEN-CN showed higher thermal stability with 5% weight loss temperatures (*T*_{5%}) up to 430°C.

The glass transition temperature of PEN-CN was improved from 211 to 235°C measured by differential scanning calorimetry (DSC). In addition, it also exhibited excellent mechanical properties that Young's modulus reached to 3.5 GPa. Meanwhile, the effects of different aromatic amines and Lewis acid on the crosslinking behavior of PEN-CN were investigated by DSC. The results indicated that anhydrous Zinc chloride (ZnCl₂) was the best catalyst to lower the curing temperature among 2,6-bis(4-diaminobenzyloxy) benzonitrile, 4,4-diaminodiphenyl sulfone, APN and ZnCl₂. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: synthesis; high performance polymers; mechanical properties; thermal properties

INTRODUCTION

Poly(arylene ether nitriles) (PEN) is a well-known class of engineering thermoplastics for the outstanding properties such as high thermal and thermo-oxidative stability, excellent mechanical properties, radiation resistance, and chemical inertia. The first commercialized product of PEN, developed by Idemitsu with trade name PEN®, was a class of semi-crystalline polymer with pendant nitrile (CN) groups.

The pendant CN as polar groups could promote the adhesion of the polymers to many substrates such as carbon reinforcement.^{1–5} However, the poor solubility of PEN hampers its synthesis, processing and widespread application, especially for high-molecular weight materials. In addition, the CN groups as potential sites for the crosslinking reaction of PEN had been proved, but this reaction are usually conducted at high-temperature (200–500°C) under super-high pressures (3000–50,000 atm) to obtain S-triazine structures.⁶ The modest trimerization of aromatic nitrile compounds can be achieved through adding a Lewis acid catalyst under normal pressure. For example, the cyclization of the pendant CN groups in poly(phenylene sulfide)s was conducted at 290–300°C under atmosphere pressure in the presence of Zinc chloride (ZnCl₂).^{7–9}

Recently, many researches focused on improving the solubility of poly(arylene ethers) to expand their widespread application by evolving the incorporation of flexible linkages, kink groups, alkyl pendant groups, or noncoplanar units into the polymer backbones. Besides, introduction of bulky pendant groups into polymer backbone has been recognized

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Correspondence to: X. Liu (liuxb@uestc.edu.cn).

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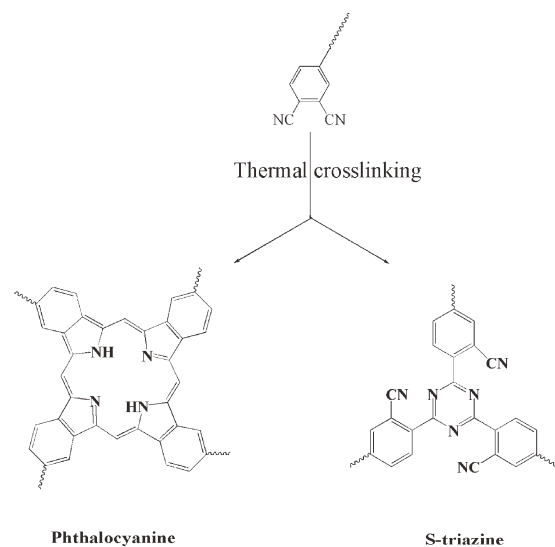
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as one of the successful approaches to increase the solubility of these high performance polymers.^{10–13} Meanwhile, to develop polymers for high performance applications, lots of investigations were concentrated on improving the glass transition temperature (T_g) and the thermal stability via synthesis of oligomers, macromonomers or polymers with terminal —CN groups or other activated groups like benzoxazine and epoxy groups. For example, 4-chlorobenzonitrile was introduced to the poly(arylene ether)s chain as terminal groups to obtain crosslinkable polymers, which can occur thermal crosslinking reaction and form triazine rings. However, the concentration of activated terminal groups was in conflict with the molecular weight of the polymer chains. Increasing concentration of the activated terminal groups would lead to a decrease in molecular weight, which resulted in poor mechanical properties even if these polymers were heat-treated by thermal crosslinking.^{14–16}

On the other hand, phthalonitrile-based polymers as a class of high-temperature materials that has series of excellent properties such as high T_g s, outstanding thermal and thermo-oxidative stability, excellent mechanical properties, superior fire resistance, and good moisture resistance. The many outstanding properties make the phthalonitriles attractive for many military and civilian advanced technological applications.¹⁷ Furthermore, the crosslinking of phthalonitriles can be promoted using curing additives such as phenols, organic amines, strong organic acids, metals, and their salts. Their crosslinked products such as triazine and phthalocyanine (Scheme 1) will bring high T_g s and thermo-oxidative stability to PEN. Therefore, introduction phthalonitriles into the backbone of PEN as pendant groups is a useful approach to enlarge the concentration of activated nitrile and obtain crosslinkable polymers.

In this study, we present the synthesis of a new acid-contained copoly(arylene ether nitriles) (PEN—COOH) based on phenolphthalein and bisphenol-A. The carboxyl groups as functional group reacted with 4-(4-aminophenoxy)phthalonitrile (APN) via the Yamazaki-Higashi phosphorylation route and PEN with pendant phthalonitrile (PEN—CN) groups have been successfully obtained and characterized. Phthalonitrile was first introduced into PEN as pendant group, which was chosen as the model polymer system. Our purpose is to obtain a high molecular weight PEN while the concentration of activated groups is sufficient for improving thermal properties by crosslinking. Furthermore, the properties of PEN—COOH and PEN—CN, such as solubility, mechanical strength of their films, and thermal stability were investigated. We also studied the crosslinking reaction of PEN—CN with variable catalysts such as $ZnCl_2$, 2,6-bis(4-diaminobenzoxy) benzonitrile (BDB), 4,4-diaminodiphenylsulfone (DDS), and APN.



Scheme 1 Thermal crosslinking reaction of phthalonitriles.

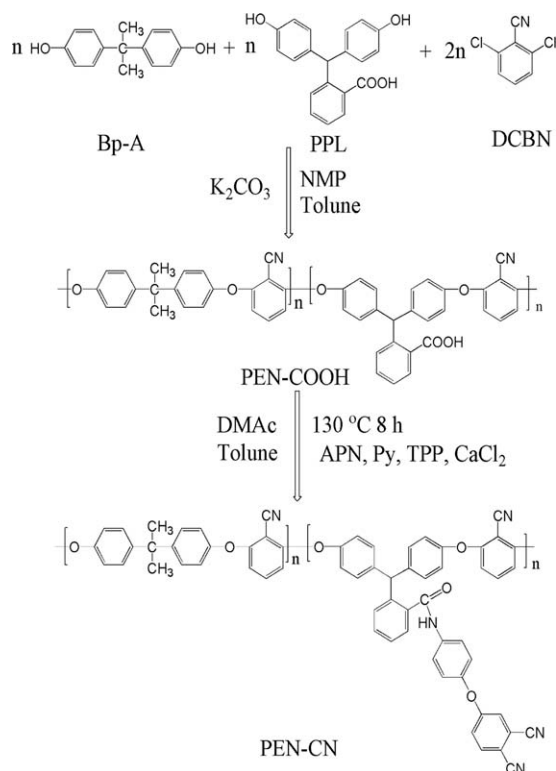
EXPERIMENTAL

Materials

2,6-Dichlorobenzonitrile (DCBN) was obtained from Yangzhou Tianchen chemicals (Jiangsu, China). *N,N'*-dimethylformamide (DMF, AR), *N,N'*-dimethylacetamide (DMAc, AR), *N*-methylpyrrolidone (NMP, AR), toluene (AR), zinc powder, sodium hydroxide (NaOH, AR), potassium carbonate (K_2CO_3 , AR), pyridine (Py, Ar), triphenyl phosphite (TPP, Ar), and anhydrous calcium chloride ($CaCl_2$) were purchased from Tianjin BODI chemicals. 4-Nitrophthalonitrile (99%) was supplied by Alpha chemicals (Dezhou). Phenolphthalein and bisphenol-A were gained from Chengdu Haihong chemicals. The DDS was purchased from Sichuan Dongcai chemicals. Synthesis of phenolphthalin (PPL), APN, and 2,6-bis(4-diaminobenzoxy)benzonitrile were carried out according to reference reported before.^{18–20} All the materials were used without further purification.

Characterizations

The Fourier Transform Infrared (FTIR) spectra of polymers were recorded on NICOLET MX-1E FTIR 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. Gel permeation chromatography (GPC) analysis was conducted with a PL-GPC220 system using polystyrene as standard and THF as the eluent. The thermal curing behavior of the polymers were measured by the TA Instruments Modulated differential scanning calorimetry-Q100 (DSC-Q100) at a



Scheme 2 Synthesis route of poly(arylene ether nitrile) with pendant phthalonitriles.

heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min from 100 to 370°C. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were used to determine the thermal decomposition of the polymers by using TA Instruments Q50 with a heating rate of 20°C/min in nitrogen. 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 was 5 mm/min, and the measurement temperature was about 20°C. All the reported values were calculated as averages of five specimens for each sample.

Synthesis of PEN-COOH

PEN-COOH was synthesized via nucleophilic aromatic substitution according to the modified method we reported before,²¹ as depicted in Scheme 2. In a 250 mL three-necked round-bottom flask fitted with a condenser, a Dean Stark trap and an overhead mechanical stirrer, DCBN (0.4 mol, 68.8 g), bisphenol-A (0.2 mol, 45.6 g), PPL (0.2 mol, 64 g), and K₂CO₃ (0.048 mol, 66 g) were mixed in the flask with 150 mL NMP and 50 mL toluene. The mixture were stirred and heated to the reflux temperature about 150°C for 2 h to promote the phenolate forma-

tion. After the water-toluene azeotrope was distilled off, the reaction mixture was gradually heated to the 200°C for about 2 h until the stir became difficulty in increasing the viscosity. The mixture was precipitated into 500 mL methanol with 50 mL hydrochloric acid. The aqua solid polymer was washed thoroughly with hot water. After filtration, it was dried at 120°C under vacuum overnight.

Analysis for PEN-COOH: FTIR (KBr, cm⁻¹): 3411 (—OH), 3036 (C—H aromatic ring), 2967, 2926 (—CH₃), 2230 (—CN), 1716, 1645 (—COOH), and 1245 (Ar—O—Ar); ¹H-NMR (300 MHz, DMSO-d₆, ppm): 1.67 (s, 6H), 6.56–6.61 (m, 6H), 6.72 (m, 2H), 7.04–7.11 (m, 2H), 7.15 (m, 2H), 7.32–7.34 (m, 4H), 7.49–7.51 (m, 2H), and 7.80–7.82 (m, 1H).

Synthesis of PEN-CN

The synthesis of PEN-CN was performed as showed in Scheme 2. The typical reaction was carried out as follows: in a 100 mL three-necked flask, equipped with mechanical stirrer and nitrogen gas inlet and outlet, PEN-COOH (6 g containing about 8 mmol carboxyl group), excess APN (2.82 g, 12 mmol), CaCl₂ (1.11g, 10 mmol), TPP (6.0 mmol), and Py (4 mL) were dissolved in 50 mL DMAc and 15 mL toluene. The mixture was stirred at 130°C for 8 h to promote the amido bond formation. Subsequently, the product was slowly poured into a mixture of methanol and the precipitated polymer (PEN-CN) was washed thoroughly with hot water. Finally, PEN-CN was dried at 110°C under vacuum for 24 h. The yield was calculated: 91 wt %. Selected data of PEN-CN: FTIR (KBr, cm⁻¹): 3411 (—OH), 3100 (N—H), 3064 (C—H aromatic ring), 2967, 2926 (—CH₃), 2230 (—CN), 1674 (C=O), 1245 (Ar—O—Ar); ¹H-NMR (300 MHz, DMSO-d₆, ppm): 7.43–7.50 (m, 4H), 7.68–7.66 (m, 3H), 10.40 (s, 1H, H_a) (see the ESI*).

RESULTS AND DISCUSSION

Synthesis and characterization of PEN-COOH and PEN-CN

The acid-contained PEN was prepared by the nucleophilic aromatic substitution polymerization of PPL and bisphenol-A with DCBN in NMP in the presence of potassium carbonate (Scheme 2). The pendant carboxyl group of PEN-COOH as an active and functional group would bring some surprising physical and chemical functions. The PEN-CN containing pendant phthalonitrile group was obtained via the Yamazaki-Higashi phosphorylation route of APN with PEN-COOH in the presence of CaCl₂, showed in Scheme 2.²²

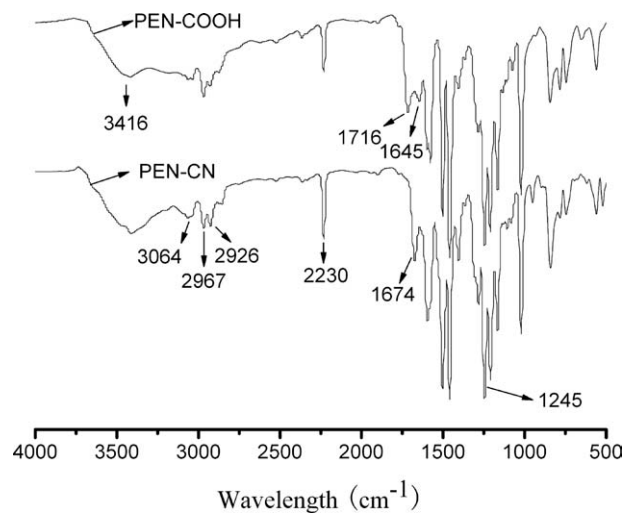


Figure 1 FTIR spectrum of PENs.

The structures of PENs were identified by FTIR spectroscopy and $^1\text{H-NMR}$ spectra. As shown in Figure 1, the FTIR spectra of PEN-COOH showed the characteristic absorptions of $-\text{CN}$ groups near 2230 cm^{-1} , of the aromatic ether near 1245 cm^{-1} , of the carboxyl group ($-\text{COOH}$) near 1716 and 1645 cm^{-1} . These characteristic absorptions suggested that the acid-contained polymer were synthesized as shown in Scheme 2. The FTIR spectra of PEN-CN showed an obvious change that the absorption peaks at 1716 and 1645 cm^{-1} disappeared but a new absorption peak appeared at 1674 cm^{-1} , which was attributed to the $-\text{CONH}-$ group. Besides, Figures 2 and 3 showed the $^1\text{H-NMR}$ spectra of PEN-COOH and PEN-CN, respectively. Compared with Figure 2, there was a new signal at 10.40 ppm in Figure 3, which was assigned to the amide group. Therefore, the structures of PENs were confirmed by the data of FTIR and $^1\text{H-NMR}$ spectra.

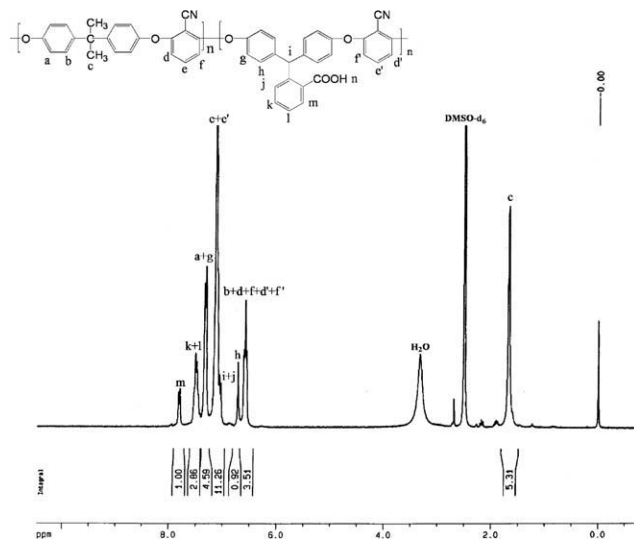


Figure 2 $^1\text{H-NMR}$ spectrum of PEN-COOH.

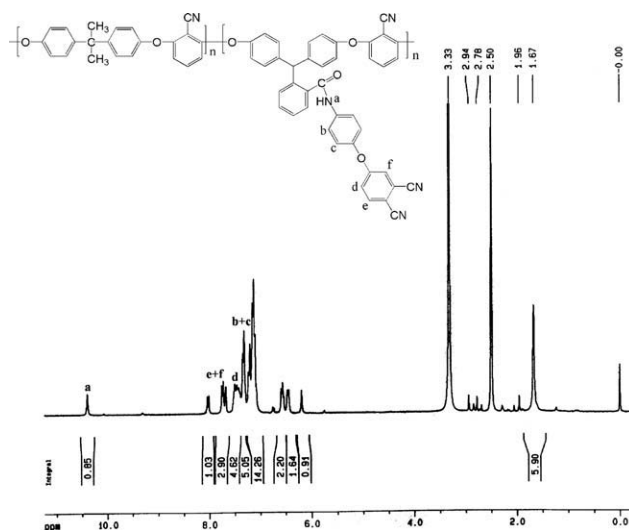


Figure 3 $^1\text{H-NMR}$ spectrum of PEN-CN.

The inherent viscosities (η_{inh}) were evaluated in DMAc solvent at 30°C with Ubbelohde viscometer. The values of PEN-COOH and PEN-CN were 0.60 and 0.57 dL/g (Table I), respectively. It is observed that the η_{inh} of PEN-CN decreased with the incorporation of bulky phthalonitrile groups as side chains. This was attributed to the bulky groups impede PEN chain packing, and therefore enhancing the "molecular intervals" between the chains. In addition, the molecular weights of PENs were determined by GPC. The values of M_n , M_w , and dispersity are shown in Table I. PEN-COOH showed that M_n value was $51,683\text{ g mol}^{-1}$, and M_w value was $76,967\text{ g mol}^{-1}$. After attaching phthalonitrile groups to the backbone, the M_n and M_w of PEN-CN increased to $59,634\text{ g mol}^{-1}$ and $88,593\text{ g mol}^{-1}$, respectively. These results clearly revealed that APN were reacted with PEN-COOH successfully. Furthermore, the dispersities (M_w/M_n) of PEN-COOH and PEN-CN were 1.49 and 1.48 , respectively (see the ESI*).

Solubility of PENs

The solubility behaviors of PEN-COOH and PEN-CN synthesized were examined in various solvents by dissolving 0.03 g of the PENs in 10 mL solvent, and the results were summarized in Table II. Compared to the semicrystalline PEN (RS-PEN), which was synthesized from resorcinol and DCBN

TABLE I
Characterization of PENs

	η_{inh} (dL g^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n
PEN-COOH	0.60	51,683	76,967	1.49
PEN-CN	0.57	59,634	88,593	1.48

TABLE II
Solubility of PENs

Polymer	Solubility ^a					
	NMP	DMAc	DMF	THF	CHCl ₃	DMSO
PEN-COOH	++	++	++	++	+	++
PEN-CN	++	++	++	++	+	++
RS-PEN ^b	-	-	-	-	-	-

^a Solubility: ++, soluble at room temperature; +, soluble on heating; -, insoluble.

^b RS-PEN was synthesized according to the method in Ref. 4.

according to the method in Matsuo et al.,⁴ both of PEN-COOH and PEN-CN have good solubility in many polar aprotic solvents such as NMP, DMF, DMSO, and DMAc at room temperature, and they also can be dissolved in some low-boiling solvents like THF. Besides, these polymers could be dissolved in CHCl₃ by heating. The excellent solubility of PEN-COOH is attributed to the structurally unsymmetrical nature and noncoplanar conformation of the PPL. Additionally, the superior solubility of PEN-CN also can be 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 reduces the chain interactions due to the increase in the chain distances. Consequently, the solvent molecules were able to penetrate more easily to solubilize the polymer chains.¹²

Thermal properties

The T_g of PEN-COOH and PEN-CN were measured by DSC. As shown in Figure 4, the T_g of PEN-COOH was 211°C resulting from the typical second heating cycle. The DSC curves of PEN-CN were also showed in Figure 4, including the first and second heating cycle. In the first curve of

PEN-CN, there is an obvious exothermic peak at 267.4°C, which was caused by the thermal crosslinking reaction of phthalonitrile attached in the backbone of PEN. The second DSC curve of PEN-CN (marked PEN-CN sec in Fig. 4) had no evident T_g point in the range of 200–350°C. This result was for that the formed phthalocyanine or triazine rings through thermal crosslinking reaction between -CN groups of pendant phthalonitrile would hamper the movement of polymer chains. As a result, the T_g of PEN-CN was improved.

The thermal stabilities of PENs were evaluated using TGA and DTG, and their curves were shown in Figures 5 and 6. Besides, the thermal data such as the temperatures corresponding to the weight loss of 5 wt % ($T_{5\%}$), 10 wt % ($T_{10\%}$), the maximum rate of decomposition (T_{max}), and the amounts of carbonized residue (C_y) values were summarized in Table III. As shown in Figure 5, the sample of PEN-CN possessed higher thermal stability than that of PEN-COOH. The $T_{5\%}$ and $T_{10\%}$ values of PEN-COOH are just only 253 and 383°C, respectively, which are much lower than those of PEN-CN ($T_{5\%} = 434^\circ\text{C}$; $T_{10\%} = 476^\circ\text{C}$). These results are 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 heated up to $\sim 250^\circ\text{C}$. Compared with pendant carboxyl groups, the pendant

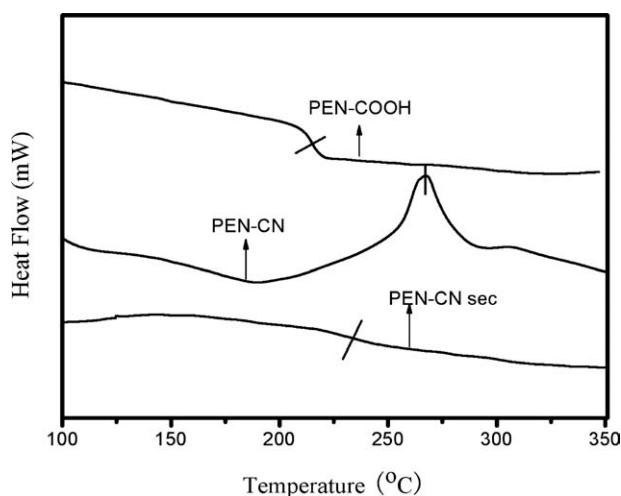


Figure 4 DSC cures of PENs.

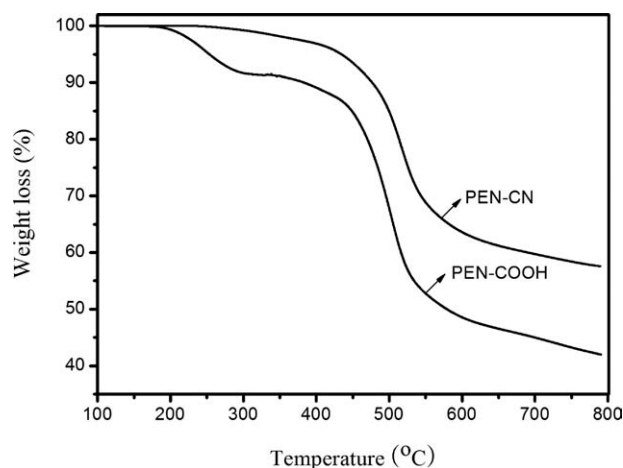


Figure 5 TGA curves of PENs.

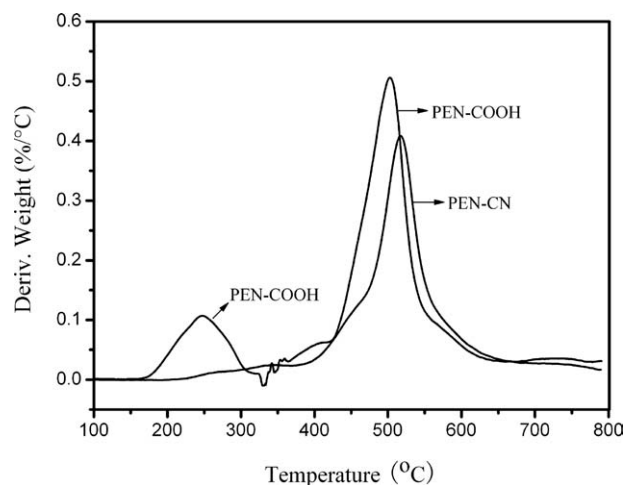


Figure 6 DTG curves of PENs.

phthalonitrile groups have higher thermal stability. Furthermore, as the temperature was heated up to about 275°C, the crosslinking of phthalonitrile would occur and form better thermal stability structures, such as phthalocyanine or triazine rings. The carbonized residue (C_y) of PEN-COOH and PEN-CN are calculated and listed in Table III. These C_y values showed that the introduction of APN as pendant groups to the PEN chain would improve the char yield of PEN from 42 to 57%.

As can be seen from the DTG curves showed in Figure 6, the PEN-COOH decomposed in two-stage weight loss process. The temperature of the first maximum speed of decomposition ($T_{\max 1}$) is situated at 247°C, which is due to the degradation of the carboxyl groups. The temperature of the second maximum speed of decomposition ($T_{\max 2}$) is 503°C, which is lower than the only T_{\max} of PEN-CN ($T_{\max} = 517^\circ\text{C}$). The clear differences in the thermal decomposition behaviors of the PEN-CN are mainly due to the different nature of the side groups along the PEN-CN chains.

Mechanical properties of PENs

The mechanical properties of PENs were measured through their films cast from their DMAc solutions (10% w/v), according to GB/T 1040-2006. The mechanical properties of PENs were summarized

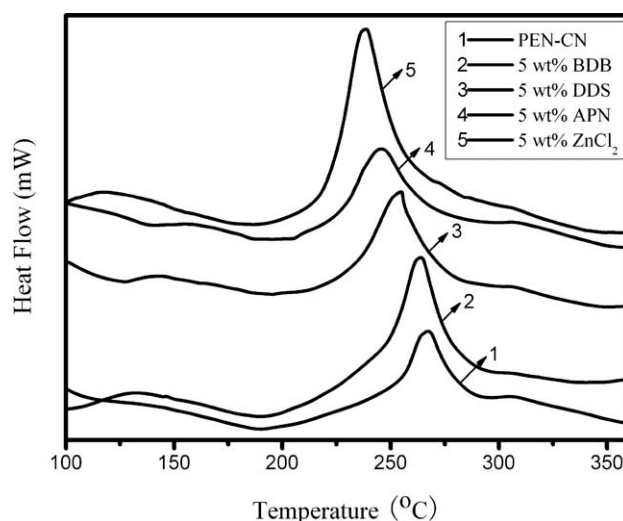


Figure 7 DSC curves of PEN-CN after adding various catalysts.

in Table III. As shown in Table III, the average tensile strength and Young's modulus values of PEN-COOH were 83.1 MPa and 2.9 GPa, respectively. Meanwhile, those of PEN-CN were enhanced to 89.7 MPa and 3.5 GPa. These results showed the excellent mechanical properties of synthesized PEN-COOH and PEN-CN, and also confirmed their high molecular weights and good film-forming abilities. The elongation at break values of PEN-COOH and PEN-CN are 4.4 and 3.1%, respectively. Compared with other polymers with terminal nitrile or benzoxazine groups, PEN-CN showed much better film-forming abilities, mechanical properties, and flexibility.¹⁵ For these reasons, this kind of PEN-CN would be applied widely as a potential high-performance and functional polymeric materials.

Crosslinking behavior of PEN-CN with different catalysts

As showed in Figure 4, the curve of PEN-CN has a very obvious exothermic peak at about 267.4°C, which indicated that the phthalonitrile is more active than the -CN groups attached to the backbone of PEN.^{7,23} Therefore, investigation of the crosslinking reaction of PEN-CN would be a more practical and available research on improving the properties of PEN-CN. In the previous researches, phenols, organic amines,

TABLE III
The Thermal and Mechanical Properties of PENs

Polymer	Thermal properties						Mechanical properties		
	T_g (°C)	T_c (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{\max} (°C)	C_y (%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
PEN-COOH	211		253	383	247,503	42	83.1	4.4	2.9
PEN-CN	235	267	434	476	517	57	89.7	3.1	3.5

TABLE IV
Thermal Characteristics Related with Crosslinking Reaction of PEN-CN in the Presence of Different Catalysts

PEN-CN with catalysts	Pure PEN-CN	5 wt % APN	5 wt % DDS	5 wt % BDB	5 wt % ZnCl ₂
T_c (°C)	267.4	245.9	254.8	264.0	238.6
T_g (°C)	235.6	225.2	226.2	223.0	229.6
ΔH (J/g)	-14.0	-19.6	-22.0	-25.1	-57.1

strong organic acids, metals, and their salts would promote the curing reaction of phthalonitrile and lower the curing temperature.²⁴⁻²⁶ For this reason, in this study, the crosslinking reaction of PEN-CN with different catalysts, including BDB, DDS, APN and ZnCl₂, were investigated by DSC. Among these catalysts, BDB is a diamine with one nitrile as pendant group, DDS is also a diamine with one sulfone group, APN is monoamine with double nitriles and ZnCl₂ is a Lewis acid. For this research, PEN-CN films with different catalysts were prepared by solvent casting method. Appropriate solutions containing 1 g of PEN-CN and 0.05 g (5 wt %) of catalysts in 10 mL DMAc were allowed to cast onto a clean glass plate and dried in 60°C for 2 h, 90°C for 2 h, 120°C for 2 h, 140°C for 2 h, and at last heated to 160°C for 2 h. Then the crosslinked samples were obtained.

The DSC curves of samples were measured and showed in Figure 7. Additionally, the maximum curing temperatures (T_c , °C) and the enthalpy change (ΔH , J/g) of samples were listed in Table IV. It was clear that the T_c s of samples with catalysts were in the range of 238.6–264.0°C, which were lower than that of PEN-CN. Among these catalysts, ZnCl₂ was the best one to lower the reaction activation energy, thereby decreasing the crosslinking temperature. Second, APN was better than BDB and DDS, which can be attributed to the increasing concentration of phthalonitrile after adding 5 wt % of APN in the PEN-CN. The enthalpies changes (ΔH , J/g) of crosslinking reaction of samples were calculated and summarized in Table IV. The ΔH value of PEN-CN with ZnCl₂ was the highest among these catalysts, which indicated that the conversion degree of the crosslinking reaction with ZnCl₂ was higher than others. Among the organic amines, by contrast, the ΔH values of PEN-CN with BDB and DDS were higher than that of PEN-CN with APN. This result may be attributed to the higher concentrations of amino-group than that of APN.

CONCLUSION

A novel PEN with pendant phthalonitrile groups was successfully synthesized from acid-contained

PEN via the Yamazaki-Higashi method. The chemical structures of PEN-CN were characterized by ¹H-NMR, FTIR, and GPC. This kind of polymer has superior solubility in polar solvents, such as NMP, DMAc, DMF, DMSO, and even in less polar solvent such as THF. The T_g and thermal stability of PEN-CN were improved compared with those of PEN-COOH. In addition, the film of PEN-CN exhibited excellent mechanical properties that the tensile strength was 89.7 MPa and Young's modulus was 3.5 GPa. The effect of different catalysts, including ZnCl₂, APN, BDB and DDS on the thermal crosslinking behavior of PEN-CN was investigated. All of these attributes make it a good candidate for high performance materials.

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