Polym. Bull. (2012) 68:1879–1888
DOI 10.1007/s00289-011-0663-0

ORIGINAL PAPER

Synthesis and thermal polymerization of new polyimides with pendant phthalonitrile units

Ke Zeng · Li Li · Shourong Xiang · Yun Zhou · Gang Yang

Received: 12 July 2011 / Revised: 25 October 2011 / Accepted: 1 November 2011 /

Abstract New polyimides with pendant phthalonitrile units were synthesized via the conventional two-step polymerization approach. The chemical structure of the PIs was confirmed by IR and ^{1}H NMR spectra. The thermogravimetric analysis and differential scanning calorimetry revealed that the thermal properties of the new PIs along with their solvent-resistance can be promoted after thermal treatment at 300 °C. This promotion can be attributed to the nitrile cure reaction of the phthalonitrile units indicated by the decrease in nitrile absorptions at around 2231 cm^{-1} of the IR spectra.

Keywords Polyimide · Phthalonitrile · Thermal polymerization · Thermal properties · Solvent-resistance

Introduction

Polyimide (PI) have received much attention over half a century because of their unique properties, such as superior thermal stability, mechanical properties, and chemical and irradiation resistance [1]. Despite these outstanding properties, unmodified PIs are infusible and insoluble in common organic solvents due to their rigid backbones and strong chain–chain interactions. To overcome these problems, much effort has been focused on the improvement of the solubility or the fusibility via the concept of the molecular design. These studies include introducing flexible

---

K. Zeng · L. Li · S. Xiang · Y. Zhou · G. Yang (✉)
State Key Laboratory of Polymer Materials Engineering, College of Polymer Science
and Engineering, Sichuan University, Chengdu 610065, China
e-mail: yanggang65420@163.com

K. Zeng
The Key Laboratory of Leather Chemistry and Engineering, Ministry of Education, College of Light
Industry, Textile and Food Engineering, Sichuan University, Chengdu 610065, China

segments into the polymer chain [2, 3]; replacing symmetrical aromatic rings by unsymmetrical ones [4–6]; introducing bulky pendant substituents [7–9]; and forming a non-coplanar structure [10, 11]. Among these, introduction of bulky pendant groups into polymer backbone has been recognized as one of the successful approaches to increase the solubility of PIs. The steric hindrance of bulky pendant groups inhibits the chain packing and crystallization, and thus increases the solubility. However, in most cases, the properties, such as thermal properties or solvent-resistance of these PIs were deteriorated [8, 9].

On the other hand, oligomer or monomer with phthalonitrile end group have been confirmed to be able to undergo thermal polymerization through the nitrile groups on phthalonitrile units by an addition mechanism to afford heterocyclic crosslinked products, such as triazine, phthalocyanine, and isoindoline [12–17]. Aromatic diamine, phenol, and strong organic acid were frequently used as the curing agents [18].

In our previous study, a new wholly aromatic polyamide with pendant phthalonitrile units (CN-PA) was synthesized. The solubility of the CN-PA was improved, while its solvent-resistance and thermal properties can be controlled via the thermal polymerization of the pendant phthalonitrile group [19]. In this article, the phthalonitrile units were introduced into PI system as pendant substituents with an aim to balance the contradiction between the processability and properties of the PIs through phthalonitrile thermal polymerization. The result also implied that the thermal polymerization of the pendant phthalonitrile units in macromolecular system can be realized through end groups, such as amino or carboxyl.

Experimental section

Materials

4-Nitrophthalonitrile were obtained from Aldrich Chemical Co. and used without further purification. *p*-Nitrophenol was purchased from Tianjin BoDi Co. Ltd. 4,4′-Oxydiphthalic anhydride (ODPA) was purchased from Shanghai Research Institute of Synthetic Resins and was purified by sublimation. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Alfa Aesar and was purified by recrystallization from acetic anhydride. *N*-methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride. Other chemicals were used as received unless otherwise stated.

Synthesis of diamine

Synthesis of compound ***1***

To a 250 mL three-neck flask were charged into *p*-nitrophenol (18.00 g, 0.1294 mol) and concentrated sulfuric acid (205 mL). Then, $NaNO_3$ (12.10 g, 0.1423 mol) and $NaNO_2$ (9.87 g, 0.1430 mol) were added slowly into the flask while keeping the inner temperature below 5 °C using ice/water bath. After the addition was complete, the solution was allowed to warm to room temperature and stirred for 2 h. Yellow crude product was obtained by pouring the solution into 3000 mL ice/water, filtration and washed with water. After recrystallization from ethanol, the yellow needle crystals were dried under vacuum for 24 h at 60 °C. Yield 14.28 g (60%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.0–14.0 (br,1H); 8.71 (s, 1H); 8.36–8.39 (d, 1H); 7.29–7.31 (d, 1H).

Synthesis of diamine $\underline{\mathbf{3}}$

To a three-neck flask were charged into compound **1** (3.66 g, 19.88 mmol), stannous chloride dihydrate (40.70 g, 0.2147 mol), ethanol (54.45 mL), and concentrated hydrochloric acid (34.11 mL) under nitrogen. The mixture was heated to reflux and maintained for 4 h. After the solution was cooled to room temperature, concentrated hydrochloric acid (82 mL) was added into the solution. Then, white precipitate formed and was collected by filtration, washed with ethanol, and dried under vacuum for 24 h at 60 °C. The crude product compound **2** was used in the next reaction without further purification.

To a 100 mL three-neck flask were added 4-nitrophthalonitrile (2.48 g, 14.32 mmol), anhydrous potassium carbonate (7.76 g, 56.23 mmol), and 50 mL of DMF. The compound **2** (2.84 g, 14.32 mmol) was added into the flask under nitrogen. The mixture was stirred at 30 °C under nitrogen for 9 h and then poured into 500 mL water. The resulting precipitate was collected by filtration, washed with water until the filtrate was neutral, dried at 70 °C under reduced pressure for 12 h. The crude product was obtained as brown powders in 76% yield. The diamine $\underline{\mathbf{3}}$ was purified by column chromatography over silica gel with ethyl acetate/hexane as the mobile phase and subsequent recrystallization in acetonitrile in 43% yield. IR (KBr, cm^{-1}): 3468, 3379 (N–H str), 2238 ($C{\equiv}N$ str). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.02–8.04 (d, 1H); 7.53 (s, 1H); 7.16–7.19 (d, 1H); 6.59–6.61 (d, 1H); 6.03 (s, 1H); 5.83–5.86 (d, 1H); 4.77–4.87 (d, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.53, 147.6, 140.74, 135.97, 130.01, 121.78, 121.37, 120.32, 116.16, 115.98, 115.66, 106.43, 103.12, 101.04. Elemental analysis: Calcd for $C_{21}H_{14}N_4O_3$: C, 67.19; H, 4.03; N, 22.39. Found: C, 66.93; H, 4.04; N, 22.04.

Polymer synthesis

To a completely dry 25 mL three-neck flask equipped with a nitrogen-inlet, a drying tube and a magnetic stirrer were charged into diamine **3** (0.7145 g, 2.86 mmol) and NMP (5.3 mL). After the diamine **3** was dissolved completely, the dianhydride (2.86 mmol) was added to the solution in one portion. The mixture was stirred at room temperature for 6 h and at 50 °C for another 6 h. Then, after the solution was cooled to room temperature and diluted with extra NMP (11.6 mL), a mixture of acetic anhydride (8.2 mL), and pyridine (7.2 mL) was added slowly and the solution was stirred at room temperature for 10 h, 80 °C for 9 h, and 120 °C for 3 h. After cooling, the solution was poured into acetone. The precipitate was filtered, washed thoroughly with acetone. The precipitation procedure was carried out several times. The polymer was further purified by Soxhlet extraction from acetone for 24 h and then dried under vacuum at 150 °C for 24 h.

CN-PI **4**: inherent viscosity 0.35 dL/g in NMP at 30 ± 0.1 °C; Yield: 96%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.07–8.12 (m, 2H); 8.01–8.03 (d, 1H); 7.86 (s, 1H); 7.76 (s, 1H); 7.70–7.72 (d, 1H); 7.59–7.66 (m, 4H); 7.48–7.53 (q, 2H). FT-IR (KBr, cm^{-1}): 3071 (Ar–H str); 2232 (C≡N str); 1783, 1722 (C=O str); 1354 (C–N str).

CN-PI **5**: inherent viscosity 0.43 dL/g in NMP at 30 ± 0.1 °C; Yield: 95%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11–8.28 (m, 7H); 7.89 (s, 1H); 7.84 (s, 1H); 7.75–7.77 (d, 1H); 7.50–7.57 (q, 2H). FT-IR (KBr, cm^{-1}): 3073 (Ar–H str); 2233 (C≡N str); 1783, 1726 (C=O str); 1673 (C=O str); 1359 (C–N str).

Characterization

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Bruker Avance-400 NMR spectrometer with DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded with a Nicolet FTIR-460 Fourier transform infrared spectrometer by KBr pellet. Thermogravimetric analysis (TGA) was carried out with a TA instrument Q500 Thermogravimetric analyzer under a nitrogen stream at a flow rate of 50 mL/min and a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a TA instrument Q200 Differential Scanning Calorimeter under a nitrogen stream at a flow rate of 40 mL/min and a heating rate of 20 °C/min. The inherent viscosities were determined at a concentration of 0.5 g/dL in NMP with an Ubbelohde viscometer at 30.0 ± 0.1 °C.

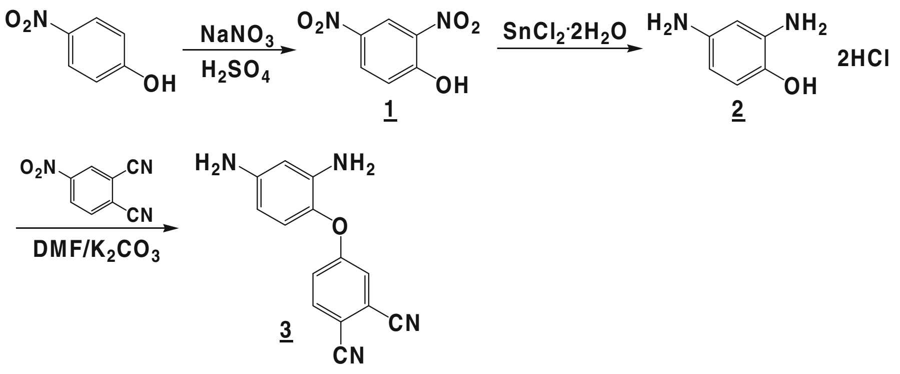
Results and discussion

Monomer synthesis

First, the phthalonitrile-containing diamine **3** was synthesized in three steps (Scheme 1). Compound **1** was obtained in good yield by nitration in concentrated sulfuric acid and was reduced to compound **2** using $SnCl_2 \cdot 2H_2O$, which was used in the next reaction without further purification. The subsequently nucleophilic displacement reaction with 4-nitrophthalonitrile produced diamine **3** in moderate yield. Its structure was unambiguously confirmed by FTIR and ^{1}H NMR spectroscopies, shown in "Experimental section". Absorption bands at 3468, 3379, and 2238 cm^{-1} are assigned to amino group and cyano group. The doublet peaks at 4.77–4.87 are corresponding to primary amine protons, indicating the asymmetric nature of the diamine **3**.

Polymer synthesis

The PIs with pendant phthalonitrile units (CN-PI) were prepared via the conventional two-step polymerization approach, as shown in Scheme 2, involving ring-opening polyaddition forming poly(amic acid) in NMP and subsequent chemical imidization. The ring-opening polyaddition reaction was performed at room temperature and subsequently higher temperature of 60 °C, respectively, due to the low reactivity of the diamine **3**. The chemical imidization of the poly(amic

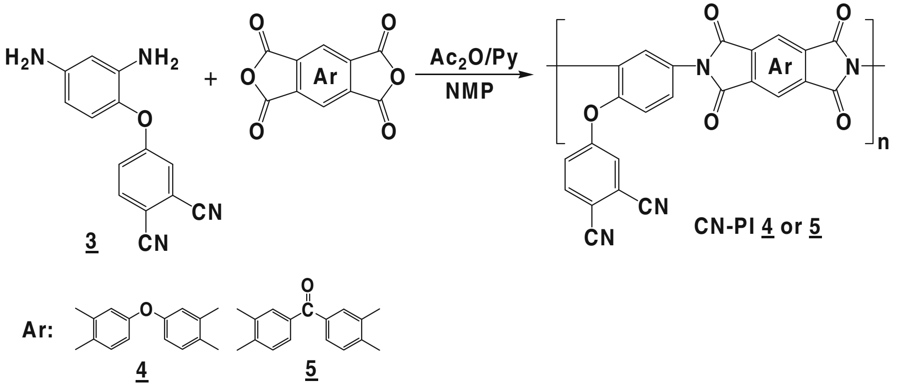


Scheme 1 Synthesis of diamine 3

acid)s proceeded with a dehydrating agent, such as a mixture of acetic anhydride and pyridine. Extra NMP was added to the poly(amic acid) solutions to prevent gelation, before addition of dehydrating agent. The CN-PIs were separated by precipitation of their polymer solution in acetone and purified by Soxhlet extraction. The yields were around 95%. The polymers obtained by chemical method had inherent viscosities in the range of 0.35–0.43 dL/g in NMP. The IR spectra of the CN-PIs confirmed the completeness of the imidization. The IR spectrum of CN-PI **4** showed characteristic absorptions at 1783 and 1722 cm^{-1} due to the asymmetric and symmetric stretches of imide carbonyl groups. The ^{1}H NMR spectrum, as shown in Fig. 1, further verified its structure and all the protons can be assigned.

Thermal polymerization behavior

The thermal polymerization behaviors of CN-PIs were investigated by TGA and DSC techniques. As shown in Figs. 2 and 3, the thermal properties of the cured polymer were significantly enhanced compared with original polymer CN-PI **4**. The



Scheme 2 Preparation of CN-PI 4 and 5

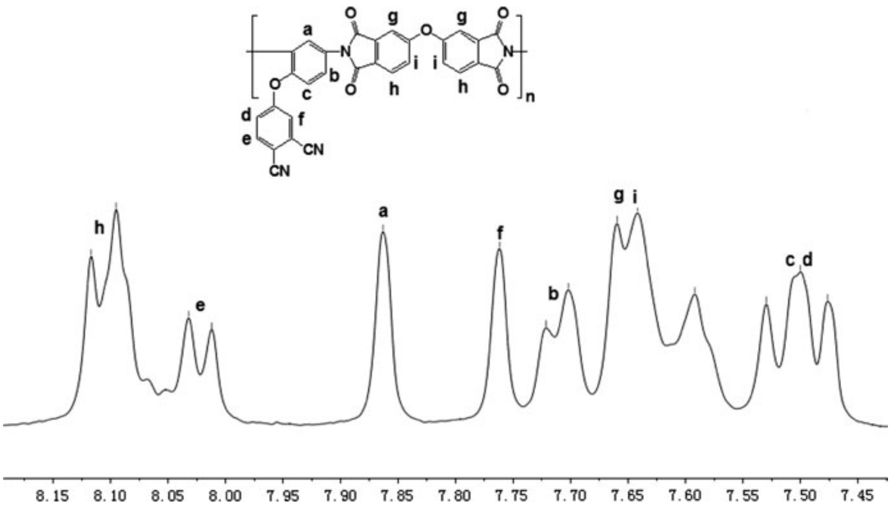


Fig. 1 ^{1}H NMR spectrum of CN-PI **4** in DMSO-d_6

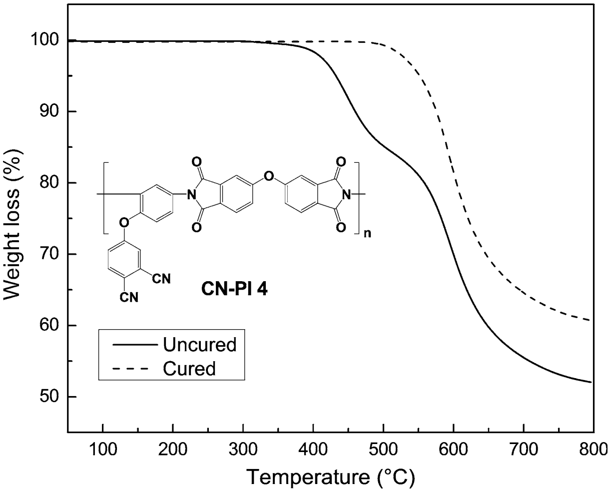


Fig. 2 TGA curves of CN-PI **4** and cured CN-PI **4**

similar thermal polymerization behavior was also found for CN-PI **5**. Table 1 summarized the thermal properties of the CN-PIs and cured polymers. The 5 and 10% weight loss temperature ($T_{5\%}$ and $T_{10\%}$) of CN-PI **4** increased from 438 and 462 °C to 548 and 575 °C after thermal treatment at 300 °C for 10 h in N_2 (curing procedure). The char yield of the cured CN-PI **4** was also improved. For CN-PI **5**, the $T_{5\%}$, $T_{10\%}$ and char yield increased to 588, 609 °C and 68% after thermal treatment (Table 1). On the other hand, the glass transition temperatures (T_g) of CN-PI **4** and **5** centered at 266 and 277 °C. The higher T_g of CN-PI **5** compared with

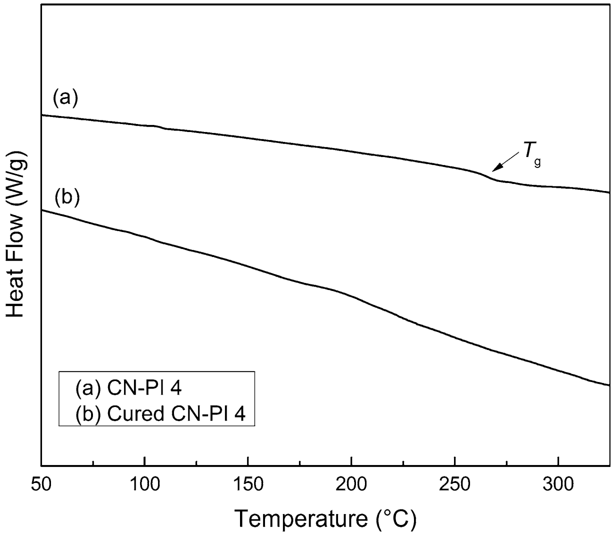


Fig. 3 DSC curves of CN-PI **4** and cured CN-PI **4**

Table 1 Thermal properties of CN-PIs

Polymer code[a]	$T_{5\%}$ (°C) in N_2	$T_{10\%}$ (°C) in N_2	Char yields at 800 °C (%)	T_g (°C)
CN-PI **4**	438	462	51	266
CN-PI **4** (cured)	548	575	61	/
CN-PI **5**	504	542	55	277
CN-PI **5** (cured)	588	609	68	/

The CN-PIs were cured at 300 °C for 10 h under nitrogen atmosphere

/ not detected within the tested temperature range (measured by DSC)

that of CN-PI **4** can be attributed to a restriction of molecular mobility caused by aromatic ketone moiety, which was also observed in other PI system [6]. Noticeably, the T_gs of the cured CN-PI **4** and **5** can not be detected within the tested temperature range (measured by DSC). Such an improvement in thermal properties indicated that more thermally stable crosslinking sites were formed probably through the pendant phthalonitrile cure reactions, when the CN-PIs were subjected to thermal treatment. This supposition can be confirmed by the decrease in nitrile absorbance (around 2230 cm^{-1}) on their FTIR spectra (Figs. 4, 5). Clearly, after normalized to internal standard peaks at 1722 cm^{-1} for CN-PI **4** and 1726 cm^{-1} for CN-PI **5**, nitrile absorptions at around 2230 cm^{-1} significantly diminished in intensity. Unfortunately, no peaks on the IR spectra of the cured polymers can be assigned to characteristic absorptions representative of triazine, phthalocyanine, and isoindoline formations [20, 21], because these characteristic absorptions overlap strong bands in the original polymers. However, it has been

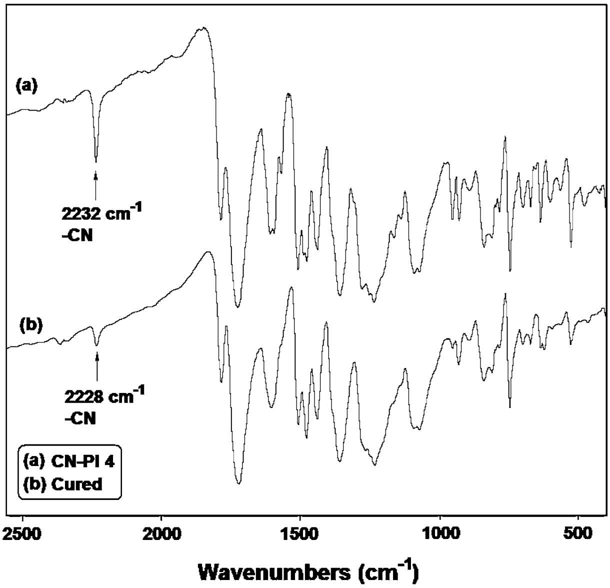


Fig. 4 IR spectra of CN-PI **4** and cured CN-PI **4**

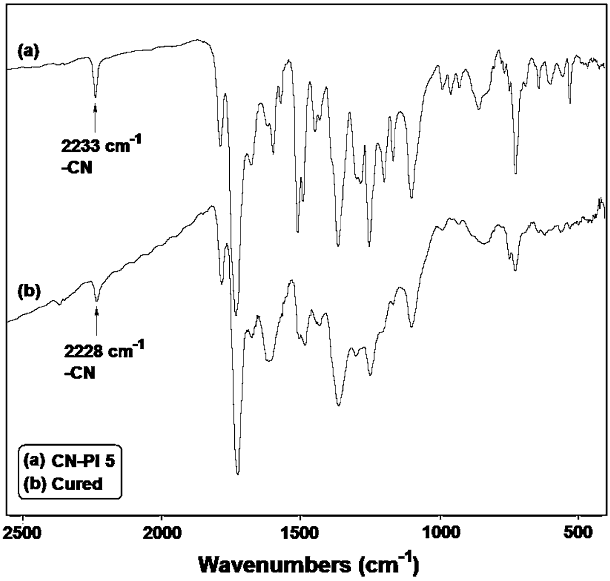


Fig. 5 IR spectra of CN-PI **5** and cured CN-PI **5**

reported that the nitrile absorptions would shift to lower wavenumbers, when cyano groups are converted to triazine derivatives [21]. The shifts were observed for cured CN-PI **4** and **5**. In our previous study, triazine formation was confirmed in CN-PA

Table 2 Solvent-resistance of CN-PIs

Polymer code	H_2SO_4	NMP	DMAc	DMSO
CN-PI **4**	++	++	++	++
CN-PI **4** (cured)	+−	−−	−−	−−
CN-PI **5**	++	++	++	++
CN-PI **5** (cured)	+−	−−	−−	−−

Solubility: ++ = soluble at room temperature; +− = partly soluble; – = insoluble even on heating

system [19]. Therefore, triazine formation was probably responsible for the crosslinking of the cured CN-PI **4** and **5**.

The solvent-resistance of CN-PIs was investigated and summarized in Table 2. CN-PIs were found to be readily soluble in a variety of polar solvents including NMP, DMAc, and DMSO, indicating their good processability. The solubility of the CN-PIs decreased when it is subjected to thermal treatment, as shown in Table 2. It is noted that the cured polymers was partly or insoluble in polar solvents mentioned above and partly soluble in concentrated sulfuric acid. Therefore, the solvent resistance was enhanced for CN-PIs when subjected to thermal treatment. Apparently, such an improvement in solvent resistance can be attributed to the formation of crosslinking sites through the nitrile cure reactions.

Conclusions

Two new PIs with pendant phthalonitrile units were successfully prepared via conventional two-step method. The as-made polymer CN-PIs were readily soluble in polar solvents, while its solvent resistance and thermal properties can be promoted by thermal treatment at 300 °C for an extended period of time. Such an enhancement in polymer properties can be attributed to the crosslinking site formations through the thermal polymerization of the nitrile groups on pendant phthalonitrile units, indicating that the nitrile cure reactions in PI system can be realized. Further studies on the relationship between the cure procedure and other properties, such as mechanical and electric properties are in progress.

Acknowledgment The authors thank the National Natural Science Foundation of China (No. 21074077) for the financial support.

References

1. Cassidy PE (1980) Thermally stable polymer. Marcel Dekker, New York
2. Hilborn JG, Labadie JW, Hedrick JL (1990) Poly(aryl ether-benzoxazoles). Macromolecules 23:2854–2861
3. Hergenrother PM, Havens SJ (1994) Polyimides containing quinoxaline and benzimidazole units. Macromolecules 27:4659–4664

4. Chung IS, Kim SY (2000) Soluble polyimides from unsymmetrical diamine with trifluoromethyl pendent group. Macromolecules 33:3190–3193
5. Zheng HB, Wang ZY (2000) Polyimides derived from novel unsymmetric dianhydride. Macromolecules 33:4310–4312
6. Chern YT, Tsai JY (2008) Low dielectric constant and high organosolubility of novel polyimide derived from unsymmetric 1,4-bis(4-aminophenoxy)-2,6-di-tert-butylbenzene. Macromolecules 41:9556–9564
7. Li WM, Li SH, Zhang QY, Zhang SB (2007) Synthesis of bis(amine anhydride)s for novel high T_{gs} and organosoluble poly(amine imide)s by palladium-catalyzed amination of 4-chlorophthalide anhydride. Macromolecules 40:8205–8211
8. Liaw DJ, Chang FC, Leung MK, Chou MY, Muellen K (2005) High thermal stability and rigid rod of novel organosoluble polyimides and polyamides based on bulky and noncoplanar naphthalene-biphenyldiamine. Macromolecues 38:4024–4029
9. Mikroyannidis JA (1995) Aromatic polyamides and polyimides with benzoxazole or benzothiazole pendent groups prepared from 5-(2-benzoxazole)-or 5-(2-benzothiazole)-1,3-phenylenediamine. Macromolecules 28:5177–5183
10. Liou GS, Maruyama M, Kakimoto M, Imai Y (1993) Preparation and properties of aromatic polyamides from 2,2′-bis(p-aminophenoxy) biphenyl or 2,2′-bis(p-aminophenoxy)-1,1′-binaphthyl and aromatic dicarboxylic acids. J Polym Sci A Polym Chem 31:2499–2506
11. Liou GS, Maruyama M, Kakimoto M, Imai Y (1993) Preparation and properties of aromatic polyimides from 2,2′-bis(p-aminophenoxy)biphenyl or 2,2′-bis (p-aminophenoxy)-1,1′-binaphthyl and aromatic tetracarboxylic dianhydrides. J Polym Sci A Polym Chem 31:3273–3279
12. Keller TM, Price TR (1982) Amine-cured bisphenol-linked phthalonitrile resins. J Macromol Sci Chem A18:931–937
13. Keller TM (1994) Synthesis and polymerization of multiple aromatic ether phthalonitriles. Chem Mater 6:302–305
14. Sumner MJ, Sankarapandian M, McGrath JE, Riffle JS, Sorathia U (2002) Flame retardant novolac-bisphthalonitrile structural thermosets. Polymer 43:5069–5076
15. Zeng K, Zhou K, Tang WR, Yang G et al (2007) Synthesis and curing of a novel amino-containing phthalonitrile derivative. Chin Chem Lett 18:523–526
16. Zeng K, Zhou K, Zhou SH, Hong HB, Zhou HF, Wang YP, Miao PK, Yang G (2009) Studies on self-promoted cure behaviors of hydroxy-containing phthalonitrile model compounds. Eur Polym J 45:1328–1335
17. Zhou SH, Hong HB, Zeng K, Yang G (2009) Synthesis, characterization and self-promoted cure behaviors of a new phthalonitrile derivative 4-(4-(3,5-diaminobenzoyl)phenoxy) phthalonitrile. Polym Bull 62:581–591
18. Zeng K, Yang G (2011) Phthalonitrile matrix resins and composites. Encyclopedia of composites. Wiley, New York
19. Zeng K, Hong HB, Zhou SH, Wu DM, Miao PK, Huang ZH, Yang G (2009) A new soluble aramide with pendant phthalonitrile units and polymer property enhancement by nitrile cure reactions. Polymer 50:5002–5006
20. Burchill PJ (1994) On the formation and properties of a high-temperature resin from a bisphthalonitrile. J Polym Sci A Polym Chem 32:1–8
21. Griffith JR, Snow AW, Marullo NP (1984) Syntheses and characterization of heteroatom-bridged metal-free phthalocyanine network polymers and model compounds. Macromolecules 17:1614–1624