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A new soluble aramide with pendant phthalonitrile units and polymer property enhancement by nitrile cure reactions

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ABSTRACT

A new soluble aramide with pendant phthalonitrile units was prepared, while its properties including solvent resistance and thermal properties can be enhanced by further thermal treatment around the glass transition temperatures of the polymers for an extended period of time. The cured polymers were characterized by thermogravimetric analysis, differential scanning calorimetry and FTIR techniques. Such improvement in polymer properties can be attributed to the nitrile cure reactions, indicated by the observation of the decrease in nitrile absorbance and the characteristic triazine band on the FTIR spectra.

1. Introduction

High performance polymers such as wholly aromatic polyamide (aramide), polyimide (PI) and polybenzoxazole (PBO) have received much attention over the past decades because of their unique properties such as superior thermal stability, mechanical properties and chemical resistance. However, rigidity of the backbone and strong chain–chain interactions result in high melting or glass transition temperature and limited solubility in most organic solvent [1]. These characteristics make them generally difficult to fabricate into useful forms, thus restricting their applications. To overcome these problems, much effort has been focused on the synthesis of soluble polymers without deterioration of their outstanding properties. These studies include introducing flexible segments into the polymer chain [2]; replacing symmetrical aromatic rings by unsymmetrical ones [3]; introducing bulky pendant substitutes [4]; and forming a non-coplanar structure [5]. Among these, introduction of bulky pendant groups into polymer backbone has been recognized as one of the successful approaches to increase the solubility of these high performance polymers. The steric hindrance of bulky pendant groups inhibits the chain packing and crystallization, and thus increases their solubility. However, this approach generally compromises their inherent solvent resistance and (or) thermal properties due to the reduced chain–chain interactions [4]. Their applications are limited in many fields. Therefore, development of approaches that can improve the solubility of these polymers while maintaining their inherent properties are highly desirable [6].

In the development of polymers for high performance applications, much effort has been focused over the past decades on oligomers and polymers containing reactive phenylethynyl groups as terminal, pendant and both terminal and pendant substituents [7]. The cured forms of these materials can exhibit an attractive combination of properties. Their cure reaction exothermic peaks on the DSC curves were extremely sharp and the reaction can be basically accomplished by heating at 350–430 °C for about 1 h [7c,7d].

On the other hand, phthalonitrile-based small molecular monomers or oligomers have been confirmed to be able to undergo thermal polymerization leading to a class of high performance resins [8]. Polymerization occurs through the nitrile groups on phthalonitrile units by an addition mechanism to afford heterocyclic crosslinked products, such as triazine, phthalocyanine and isoindoline [9]. The polymerization of the neat resins is extremely sluggish and can be controlled as a function of concentration of cure additives and processing temperature [8]. Amide, imide or ether–ketone containing monomers or oligomers end-capped with phthalonitrile units have been fully developed by workers at Naval Research Laboratory (NRL) [10].

Furthermore, phthalonitrile units have also been introduced into the main chains of the polymer system (poly(aryl ether)s) by Hay et al. [11]. However, no results with regard to the nitrile cure

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behaviors and property enhancement of the polymer by the nitrile cure reactions were reported in this investigation. Therefore, whether nitrile cure reactions in the polymer system can be realized and the effects of the nitrile cure behaviors on the processabilities and properties of the polymers are still unclear. If it can be realized, a new class of thermosetting polymers would be developed, which may show different cure characteristics and processabilities compared to polymers with pendant phenylethynyl groups [7d]. Clearly, this remaining issue would be particularly attractive both in the view of science and applications for high performance polymer.

In this communication, pendant phthalonitrile units were firstly introduced into the aramide (**CN-PA**), which was chosen as the model polymer system [12]. The aim is to obtain a soluble aramide while the solvent resistance and thermal properties can be enhanced by realization of cure reactions of the nitrile groups on pendant phthalonitrile units (**nitrile cure reactions**). Moreover, it affords a new potential approach to modify other series of high performance polymers such as PEEKs, PIs or PBOs. A new class of thermosetting polymers, showing various cure behaviors and processabilities, can be developed. Here, the preliminary results with regard to the thermal behaviors and properties of **CN-PA** are reported. The results show that the nitrile cure reactions can be realized at moderate temperatures around the glass transitions of the polymers for an extended period of time. The nitrile cure reactions contributed to the polymer property enhancement.

2. Experimental section

2.1. Materials

3,5-Dinitrobenzoyl chloride (**1**) was obtained from Aldrich Chemical Co. and used without further purification. 4-(4-Hydroxyphenoxy)phthalonitrile (**2**) was synthesized according to a published literature [13]. Isophthaloyl chloride was prepared by the reaction of the corresponding aromatic dicarboxylic acids with thionyl chloride in the presence of a few drops of *N*,*N*-dimethylformamide (DMF) as a catalyst and was purified by recrystallization from petroleum ether. DMF, *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride. Other chemicals were used as received unless otherwise stated.

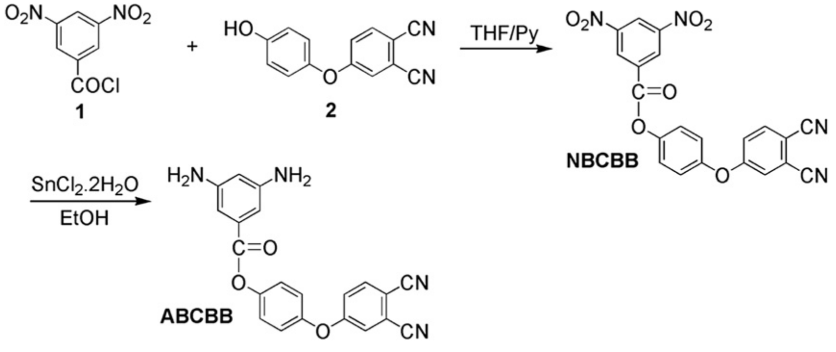
2.2. Synthesis of diamine *ABCBB*

(a) To a 1 L three-neck flask were added 4-(4-hydroxyphenoxy) phthalonitrile (20 g, 86.7 mmol), tetrahydrofuran (180 mL) and pyridine (21 mL). The solution was stirred and cooled to 0 °C in an ice/water bath. A solution of 3,5-dinitrobenzoyl chloride (22.47 g, 97.5 mmol) in tetrahydrofuran (60 mL) was added dropwise to the flask from a dropping funnel over 30 min. After addition was complete, the mixture was allowed to warm to room temperature and stirred for additional 24 h. The resulting mixture was diluted with water (400 mL), and the off-white solids were collected by suction filtration, washed with a large amount of water. After recrystallization from tetrahydrofuran/ethanol (2:1 in volume) mixed solvents, product **NBCBB** was obtained as a kelly crystal (Yield: 18 g, 49.3%). IR (KBr, cm^{-1}): 2228 (C≡N stretching), 1746 (C=O stretching), 1544, 1347 (NO_2). ^1H NMR (400 MHz, DMSO-d_6): δ 9.13 (d, $^4J_{H,H} = 1.6$, 1H), 9.09–9.12 (d, $^4J_{H,H} = 2.5$, 2H), 8.13–8.15 (d, $^3J_{H,H} = 8.4$, 1H), 7.86 (d, $^4J_{H,H} = 2.8$, 1H), 7.53–7.55 (d, $^3J_{H,H} = 8.8$, 2H), 7.44–7.47 (dd, $^3J_{H,H} = 8.8$, $^4J_{H,H} = 2.4$, 1H), 7.34–7.37 (d, $^3J_{H,H} = 9.2$, 2H).

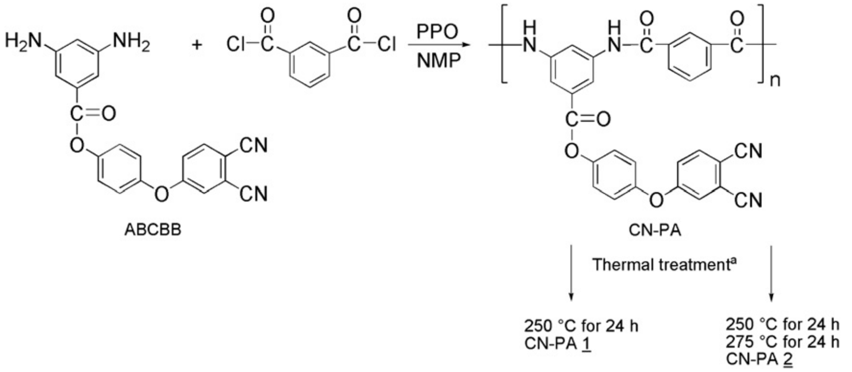
(b) To a 1 L three-neck flask were charged into **NBCBB** (15 g, 34.85 mmol), $SnCl_2 \cdot 2H_2O$ (78 g, 345.68 mmol) and ethanol (750 mL). The mixture was stirred at 30 °C for 20 h under nitrogen. Then, the solvent was removed by rotary evaporation, and 1.5 L of ethyl acetate was added into the reaction system. The pH of the solution was adjusted to 7 using 5 wt% aqueous solution of sodium carbonate. The organic layer was separated, washed with saturated brine solution and dried with anhydrous magnesium sulfate. Then, the solvent was removed by rotary evaporation. The product **ABCBB** was obtained as a yellow needle crystal after recrystallization from acetonitrile (5.14 g, 40%). IR (KBr, cm^{-1}): 3373, 3468 (N–H symmetrical and asymmetrical stretching), 2230 (C≡N stretching), 1729 (C=O stretching). ^1H NMR (400 MHz, DMSO-d_6): δ 8.13–8.14 (d, 1H), 7.84 (d, 1H), 7.40–7.43 (dd, 1H, $^3J_{H,H} = 8.8$, $^4J_{H,H} = 2.8$), 7.27–7.35 (m, 4H), 6.59 (d, 2H, $^4J_{H,H} = 1.6$), 6.11 (s, 1H), 5.11 (S, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 104.59, 104.80, 108.75, 115.86, 116.37, 117.19, 121.87, 122.41, 123.16, 124.48, 129.96, 136.78, 148.61, 150.06, 151.54, 161.52, 166.01. Elemental analysis: Calcd for $C_{21}H_{14}N_4O_3$: C, 68.10; H, 3.81; N, 15.13. Found: C, 67.78; H, 3.86; N, 15.05.

2.3. Synthesis of *CN-PA* by low-temperature solution polycondensation

To a completely dry 25 mL three-neck flask equipped with a nitrogen-inlet, a dry tube and a mechanical stirrer were charged into **ABCBB** (0.5925 g, 1.6 mmol), NMP (4 mL) and propylene oxide (0.4 mL). The solution was cooled to 0 °C in an ice/water bath. To this solution of diamine was added isophthaloyl chloride (0.3248 g, 1.6 mmol) with stirring under nitrogen. The mixture was stirred at 0 °C for 1 h and then at room temperature for additional 12 h under nitrogen. The resulting mixture was trickled slowly into 300 mL of methanol producing a spherical yellow precipitate. The polymer



Scheme 1. Synthesis of diamine **ABCBB**.



Scheme 2. Preparation of **CN-PA** and **CN-PA 1**, **CN-PA 2**. [a] The thermal treatment was performed by heating powdered samples (15 mg) at a heating rate of 4 °C/min under nitrogen atmosphere.

was collected by filtration, washed with hot methanol thoroughly and then dried to afford crude polymer. The yield was nearly quantitative. The polymer was further purified by Soxhlet extraction from tetrahydrofuran (THF) for 24 h and then dried in vacuo at 150 °C for 24 h; The inherent viscosity of the polymer was 0.38 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30.0 ± 0.1 °C. IR (KBr, cm^{-1}): 3304 (N–H stretching), 2230 (C≡N), 1736 (C═O), 1655 (C═O). ^1H NMR (400 MHz, DMSO-d_6): δ 10.81 (s, 2H), 8.90 (s, 1H), 8.67 (s, 1H), 8.41 (s, 2H), 8.23–8.25 (d, 2H), 8.08–8.11 (d, 1H), 7.81–7.82 (d, 1H), 7.74 (s, 1H), 7.40–7.46 (m, 3H), 7.29–7.32 (d, 2H). Elemental analysis: Calcd for $(C_{29}H_{16}N_4O_5)_n$: C, 69.60; H, 3.22; N, 11.20. Found: C, 67.82; H, 3.38; N, 10.75.

2.4. Characterization

^1H 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. Elemental analyses were performed on an Italy CARLO ERBA 1106 elemental analyzer. Thermogravimetric analysis (TGA) was carried out with a TA instrument Q500 Thermogravimetric analyzer at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a TA instrument Q200 Differential Scanning Calorimeter at a heating rate of 20 °C/min. The inherent viscosities were determined at a concentration of 0.5 g/dL in DMAc with an Ubbelohde viscometer at 30.0 ± 0.1 °C.

3. Results and discussion

3.1. Monomer synthesis

First, a new phthalonitrile-containing diamine **ABCBB** was designed and readily synthesized in two steps from 3,5-dinitrophthaloyl chloride and 4-(4-hydroxyphenoxyl) phthalonitrile (Scheme 1). Its structure was unambiguously confirmed by FTIR, ^1H and ^{13}C NMR spectroscopies and elemental analysis.

3.2. Synthesis and solubility of polymer

Then the new aramide was prepared via two approaches. First, high-temperature direct polycondensation method was used to prepare this polymer from **ABCBB** and isophthalic acid. However, this approach only affords a polymer with low molecular weight, indicated by its low inherent viscosity of 0.17 dL/g. Therefore, the polymer was prepared by low-temperature solution polycondensation from diamine **ABCBB** and isophthaloyl chloride in NMP with propylene oxide (**PPO**) as an acid acceptor (Scheme 2). The polymerization proceeded homogeneously throughout the reaction and afforded a clear, viscous polymer solution. The as-made aramide **CN-PA** has an inherent viscosity of 0.38 dL/g and can be solution cast into flexible but a little brittle film, indicative of the formation of moderate molecular weight polymer. The structure of the **CN-PA** was verified by IR, ^1H NMR and elemental analysis. The absence of nonassignable peaks on its ^1H NMR spectrum indicated that a sufficient degree of polymerization was achieved for this new aramide. **CN-PA** was found to be readily soluble in a variety of polar solvents including NMP, DMAc, DMSO and *m*-cresol (Table 1). This indicates that the solubility of the polymer was moderately improved by the introduction of the side substituents containing phthalonitrile units into the polymer backbone. Interestingly, the solubility of **CN-PA** decreased when it is subjected to thermal treatment (Scheme 2), as shown in Table 1. It is noted that the thermally treated polymer (**CN-PA 1** and **CN-PA 2**) was partly soluble or insoluble in polar solvents mentioned above and partly

Table 1
Solubility of **CN-PAs** (**CN-PA**, and **CN-PA 1**, **CN-PA 2**).

CN-PAs	η_{inh} dL/g[a]	Solubility[b]						
		NMP	DMAc	DMF	DMSO	$CHCl_3$	*m*-cresol	H_2SO_4
CN-PA	0.38	+	+	+−	+	−−	+h	+
CN-PA 1	\	+−	+−	−−	\	\	\	+−
CN-PA 2	\	−−	−−	−−	\	\	\	+−

−− = Insoluble even on heating.
\: not measured.
[a] Measured at a concentration of 0.5 g/dL in DMAc at 30.0 ± 0.1 °C.
[b] Solubility: + = soluble at room temperature; +h = soluble on heating; +− = partly soluble; − − = insoluble even on heating.

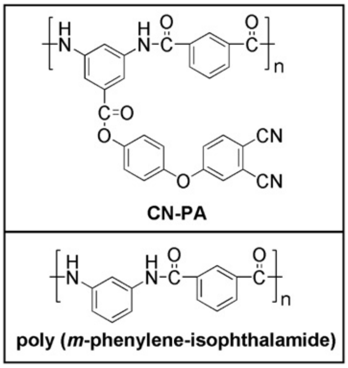


Fig. 1. Structures of **CN-PA** and parent unmodified aramide.

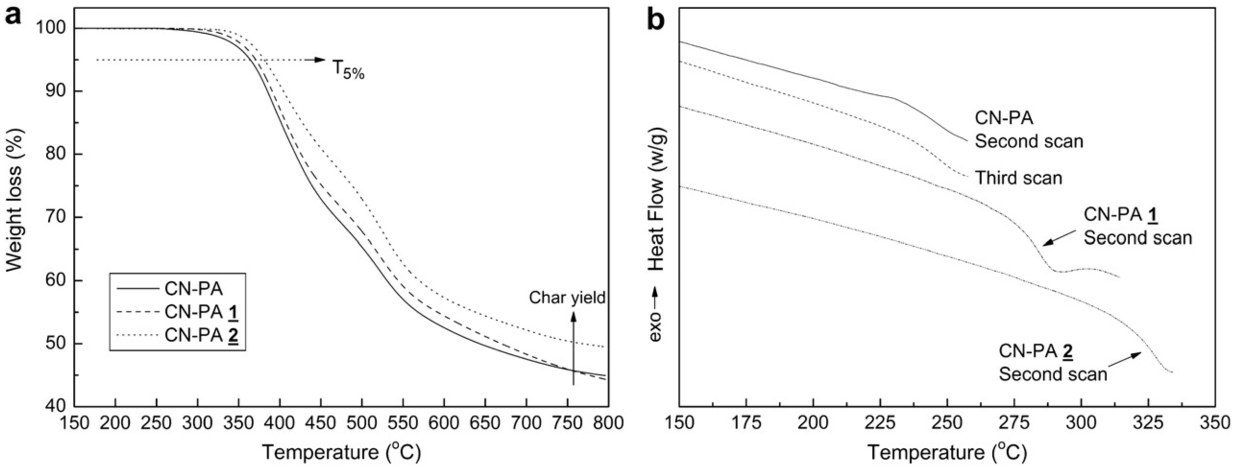


Fig. 2. (a) TGA traces of **CN-PAs** at a heating rate of 10 °C/min under nitrogen at a flow rate of 50 cc/min. (b) DSC traces of **CN-PAs** at a heating rate of 20 °C/min. First scan was conducted from 40 to 260 °C at a heating rate of 20 °C/min and followed by cooling to 40 °C at a heating rate of 20 °C/min. Glass transition temperatures were taken as the midpoint temperature of the baseline shift on the second scan DSC traces.

soluble in concentrated sulfuric acid. Therefore, the solvent resistance was enhanced for **CN-PA** when subjected to further thermal treatment. Apparently, such an improvement in solvent resistance can be attributed to the formations of crosslinking sites probably through the nitrile cure reactions.

3.2.1. *Polymer property enhancement and nitrile cure reactions*

In order to further understand the above results, thermal properties of **CN-PA** and cured polymers were investigated comparatively with parent unmodified aramide poly(*m*-phenylene-isophthalamide) (Fig. 1). The thermal properties of polymers were also enhanced when subjected to thermal treatment around their glass transition temperatures for an extended period of time (Fig. 2). The 5% weight loss temperature ($T_{5\%}$) gradually increased from around 360 °C of **CN-PA** to 380 °C of **CN-PA 2** and char yield (800 °C) of **CN-PA 2** also increased to 51% from initial 44%, which is comparable to that of the parent unmodified aramide (char yield: about 50%) [14], shown in Fig. 2(a). Such an improvement in heat resistance further indicates that more thermally stable crosslinking sites were formed probably through the nitrile cure reactions, when **CN-PA** was subjected to thermal treatment. This result is consistent with the observation of the decrease in nitrile absorbance (2230 cm^{-1}) on the FTIR spectra (Fig. 3). In addition, a weak absorption at 1357 cm^{-1} assigned to the characteristic triazine band was clearly observed for **CN-PA 2** [7], indicative of the formation of thermally stable crosslinking sites, which may be responsible for the enhancement in thermal properties of **CN-PA**. Unexpectedly, although the $T_{5\%}$ was increased for **CN-PA 1**, a slight decrease in char yield was observed, which may be related to the multiple reaction mechanisms of phthalonitrile unit such as triazine, phthalocyanine and isoindoline. The ratio of these structures may be different according to the thermal history [8] and it is known that different structures may show different degradation mechanisms and thermal properties. Probably the higher ratio of the less thermally stable structure was produced for **CN-PA 1** compared to **CN-PA** and **CN-PA 2**. At this stage, this inconsistent result cannot be fully understood. Characteristic absorptions representative of phthalocyanine and isoindoline formations were difficult to be identified in this article, because these absorptions overlap strong bands in the **CN-PAs**. On the DSC traces, no exothermic peaks were found, indicating that the nitrile cure reaction progressed at an extremely slow rate (Fig. 2(b)). It has been reported in the small molecular system that the thermal polymerization of nitrile groups was controlled as a function of the concentration of the functional groups containing active hydrogen such as amino or hydroxyl [6,8]. However, the low cure reactivity in this polymer system cannot be simply attributed to the extremely low concentration of end amino groups but also the low mobility of the side chain may contribute to the low cure reactivity, when the polymers were thermally treated around the glass transition temperatures. Because of this cure characteristic of the **CN-PA**, its original glass transition temperature (T_g) is believed to be detectable (around 245 °C). Strikingly, it was tremendously elevated to about 325 °C for **CN-PA 2** (Fig. 2(b)) much higher than that of poly(*m*-phenylene-isophthalamide) (about 275 °C) [15].

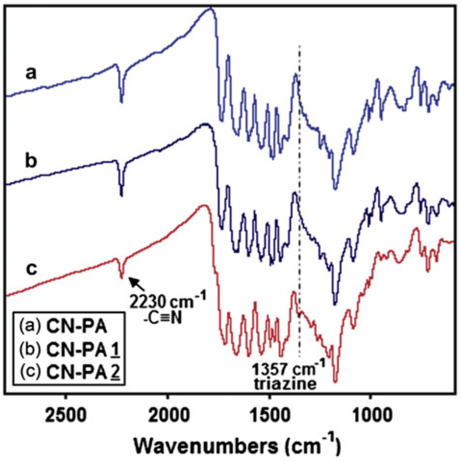


Fig. 3. FTIR spectra of **CN-PAs** (**CN-PA**, and **CN-PA 1**, **CN-PA 2**).

4. Conclusions

In conclusion, a new aramide with pendant phthalonitrile units was successfully prepared from a new diamine **ABCBB** via low-temperature solution polycondensation. The as-made polymer **CN-PA** was readily soluble in polar solvents, while its solvent resistance and thermal properties can be enhanced by thermal treatment around the glass transition temperatures of the polymers for an extended period of time. The nitrile cure reactions in this polymer system can be realized and was extremely sluggish around the glass transition temperatures. 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. This cure characteristic of **CN-PA** affords its potential as matrices for thick composite applications. Further studies on composite applications are in progress.

Acknowledgment

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.08.033.

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