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An efficient approach to prepare ether and amide-based self-catalyzed phthalonitrile resins

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Abstract

Phthalonitrile polymers with amide and ortho-, meta-, and para-substituted ether linkages in the backbone were synthesized successfully and their thermal properties were investigated. The monomer building blocks for these polymers were cured without the addition of catalysts due to the self-catalyzing nature of the monomer's amino group. The ether and amide functionalities in the chain enhanced their processability without compromising thermal stability. The resins exhibited a low complex viscosity over a wide processing window between the monomer melting temperature and the polymer cure temperature, with the processing temperature range varying significantly for para-, ortho-, and meta-substituted polymer architectures. All three systems exhibited high thermal and thermo-oxidative stability. The high char yields, which ranged from 66–75% at 900 °C under nitrogen atmosphere, and the high glass transition temperatures of the polymers indicate a high crosslinking density in the network structure.

1 Introduction

Phthalonitrile resins are a class of high temperature thermosetting polymers. They exhibit high glass transition temperatures, good thermal stability, excellent moisture resistance, superior flame resistance, and allow the creation of void-free composites. Therefore, in many regards, they are considered ideal materials for marine, aerospace, and electronic applications.[1–3] However, these polymers require high curing temperatures; they are brittle because of their high crosslinking density; they also require long curing times and offer a narrow processing window – defined as the temperature between the melting temperature of the monomer and the gelation temperature of the polymer network.[4,5] These problems can be overcome using various curing additives to reduce the curing time[6–10] and a variety of structural changes to attain low complex viscosity of the prepolymer resin and a broad processing window.[11–21] The introduction of flexible aromatic ether linkages into the polymer chain tends to result in decreased crosslinking density and thus reduced brittleness in the cured resin. At the same time the flexible aromatic ether linkages lower the viscosity of the prepolymers, allowing for improved resin flow during

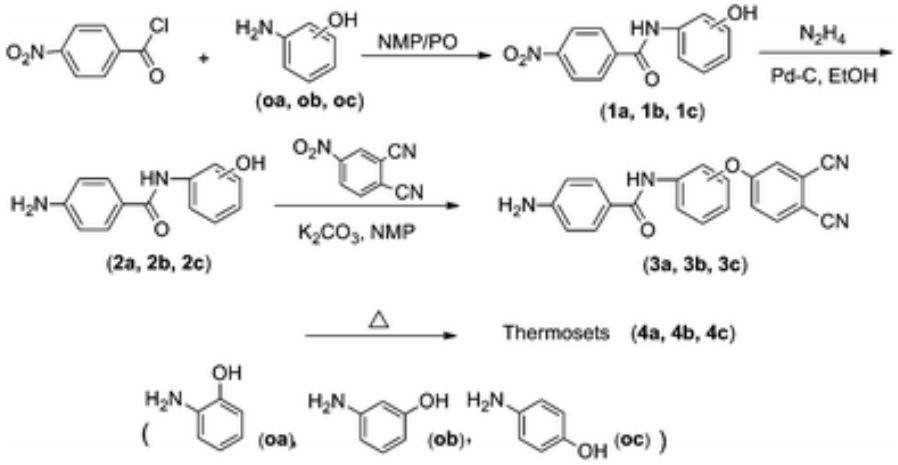
processing.[4,5] Unfortunately, these flexible ether linkages also compromise the thermal stability of phthalonitrile resins. Incorporating thermally stable groups into the polymer main chain together with ether linkages is an effective approach to improve thermal properties as well as processability.[22] Typically, phthalonitrile resins are cured in the presence of aromatic diamines.[8] However, volatilization of the diamines is observed at elevated temperature, which results in a slowdown of the curing reactions[23] and creates problems in attaining anticipated properties.

Therefore, it is desirable to modify the structure of the phthalonitrile monomers to eliminate the need for curing additives. A simple, well known, and effective method is the incorporation of auto-catalyzing groups into the reactive phthalonitrile units. Here, various hydroxyl or amino-functional phthalonitrile monomers/oligomers cross-link by self-promoted curing without the addition of curing additives.[6,24]

In this work, as well as in our previous work,[25,26] we have developed some new monomers that are not only self-catalyzing but also contain thermally stable groups along the flexible ether linkages for improved thermal properties and processability. They are superior in all aspects compared to conventional, non-catalyzed phthalonitrile monomers.[5–10]

2 Results and discussion

The 4-amino-N-[(3,4-dicyanophenoxy)phenyl]benzamides were synthesized in three steps as shown in Scheme 1. In the first step, N-(hydroxyphenyl)-4-nitrobenzamides were synthesized by the condensation reaction between commercially available aminophenol and 4-nitrobenzoyl chloride. This was followed by a catalytic reduction of the nitro group in the second step, and finally the target compounds were obtained through nucleophilic displacement of the nitro group in 4-nitrophthalonitrile by the potassium salt of N-(hydroxyphenyl)-4-aminobenzamide with continuous purging of nitrogen.



Scheme 1 Synthesis and polymerization of **3a**, **3b** and **3c**.

The formation of the synthesized products was confirmed by FT-IR and NMR spectral data. The appearance of stretching bands in the range of 3300–3450 cm^{-1} and around 1660 cm^{-1} was assigned to amide groups; the disappearance of the nitro bands and the appearance of new bands

in the range of 3270–3325 cm^{-1} were attributed to amino groups, which also confirmed the formation of the newly synthesized products. The final products were confirmed by the disappearance of the hydroxyl band and the appearance of a new band at 1252 cm^{-1} attributed to ether groups. FT-IR spectra displayed all the characteristic bands of cross-linked products, showing some additional bands around 1518 cm^{-1} and 1358 cm^{-1} and around 1012 cm^{-1} confirming the formation of triazine and phthalocyanine rings, respectively (Fig. ii and iii, ESI†). The decrease in intensity of the nitrile group and the shift to a lower wavelength around 2223 cm^{-1} compared to their corresponding precursors confirm the formation of triazine rings. In addition, conversion of such type of monomers to isoindolines and dehydrophthalocyanines has been also reported[27] (Fig. i, ESI†). ^{1}H NMR and ^{13} CNMR spectra further confirmed the formation of monomer structures (Fig. iv–ix, ESI†). Assignments for all the protons were in complete agreement with the proposed molecular structures.

The curing of the monomers was analyzed by DSC up to 400 °C, as displayed in Fig. 1. The melting transition occurred around 88 °C, 181 °C, and 239 °C for monomers **3a**, **3b**, and **3c** respectively. These differences in melting points reflect the fact that melting transitions are strongly related to the structure of the monomers. The heat absorbed during melting of monomers **3a**, **3b**, and **3c** was 5.36 J g^{-1}, 163.2 J g^{-1}, and 130.8 J g^{-1}, respectively, which was higher than the heat for their imide-based phthalonitrile[25] counterparts.

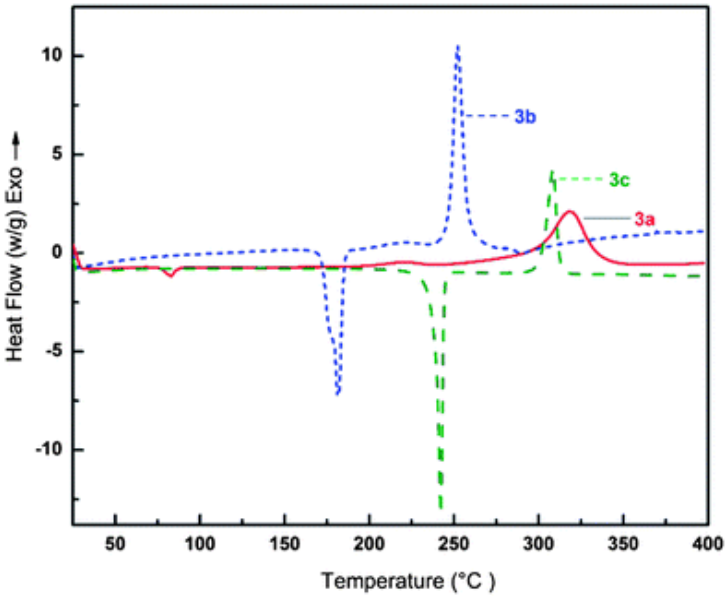


Fig. 1 DSC curves of the monomers **3a**, **3b**, and **3c**.

These higher melting enthalpies indicated that these monomers were more crystalline than their imide counterparts due to intermolecular hydrogen bonding. On the other hand, the rather low melting enthalpy of monomer **3a** compared to monomers **3b** and **3c** is due to the fact that its structure does not allow for the same levels of intermolecular interaction. Curing peaks were observed at 318.6 °C, 252.9 °C, and 308.6 °C for monomers **3a**, **3b**, and **3c**, respectively. These variations indicated the effect of different monomer linkages. The curing enthalpies were 170.7 J g^{-1}, 221.5 J g^{-1}, and 90.4 J g^{-1} for monomers **3a**, **3b**, and **3c**, respectively. This variation in

enthalpy shows the significant effect of the different substitution patterns on the structure of the monomer.

The rheometric analysis of the monomers **3a**, **3b**, and **3c** during polymerization, performed as a function of temperature, is shown in Fig. 2. These measurements were made between 75 °C and 375 °C. It was found that the complex viscosity (η*) of each monomer decreased sharply above its melting point and increased suddenly close to the curing temperature. The phenomenon coincided with the results of DSC analysis. It was found that all three monomers maintained very low viscosity in the processing window between the melting point and the initiation of polymerization. The results showed a reasonable processing window (ΔT ~ 50 to 200 °C depending on the monomer) between the melting point and curing temperature. Their low melt viscosity and large processing window make them suitable candidates for resin transfer molding or resin infusion molding, among other liquid composite processing technologies. It is noted that **3a** had the widest processing window (~200 °C) while **3c** had the narrowest window. This is due to the lower melting temperature and higher curing temperature of **3a** compared to the other monomers, as explained earlier.

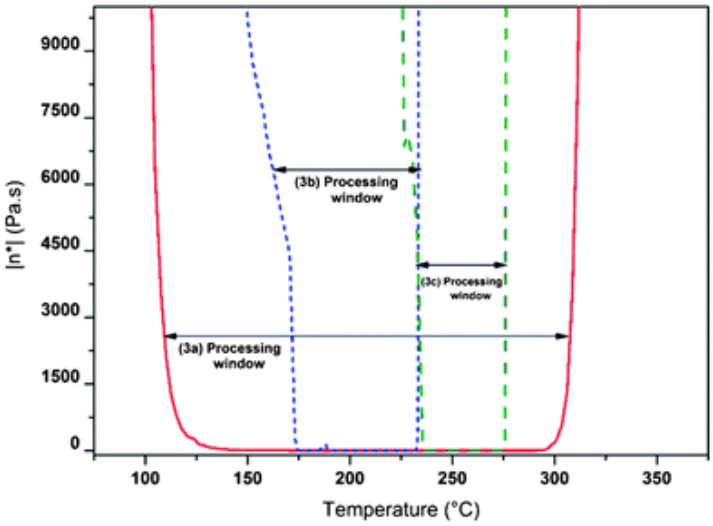


Fig. 2 Complex viscosity (η*) of the monomers **3a**, **3b**, and **3c**.

TGA of the polymers **4a**, **4b**, and **4c** were performed both under nitrogen and air atmospheres between 25 and 900 °C as shown in Fig. 3 and Table 1. The results of these studies indicated that polymers **4a**, **4b**, and **4c** exhibited 5% weight loss temperatures from 506–531 °C in a nitrogen atmosphere and from 496–502 °C in air, respectively. This indicates that polymer **4c** is comparatively more stable towards heat. Char yields ranged from 66–75% at 900 °C in nitrogen. The high char yield of polymer **4a** showed a high crosslinking density due to the high curing temperature, comparatively. Thermal stability of these polymers was lower than their imide counterparts[25] due to differences in molecular structures. However, the char yields of these polymers (66–75%) were higher than their imide[25] analogues (62.5–70%) due to the lower average molecular mass between the crosslinking groups.

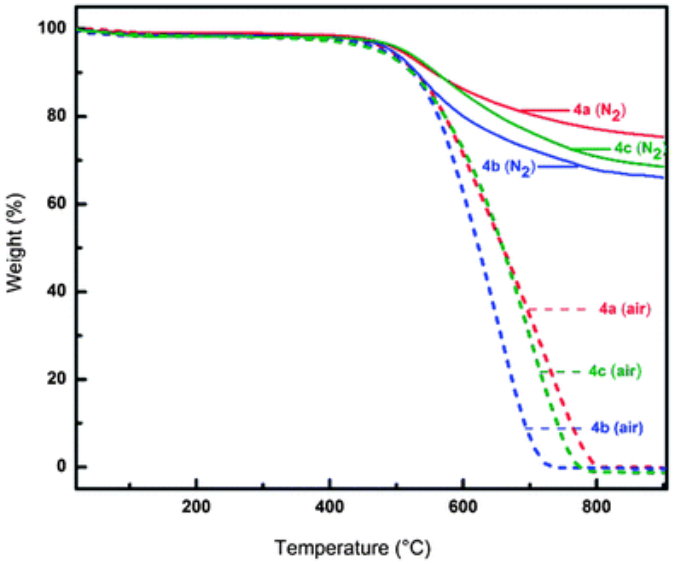


Fig. 3 TGA plots for **4a**, **4b**, and **4c** in nitrogen and air atmospheres.

Table 1 TGA and DMA results for **4a**, **4b**, and **4c**

	TGA (°C)				
Polymer code	$T_{5\%}(N_2)$[a]	$T_{5\%}(O_2)$	**% Char yield (N_2) (900 °C)**	E'[b] **(MPa) rt**	T_g **(°C)**
4a	517	496	75	2150	>500
4b	506	501	66	2070	>500
4c	531	502	69	1950	>500

a **5% weight loss temperature ($T_{5\%}$) obtained from thermogravimetric analysis (TGA).** *b* **Storage modulus (E') obtained from dynamic mechanical analysis (DMA).** *c* **The glass transition temperature (T_g) was determined by DMA and was considered as the peak of damping factor (tan δ curves).**

DMA measurements were carried out to determine the effect of structural changes on the dynamic mechanical properties as shown in Fig. 4 and Table 1. The polymers **4a**, **4b**, and **4c** cured up to 375 °C showed storage moduli of 2150, 2070, and 1950 MPa respectively at 25 °C. The high storage modulus observed for **4a** is believed to be due to the high curing temperature and thus it has a higher crosslinking density. The storage moduli of **4a** and especially **4c** remain almost flat with increase in temperature due to their high crosslinking densities. However, there was a steady decrease in storage modulus for **4b**, indicating a lower overall crosslinking density, due to cross-linking at lower temperature. Because of their structural variations and high crosslinking density, the storage moduli of these polymers are comparatively higher than those of aminophenoxy phthalonitrile[26] based polymers and their imide analogues.[25] The damping factor (tan δ) of each polymer, cured at 375 °C, remained low up to approximately 500 °C, as the materials approached the glass transition region, where the tan δ continued to increase at the end of the temperature range tested. This behavior indicated that these polymers remained below the glass transition temperature (defined by the peak in the tan δ curve) throughout the experiments and remained in a glassy state up to 500 °C.

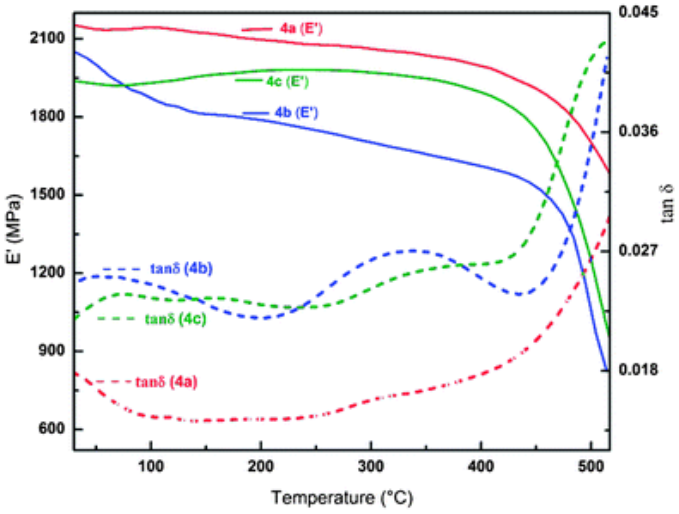


Fig. 4 Storage moduli (E′) and damping factors (tan δ) of the polymers **4a**, **4b**, and **4c**.

3 Experimental

3.1 Materials

2-Aminophenol, 3-aminophenol, 4-aminophenol, 4-nitrobenzoyl chloride, propylene oxide (PO), hydrazine monohydrate, and 10% Pd–C were obtained from Sigma-Aldrich, and used as supplied. Potassium carbonate (Fluka) was dried at 150 °C under vacuum. 4-Nitrophthalonitrile was purchased from Alpha and used as received. Dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) were obtained from Sigma-Aldrich and purified by distillation under reduced pressure over calcium hydride (CaH_2) and stored over 4 Å molecular sieves. All other solvents and reagents used were purified using standard methods.

3.2 Measurements

^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX300 NMR spectrometer. The infrared spectra of the monomers and the products were obtained on a Bruker 27 FT-IR spectrometer, using KBr disks. Differential scanning calorimetry (DSC) experiments were performed on a Mettler Toledo 822e differential scanning calorimeter at a heating rate of 10 °C min^{-1} under flowing nitrogen. The glass transition temperature (T_g) of the polymers was identified as the peak temperature of the tan δ curves obtained by dynamic mechanical analysis performed on a DMA 242 C (Netzsch, Germany) instrument with a driving frequency of 1.0 Hz, in single cantilever mode, and at a scanning rate of 5 °C min^{-1} in nitrogen. Melting points were measured using DSC. Thermogravimetric analysis (TGA) was conducted with a Netzsch STA 409PC instrument, using approximately 10 mg of samples under controlled flux of nitrogen/air at 10 °C min^{-1}. Complex viscosity measurements were performed on a Physica MCR-300 mechanical spectrometer at a ramp rate of 4 °C min^{-1} in air and the top parallel plate was oscillated at a fixed strain of 10% and a fixed angular frequency of 100 rad s^{-1}. Sample specimen discs of 2.5 cm diameter and 1 mm thickness were prepared by compression molding at room temperature under high pressure.

3.3 Syntheses

3.3.1 Syntheses of **1a**, **1b** and **1c**. Aminophenol (3.69 g, 0.0338 mol) was added to 70 mL of dry

N-methyl-2-pyrrolidone (NMP) under a constant flow of nitrogen. The reaction mixture was stirred at 0 °C for half hour and then 20 mL of propylene oxide (PO) was added. After five minutes, p-nitrobenzoyl chloride (6.24 g, 0.0338 mol) was added and the reaction mixture was stirred for an additional half hour at the same temperature. After reaching room temperature, the reaction mixture was stirred for an additional 8 h. Next, the reaction mixture was poured into water, after which the solid precipitate was filtered, washed with hot water repeatedly, and dried overnight under vacuum at 80 °C.

The reaction of (3.69 g, 0.0338 mol) 2-aminophenol (the ortho-substituted configuration) and (6.24 g, 0.0338 mol) p-nitrobenzoyl chloride resulted in light yellow color N-(2-hydroxyphenyl)-4-nitrobenzamide (**1a**) (8.5 g, 97%, mp: 206 °C). FTIR (ν_{max}, cm^{-1}): 3300–3420b (OH, –CONH–), 3035w (ArC–H) 1655s (CO, –NHCO–) 1610s (N–H) 1550m, 1522m (C=C), 1438s, 1351m (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.85 (s, 1H, NHCO), 9.74 (s, 1H, OH), 8.36 (d, J = 8.00 Hz, 2H, Ar H-1), 8.19 (d, J = 8.00 Hz, 2H, Ar H-2), 7.60 (d, J = 8.02 Hz, 1H, Ar H-7), 7.04–7.10 (m, 2H, Ar H-5,6), 6.93 (d, J = 8.00 Hz, 1H, Ar H-4), 6.81–6.86 (m, 1H, Ar H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 164.7 (C=O), 151.0 (C7), 150.0 (C1), 141.2 (C4), 130.1 (C3), 127.3 (C6), 126.0 (C9), 124.5 (C2), 121.0 (C10), 119.9, 116.9 (C8).

Using the same procedure, the reaction of (3.69 g, 0.0338 mol) 3-aminophenol (the meta-substituted configuration) and (6.24 g, 0.0338 mol) p-nitrobenzoyl chloride resulted in yellow color N-(3-hydroxyphenyl)-4-nitrobenzamide (**1b**) (8.5 g, 98%, mp: 214 °C). FTIR (ν_{max}, cm^{-1}): 3310–3405b (OH, –CONH–), 3033w (ArC–H) 1662s (CO), 1605s (N–H), 1545m, 1522m (C=C), 1440s, 1353m (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 10.44 (s, 1H, NHCO), 9.49 (s, 1H, OH), 8.37 (d, J = 8.00 Hz, 2H, Ar H-1), 8.16 (d, J = 8.00 Hz, 2H, Ar H-2), 7.35 (s, 1H, Ar H-3), 7.15 (d, J = 8.00 Hz, 2H, Ar H-5,7), 6.54 (t, J = 7.89 Hz, 1H, Ar H-1). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 165.0 (C=O), 158.7 (C8), 150.0 (C1), 141.6 (C6), 140.9 (C4), 130.2 (C3,10), 124.5 (C2), 112.1 (C9,11), 108.5 (C7).

Also using the same procedure, the reaction of (3.69 g, 0.0338 mol) 4-aminophenol (the para-substituted configuration) and (6.24 g, 0.0338 mol) p-nitrobenzoyl chloride resulted in deep yellow color N-(4-hydroxyphenyl)-4-nitrobenzamide (**1c**) (8.0 g, 92%; mp: 266 °C). FTIR (ν_{max}, cm^{-1}): 3300–3405b (OH, –NHCO–), 3030w (ArC–H), 1660s (CO), 1600s (N–H), 1550m, 1520m (C=C), 1441s, 1352m (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 10.36 (s, 1H, NHCO), 9.36 (s, 1H, OH), 8.36 (d, J = 8.00 Hz, 2H, Ar H-1), 8.15 (d, J = 8.00 Hz, 2H, Ar H-2), 7.53 (d, J = 8.02 Hz, 2H, Ar H-3,7), 6.75 (d, J = 8.02 Hz, 2H, Ar H-4,6). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 164.2 (C=O), 155.0 (C9), 149.9 (C1), 141.8 (C4), 131.2 (C6), 130.0 (C3), 124.5 (C2), 123.3 (C7,10), 116.0 (C8,10).

3.3.2 Syntheses of **2a**, **2b** and **2c**. N-(Hydroxyphenyl)-4-nitrobenzamide (7.5 g, 0.0290 mol), 0.3 g of 10% Pd–C, and 350 mL of ethanol were heated in a 500 mL flask to 85 °C. Over a period of 1 h, 10 mL of hydrazine monohydrate was added to the stirring mixture dropwise. The reaction was continued at reflux for another 4 h after addition of hydrazine monohydrate. In order to redissolve the precipitated product, 70 mL of tetrahydrofuran was added to the suspension and refluxing was continued for an additional 1 h. The mixture was filtered to remove the Pd–C and the filtrate was poured into water. The product was filtered, washed with hot water, and vacuum

dried overnight.

The reduction of (7.5 g, 0.0290 mol) N-(2-hydroxyphenyl)-4-nitrobenzamide (**1a**) resulted in an off-white powder of N-(2-hydroxyphenyl)-4-aminobenzamide (**2a**) (5.8 g, 88%, mp: 231 °C). FTIR (ν_{max}, cm^{-1}): 3270–3330b (OH, NH_2, –CONH–), 3025w (ArC–H), 1644s (CO), 1605b (NH_2, –CONH–), 1595m, 1520m (C=C). ^{1}H NMR (DMSO-d_6) δ: 9.82 (s, 1H, NHCO), 9.23 (s, OH), 7.63–7.72 (m, 3Ar H), 6.80–6.98 (m, 3Ar H), 6.58 (d, 2Ar H, J = 8.02 Hz), 5.82 (s, –NH_2). ^{13}C NMR (DMSO-d_6) δ: 166.5 (C=O), 153.4 (C1), 149.6 (C7), 130.3 (C3), 127.7 (C6), 126.0 (C9), 124.0 (C4), 121.0 (C10), 120.2 (C11), 117.4 (C8), 113.7 (C2).

The reduction of (7.5 g, 0.0290 mol) N-(3-hydroxyphenyl)-4-nitrobenzamide (**1b**) resulted in a white powder of N-(3-hydroxyphenyl)-4-aminobenzamide (**2b**) (5.8 g, 88%, mp: 221 °C). FTIR (ν_{max}, cm^{-1}): 3270–3325b (OH, NH_2, –NHCO–), 3027w (ArC–H), 1647s (CO), 1600b (NH_2, –NHCO–), 1598m, 1525m (C=C). ^{1}H NMR (DMSO-d_6) δ: 9.61 (s, 1H, NHCO), 9.30 (s, OH), 7.68 (d, 2Ar H, J = 8.05 Hz), 7.33 (s, Ar H) 7.02–7.15 (m, 2Ar H), 6.57 (d, 2Ar H, J = 8.03 Hz), 6.42 (d, Ar H, J = 7.91 Hz), 5.73 (s, –NH_2). ^{13}C NMR (DMSO-d_6) δ: 166.3 (C=O), 158.4 (C8), 153.0 (C1), 141.9 (C6), 130.3 (C3), 130.0 (C10), 122.3 (C4), 113.5 (C2), 111.9 (C9), 111.0 (C11), 108.3 (C7).

The reduction of (7.5 g, 0.0290 mol) N-(4-hydroxyphenyl)-4-nitrobenzamide (**1c**) resulted in a white powder of N-(4-hydroxyphenyl)-4-aminobenzamide (**2c**) (6.32 g, 96%, mp: 262 °C). 3285–3320b (OH, NH_2, –NHCO–), 3034w (ArC–H), 1641s (CO), 1608b, (NH_2, –NHCO–), 1598m, 1535m (C=C). ^{1}H NMR (DMSO-d_6) δ: 9.53 (s, 1H, NHCO), 9.16 (s, OH), 7.65 (d, 2Ar H, J = 8.00 Hz), 7.46 (d, 2Ar H, J = 8.00 Hz), 6.68 (d, 2Ar H, J = 8.03 Hz), 6.55 (d, 2Ar H, J = 8.03 Hz), 5.67 (s, –NH_2). ^{13}C NMR (DMSO-d_6) δ: 165.9 (C=O), 154.2 (C9), 152.8 (C1), 132.2 (C6), 130.2 (C3), 123.2 (C7,11), 122.5 (C4), 115.9 (C10,8), 113.6 (C2).

3.3.3 Syntheses of **3a**, **3b** and **3c**. 4-Nitrophthlonitrile (2.27 g, 0.0131 mol) and K_2CO_3 (1.81 g, 0.0131 mol) were added to a solution of N-(hydroxyphenyl)-4-aminobenzamide (3.00 g, 0.0131 mol) in 40 mL of DMSO. The reaction mixture was stirred under nitrogen for 40 h or until 4-nitrophthalonitrile was consumed. The contents were poured into 200 mL of ice cold water and a few drops of hydrochloric acid (HCl) were added until the solution was neutralized. The precipitated solid was filtered and washed with water and cold ethanol. The product was dried overnight under vacuum at 70 °C.

The reaction of N-(2-hydroxyphenyl)-4-aminobenzamide (3.00 g, 0.0131 mol), 4-nitrophthalonitrile (2.27 g, 0.0131 mol), and K_2CO_3 (1.81 g, 0.0131 mol) resulted in a brown powder of 4-amino-N-[2-(3,4-dicyanophenoxy)phenyl]benzamide (**3a**) (3.7 g, 80%, mp: 100 °C). FTIR (ν_{max}, cm^{-1}): 3650–3153b (NH_2, –NHCO–), 3078w (ArC–H), 2227m (CN), 1637s (CO), 1600b (NH_2, –NHCO), 1585m, 1521m (C=C), 1272s (C–O–C). ^{1}H NMR (DMSO-d_6) δ: 9.03 (s, NHCO), 7.75 (d, Ar H, J = 8.52 Hz), 7.52 (d, 2Ar H, J = 8.52 Hz), 7.25–7.40 (m, 4Ar H), 7.14 (s, Ar H), 7.03 (d, Ar H, J = 8.70 Hz), 6.52 (d, 2Ar H, J = 8.55 Hz) 6.16 (s, –NH_2). ^{13}C NMR (DMSO-d_6) δ: 164.9 (C=O), 155.2 (C12), 150.6 (C1), 146.12(C7), 135.9 (C16), 132.5 (C3), 132.2 (C6), 127.6 (C4), 127.2 (C9), 126.5 (C17), 125.4 (C10), 119.0 (C13), 118.6 (C11), 118.0 (C14), 117.0 (C8), 116.4 (CN), 114.9 (CN), 113.5 (C2), 101.7 (C15).

The reaction of N-(3-hydroxyphenyl)-4-aminobenzamide (3.00 g, 0.0131 mol), 4-nitrophthalonitrile (2.27 g, 0.0131 mol), and K_2CO_3 (1.81 g, 0.0131 mol) resulted in light yellow 4-amino-N-[3-(3,4-dicyanophenoxy)phenyl]benzamide (**3b**) (3.6 g, 78%, mp: 180 °C). FTIR (ν_{max}, cm^{-1}): 3670–3168b, (NH_2, –NHCO–), 3035w, (ArC–H), 2231m, (CN), 1639s, (CO), 1604b, (NH_2, –NHCO–), 1510m, 1485m, (C=C), 1251s, (C–O–C). ^{1}H NMR (DMSO-d_6) δ: 9.93 (s, NHCO), 8.12 (d, Ar H, J = 8.40 Hz), 7.83 (s, Ar H), 7.64–7.75 (m, 4Ar H), 7.35–7.50 (m, 2Ar H), 6.85 (d, Ar H, J = 8.75 Hz), 6.58 (d, 2Ar H, J = 8.70 Hz), 5.80 (s, $–NH_2$). ^{13}C NMR (DMSO-d_6) δ: 164.9 (C=O), 155.2 (C12), 150.6 (C1), 146.1 (C7), 135.9 (C16), 132.5 (C3), 132.2 (C6), 127.6 (C4), 127.2 (C9), 126.5 (C17), 125.4 (C10), 119.0 (C13), 118.6 (C11), 118.0 (C14), 117.0 (C8), 116.4 (CN), 114.9 (CN), 113.5 (C2), 101.7 (C15).

The reaction of N-(4-hydroxyphenyl)-4-aminobenzamide (3.00 g, 0.0131 mol), 4-nitrophthlonitrile (2.27 g, 0.0131 mol), and K_2CO_3 (1.81 g, 0.0131 mol) resulted in a white powder of 4-amino-N-[4-(3,4-dicyanophenoxy)phenyl]benzamide (**3c**) (3.5 g, 76%,mp: 240 °C). FTIR (ν_{max}, cm^{-1}): 3670–3168b, (NH_2, –NHCO–), 3035w, (ArC–H), 2231m, (CN), 1639s, (CO), 1604b, (NH_2, –NHCO–), 1510m, 1485m, (C=C), 1251s, (C–O–C). ^{1}H NMR (DMSO-d_6) δ: 9.90 (s, NHCO), 8.07 (d, Ar H, J = 8.50 Hz), 7.86 (d, 2Ar H, J = 8.59 Hz), 7.75 (s, Ar H), 7.70 (d, 2Ar H, J = 8.40 Hz), 7.34 (d, Ar H, J = 8.90 Hz), 7.14 (d, 2Ar H, J = 7.70 Hz), 6.59 (d, 2Ar H, J = 8.60 Hz), 5.78 (s, $–NH_2$). ^{13}C NMR (DMSO-d_6) δ: 164.4 (C=O), 162.0 (C12), 154.8 (C8), 153.3 (C1), 142.9 (C6), 137.3 (C16), 131.4 (C10), 130.4 (C3), 123.7 (C4), 123.0 (C17), 121.6 (C13), 117.9 (C14), 117.7 (C9), 116.9 (CN), 116.4 (C11), 115.2 (CN), 113.5 (C2), 112.3 (C7), 109.1 (C15).

3.3.4 Synthesis of polymers **4a**, **4b** and **4c**. The self-catalyzed monomers **3a**, **3b**, and **3c** were heated using the following heating profile; 170 °C for 1 h, 200 °C for 2 h, 250 °C for 3 h, 315 °C for 5 h and then post-cured at 375 °C for 5 h in an open atmosphere. The post-cured products were then characterized and analyzed using different techniques.

4 Conclusions

A new method was introduced for the preparation of self-catalyzed amide-containing phthalonitriles with a flexible ether linkage. The monomer **3a** exhibited a lower melting point and high curing temperature than the other two isomers and thus allowed for a wider processing window. The flexible ether linkage enhanced processability without compromising thermal and oxidative stability. The 5% weight loss temperature for all three cured polymers was near 500 °C in air and 520 °C in nitrogen, with more than 70% residual mass at 900 °C. None of the polymers exhibit a T_g below 500 °C when fully cured. The outstanding thermal stability of all synthesized polymers and the broad processing window of **3a** are very promising for high temperature polymer and polymer matrix composite applications.

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