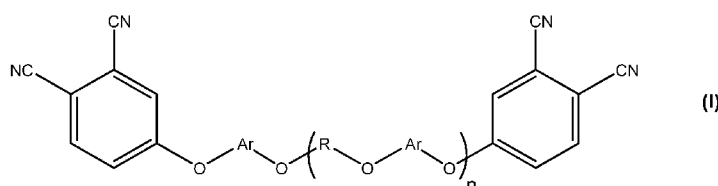




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(54) **Title:** SYNTHESIS AND POLYMERIZATION OF OLIGOMERIC ALIPHATIC-AROMATIC BASED PHTHALONITRILES



(57) **Abstract:** A phthalonitrile compound having the formula below. The value n is a positive integer. Each R has a hydrocarbon chain optionally having -O- or -SiR'₂-O-. Each R' is an aliphatic group. Each Ar is an aromatic group with the proviso that Ar contains at least two aromatic rings when n is 1 and R is an alkylene group. A method of: reacting an excess of a dihydroxyaromatic compound with a dihalocompound to form an oligomer; and reacting the oligomer with 4-nitrophthalonitrile to form the phthalonitrile compound, where Ar is an aromatic group.

SYNTHESIS AND POLYMERIZATION OF OLIGOMERIC ALIPHATIC-AROMATIC
BASED PHTHALONITRILES

This application claims the benefit of US Application No. 14/968,099, filed on
December 14, 2015, which claims the benefit of US Provisional Application No. 62/092,291,
filed on December 16, 2014. The provisional application and all other publications and patent
documents referred to throughout this nonprovisional application are incorporated herein by
reference.

TECHNICAL FIELD

The present disclosure is generally related to phthalonitrile compounds.

DESCRIPTION OF RELATED ART

Phthalonitrile resins are showing outstanding potential as matrix materials for advanced
composites. Phthalonitrile monomers polymerize through the cyano groups, with the aid of an
appropriate curing agent, to yield a crosslinked polymeric network with high thermal and
oxidative stabilities. These polymers are obtained by heating the phthalonitrile monomers and a
small amount of curing additive in the melt-state for extended periods of time at elevated
temperatures. A variety of phthalonitrile monomers containing aromatic ether, thioether, imide,
and sulfone linkages between the terminal phthalonitrile units have been synthesized and cured
or converted to crosslinked/networked polymers. The cure reaction of these monomers have
been investigated using a variety of curing additives such as organic amines, strong organic
acids, strong organic acids/amine salts, metallic salts and metals. When postcured at elevated
temperatures at about 400°C, the thermoset shows excellent long-term thermal and oxidative
stabilities to temperatures approaching 375°C. In addition, the high aromatic content of the
thermoset affords a high char yield (60-90%) when pyrolyzed to 1000°C under inert conditions.
The high thermal stability and the ability to form a high char yield upon pyrolysis contribute to
the outstanding fire performance of the phthalonitrile polymer. For instance, the fire
performance of phthalonitrile-carbon and phthalonitrile-glass composites are superior to that of
other thermoset-based composites currently in use for aerospace, ship and submarine
applications. The phthalonitriles are still the only polymeric material that meets MIL-STD-2031
for usage inside of a submarine.

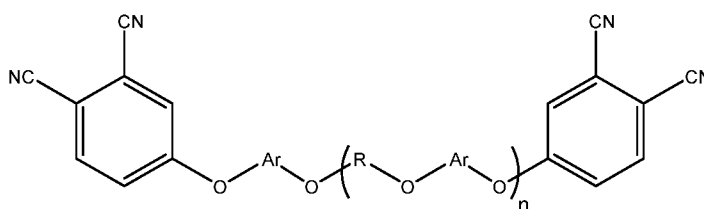
Current phthalonitrile research efforts are targeted towards developing high temperature
and flame resistant composites and addressing composite processability based on cost effective
on manufacturing techniques such as resin transfer molding (RTM), resin infusion molding

(RIM), and filament winding. One of the objectives has been concerned with the incorporation of units within the backbone to improve on the synthesis at lower temperatures and to enhance the flammability resistance and thermo-oxidative properties while retaining low temperature processability. A low viscosity resin enables composite processing by RTM and RIM

manufacturing methods. Furthermore, a low melt viscosity and a larger processing window are useful for fabrication of thick composite sections where the melt has to impregnate thick fiber preforms. Low melting oligomeric phthalonitrile monomers and curing additives that do not volatilize at elevated cure reaction temperatures such as bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS) have been shown to enhance the overall physical properties and processability of phthalonitrile-based composites.

BRIEF SUMMARY

Disclosed herein is a phthalonitrile compound having the formula below. The value *n* is a positive integer. Each *R* comprises a hydrocarbon chain optionally comprising –O– or –SiR'₂–O–. Each *R*' is an aliphatic group. Each *Ar* is an aromatic group with the proviso that *Ar* comprises at least two aromatic rings when *n* is 1 and *R* is an alkylene group.



Also disclosed herein is a method comprising: reacting an excess of a dihydroxyaromatic compound having the formula HO–Ar–OH with a dihalocompound having the formula X–R–X to form an oligomer; and reacting the oligomer with 4-nitrophthalonitrile to form a phthalonitrile compound having the formula above. Each *X* is a halide, *R* is as defined above, and each *Ar* is an aromatic group.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation will be readily obtained by reference to the following Description of the Example Embodiments and the accompanying drawings.

Fig. 1 shows the synthesis of oligomer phthalonitrile **1** and thermoset **6**.

Fig. 2 shows the structures of phthalonitriles **1a**, **1b**, and **1c**.

Fig. 3 shows the DSC thermograms of phthalonitrile resin **1a** cured with 10 mol % of

Fig. 4 shows TGA thermograms of bisphenol A siloxane phthalonitrile resin **6c** heated under air and nitrogen atmospheres.

5 DETAILED DESCRIPTION OF EXAMPLE EMBODIMENTS

In the following description, for purposes of explanation and not limitation, specific details are set forth in order to provide a thorough understanding of the present disclosure. However, it will be apparent to one skilled in the art that the present subject matter may be practiced in other embodiments that depart from these specific details. In other instances,
10 detailed descriptions of well-known methods and devices are omitted so as to not obscure the present disclosure with unnecessary detail.

Disclosed herein the synthesis and polymerization of low melting oligomeric phthalonitrile monomers containing multiple aromatic ether and aliphatic moieties between the terminal phthalonitrile units. The novel oligomeric aromatic ether-aliphatic-containing
15 phthalonitrile monomers can polymerize through the phthalonitrile units to afford high temperature, flame resistant thermosets. Desirable physical properties such as a low glass transition (T_g) temperature and high thermal and oxidation stability can be obtained at lower postcure temperatures ($\sim 300^\circ\text{C}$). Polymeric composites and coatings formulated from the new phthalonitriles should have outstanding thermo-oxidative and flammability properties for ship,
20 submarine, and aerospace applications and can withstand continuous high temperatures ($300\text{--}375^\circ\text{C}$) in oxidative environments such as air for extended periods. To date, current oligomeric phthalonitrile polymers have melting points between 50 and 100°C with the polymerization occurring in excess of 200°C . The use of low molecular weight precursor resins to obtain thermosetting polymeric materials with high thermo-oxidative properties is often advantageous
25 from a processing standpoint. Precursor resins are useful in composite fabrication by a variety of methods such as infusion, resin transfer molding, and prepreg consolidation. The phthalonitriles may be suitable for numerous aerospace and electronic applications due to their outstanding and superior thermal and oxidative properties, ease of processability, and low water absorption relative to other high temperature polymers such as polyimides. Furthermore, resins with a large
30 window between the melting point and the cure temperature are desirable to control the viscosity and the rate of curing. With these disclosed phthalonitrile monomers, processability to shaped composite components may be achieved in non-autoclave conditions potentially above 70°C and by cost effective methods.

Earlier simple bisphenol-based phthalonitriles had melting points in excess of 200°C . It

was, therefore, desirable to design and prepare low melting oligomeric phthalonitrile monomers, which upon polymerization would retain the useful thermal properties (300-375°C) exhibited by the phthalonitrile polymers but with greater thermo-oxidative and superior flammability properties. Such monomers should also exhibit a large processing window useful for composite and device fabrication. The term “oligomeric” means that more than one compound is formed during the synthesis of **1** (Fig. 1) with the average molecular weight dependent on the ratios of reactants, **2** and **3**, used. The synthesis of a series of multiple aromatic ether-linked phthalonitriles **1**, which contain aryl ether and aliphatic units in the backbone, has been achieved by a one pot reaction involving initially a nucleophilic displacement reaction between bisphenol **2**, dihaloaliphatic compound **3**, under basic conditions (K₂CO₃) in dimethylsulfoxide (DMSO) at temperatures around 90°C (Fig. 1). Once NMR spectroscopy confirmed the desired oligomeric diphenolate product **4**, the displacement reaction was considered complete. Further reaction of **4** with 4-nitrophthalonitrile **5** afforded the oligomeric phthalonitriles **1**, which were readily soluble in common organic solvents such as toluene, DMF, acetone, methylene chloride, ether, and chloroform, in 91-95% yields. The structure of the phthalonitrile monomers **1** was confirmed by IR and ¹H-NMR spectroscopy. The length of the spacer between the terminal phthalonitrile groups can be varied by changing the ratio between **2** (excess) and **3**. Oligomeric phthalonitrile resins **1** generally have melting point between 50 and 70°C. Several oligomeric phthalonitriles **1** have been synthesized by this method and the structures of **1a**, **1b**, and **1c** are shown in Fig. 2.

Polymerization studies of phthalonitrile **1** (n = 1) were achieved by DSC analyses up to 400°C in the presence of 3 weight % of bis(3-[4-aminophenoxy]phenyl)sulfone (*m*-BAPS) to afford thermosets **6**. Using a resin **1a** as an example, the DSC thermogram (Fig. 3) revealed an endothermic transition (glass transition temperature (T_g)) at approximately 50°C and an exothermic transition peaking at 250°C attributed to the reaction with *m*-BAPS. Therefore, **1a** exhibited low softening temperatures was completely free flowing above 50°C as determined by a visual melting test and DSC analysis and had a long processing window (~ 100°C) before reaction with the curing additive started to occur above 150°C. The polymerization studies of **1b** and **1c** displayed similar DSC thermograms as **1a**.

Low molecular weight diaryl ether aliphatic-containing compounds **4** were used in the preparation of novel oligomeric phthalonitriles **1**. The oligomeric phthalonitriles **1** were easily converted to polymer **6** under thermal conditions and in the presence of a curing additive. Under these curing conditions, the new phthalonitrile monomer **1** offers a broad processing window, which is important for the fabrication of complex shaped composite components. The thermosets

or cured polymers **6** show outstanding and superior thermo-oxidative properties. Fig. 4 shows TGA thermograms of the bisphenol A derived phthalonitrile thermoset **1c** containing a siloxane moiety between the phthalonitrile end groups that has been heated to 1000°C. The polymer **6c** exhibits thermal and oxidative stability to about 400°C before any significant weight loss

occurred. Table 1 shows the rheometric viscosity for all three new phthalonitriles (**1a-1c**). Upon heating **1a** to 100°C, a viscosity of 2,000 cP was observed (Table 1). Further heating precipitously decreased the viscosity to 300 cP at 150°C and to 70 cP at 200°C. Similar viscosities were observed for the other two PN resins. These viscosity values afford an optimal processing window, a distinguishing feature necessary for the molding of complex shapes using RTM or related composite processing methods. Due to the superb thermal and oxidative stability of phthalonitrile polymers **6** cured to 400°C, the materials have potential for a variety of applications (ship, aerospace, marine, and electronic) including its use in the fabrication of advanced composites by conventional prepreg consolidation, RTM, RIM, injection molding, and filament winding and as a coating for electronic devices. Thus, the phthalonitrile-based polymers would be expected to exhibit improvements in specific physical properties when used at high temperatures or in a fire environment.

Table 1 – Viscosity data for monomers **1a-1c**

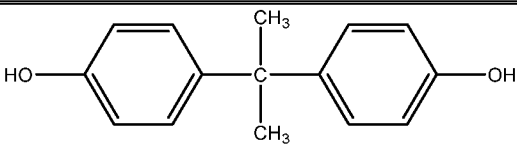
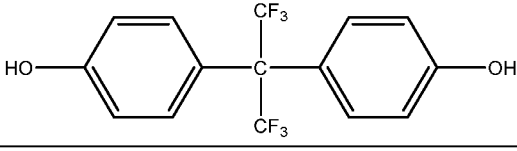
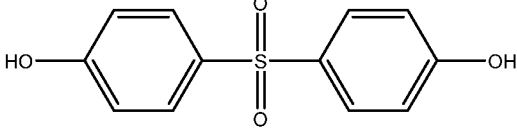
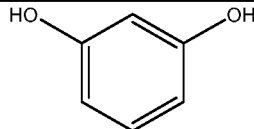
Temperature (°C)	Viscosity (cP)		
	1a	1b	1c
100	2000	2000	1400
125	600	600	350
150	300	120	180
175	90	75	100
200	70	45	50
225	50	35	30
250	40	30	20

This is the first reported synthesis of oligomeric compounds **4**, conversion to low melting oligomeric phthalonitriles **1**, and polymerization to thermosetting polymer **6** with a large processing window between the melting point and the exothermic curing temperature. The phthalonitrile monomers **1**, which display superb processability, can be readily cross-linked through the phthalonitrile groups yielding high temperature thermosetting polymers. The synthesis of a series of multiple aromatic ether-linked phthalonitriles **1**, which contain an aryl ether and aliphatic units in the backbone, has been achieved by a nucleophilic displacement reaction utilizing a dihaloaliphatic compound **3** and bisphenol A **2** followed by end-capping with 4-nitrophthalonitrile **5** (Fig. 1). Other dihaloaliphatic compound and bisphenols can be used in

the synthesis.

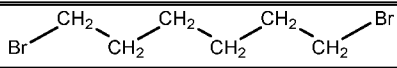
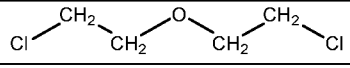
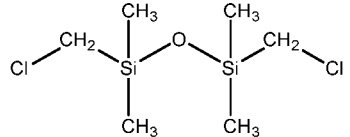
The method involves the formation of a phthalonitrile compound, including diphthalonitrile compounds, from a dihydroxyaromatic compound and a dihalo compound. The dihydroxyaromatic compound has the formula HO–Ar–OH, where Ar is an aromatic group. The Ar group can be any divalent radical with or without substituents containing one or more fused aromatic rings, one or more non-fused aromatic rings with or without intervening functional groups, or combinations thereof wherein the hydroxyl groups are on the same or different aromatic rings. Suitable dihydroxyaromatic compounds include those shown in Table 2, as well as those disclosed in U.S. Pat. No. 3,730,946, U.S. Pat. No. 3,763,210, U.S. Pat. No. 3,787,475, U.S. Pat. No. 3,869,499, U.S. Pat. No. 3,972,902, U.S. Pat. No. 4,209,458, U.S. Pat. No. 4,223,123, U.S. Pat. No. 4,226,801, U.S. Pat. No. 4,234,712, U.S. Pat. No. 4,238,601, U.S. Pat. No. 4,259,471, U.S. Pat. No. 4,304,896, U.S. Pat. No. 4,307,035, U.S. Pat. No. 4,315,093, U.S. Pat. No. 4,351,776, U.S. Pat. No. 4,408,035, U.S. Pat. No. 4,409,382, U.S. Pat. No. 4,410,676, U.S. Pat. No. 5,003,039, U.S. Pat. No. 5,003,078, U.S. Pat. No. 5,004,801, U.S. Pat. No. 5,132,396, U.S. Pat. No. 5,159,054, U.S. Pat. No. 5,202,414, U.S. Pat. No. 5,208,318, U.S. Pat. No. 5,237,045, U.S. Pat. No. 5,242,755, U.S. Pat. No. 5,247,060, U.S. Pat. No. 5,292,854, U.S. Pat. No. 5,304,625, U.S. Pat. No. 5,350,828, U.S. Pat. No. 5,352,760, U.S. Pat. No. 5,389,441, U.S. Pat. No. 5,464,926, U.S. Pat. No. 5,925,475, U.S. Pat. No. 5,965,268, U.S. Pat. No. 6,001,926, U.S. Pat. No. 6,297,298, U.S. Pat. No. 6,756,470, U.S. Pat. No. 6,891,014, U.S. Pat. No. 7,452,959, U.S. Pat. No. 7,511,113, U.S. Pat. No. 8,039,576, U.S. Pat. No. 8,222,403, U.S. Pat. No. 8,362,239, U.S. Pat. No. 8,530,607, U.S. Pat. No. 8,735,532, U.S. Pat. No. 8,859,712, U.S. Pat. No. 8,981,036, U.S. Pat. No. 8,921,510, and U.S. Pat. Appl. No. 14/926,429, all incorporated herein by reference. The Ar group may include at least two aromatic rings, either fused or non-fused as in bisphenols.

Table 2

Name	Structure
bisphenol A (2,2-bis(4-hydroxyphenyl)propane)	
bisphenol A6F (1,1,1,3,3,3-hexafluoro-2,2-bis(4-hydroxyphenyl)propane)	
bisphenol S (bis(4-hydroxyphenyl)sulfone)	
resorcinol	

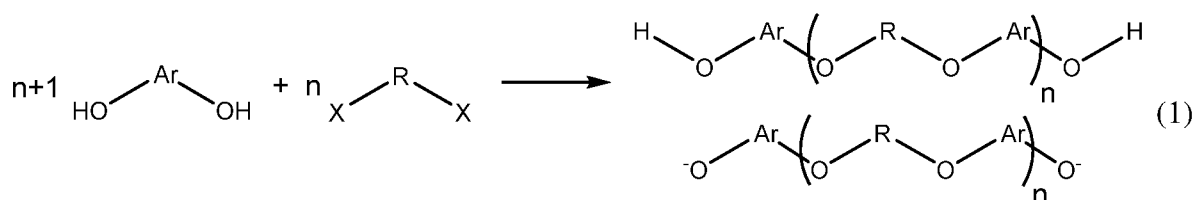
The dihalocompound has the formula $X-R-X$, where each X is a halogen, such as chlorine or bromine, and R is an aliphatic group. As used herein, an aliphatic group of the R group comprises a hydrocarbon chain and may optionally comprise an ether group ($-O-$) or a siloxane group ($-\text{SiR}'_2-\text{O}-$, wherein R' is an aliphatic group). The R group may be limited to the hydrocarbon, ether, and siloxane groups. The hydrocarbon chain may be a straight chain alkylene group. Suitable dihalocompounds include those shown in Table 3, as well as those disclosed in the patents listed above.

Table 3

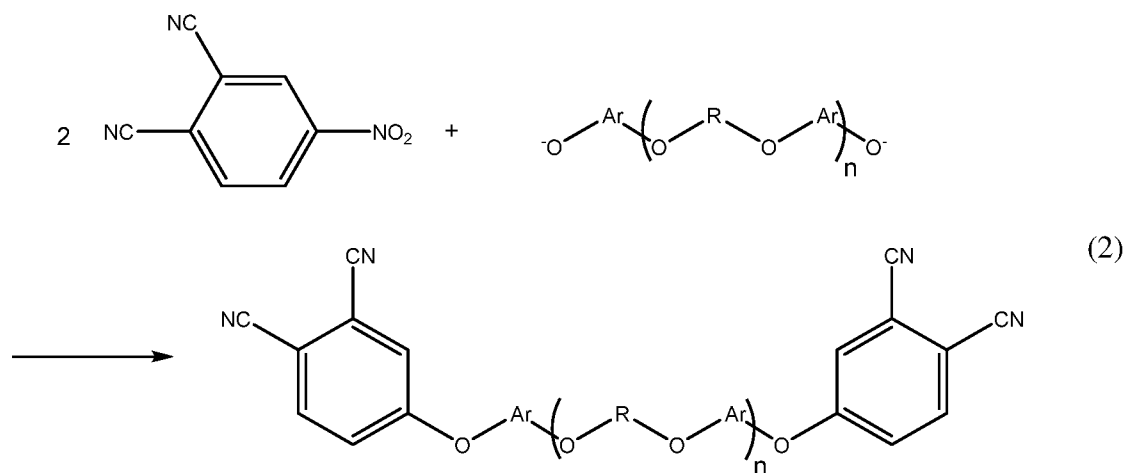
Name	Structure
1,6-dibromohexane	
bis(2-chloroethyl) ether	
bis(chloromethyl)tetramethyl disiloxane	

In the first step the dihydroxyaromatic compound is reacted with the dihalocompound to form an oligomer as shown in formula (1). The Ar and R groups may all be the same, all different, or any combination thereof in the oligomer. The dihydroxyaromatic compound is present in an excess amount to form an oligomer with terminal hydroxy groups. As used herein, the oligomer can include a mixture of molecules having different values of n , including unreacted

5 dihydroxyaromatic compound. The oligomer also includes either of both of the hydroxyl form and the ionic form as shown in formula (1). The average value of n depends on the amount of excess dihydroxyaromatic compound. For example, 2:1 molar ratio of dihydroxyaromatic compound to dihalocompound produces an average n of 1 and a 3:2 ratio produces an average n of 2. Methods of performing this reaction are known in the art, including as described in the examples herein and in the above listed patents.

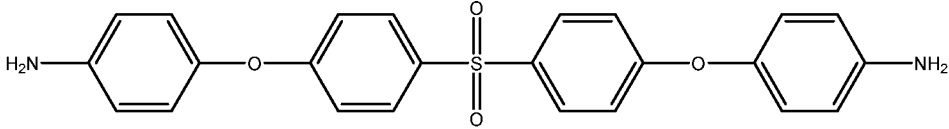
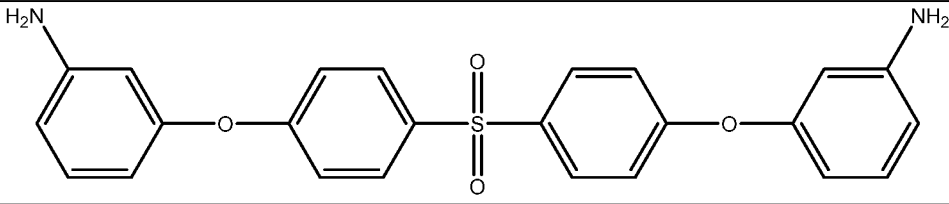
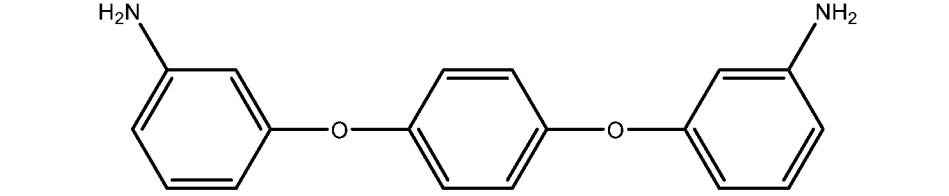
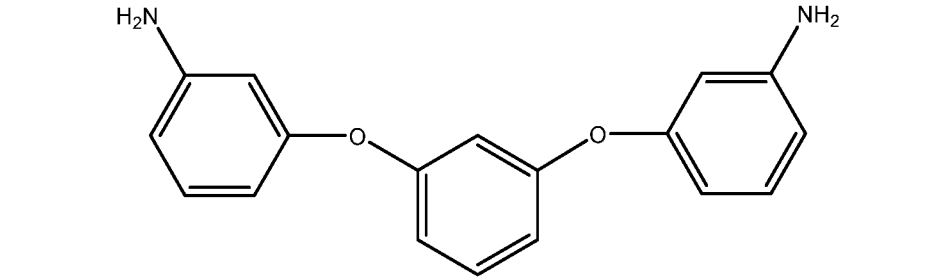


10 In the next step, the oligomer is reacted with 4-nitrophthalonitrile to form a phthalonitrile compound as shown in formula (2). Methods of performing this reaction are known in the art, including as described in the examples herein and in the above listed patents.



15 Optionally, the phthalonitrile compound may be cured with a curing additive to form a thermoset. Such curing agents are known in the art and include, but are not limited to, those disclosed in the patents listed above and those listed in Table 4.

Table 4

Name	Structure
bis[4-(4-aminophenoxy)phenyl]sulfone (<i>p</i> -BAPS)	
bis[4-(3-aminophenoxy)phenyl]sulfone (<i>m</i> -BAPS)	
1,4-bis(3-aminophenoxy)benzene (<i>p</i> -APB)	
1,3-bis(3-amino-phenoxy)benzene (<i>m</i> -APB)	

The following examples are given to illustrate specific applications. These specific examples are not intended to limit the scope of the disclosure in this application.

5

Example 1

Synthesis of 2:1 oligomeric hydroxyl compound based on bisphenol A and 1,6-dibromohexane isolated as the dipotassium salt – To a 2000 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added bisphenol A (100 g, 0.298 mol), 1,6-

10 dibromohexane (53.4 g, 0.219 mol), powdered anhydrous K₂CO₃ (150 g, 1.09 mol), and dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled and the dipotassium salt of the 2:1 oligomeric hydroxyl compound was left in solution to use in further reactions.

15

Example 2

Synthesis of 2:1 oligomeric phthalonitrile based on bisphenol A and 1,6-dibromohexane in one reaction pot

To a 2000 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added bisphenol A (100 g, 0.298 mol), 1,6-dibromohexane (53.4 g, 0.219 mol), powdered anhydrous K₂CO₃ (150 g, 1.09 mol), and dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled to 50°C. At this time, 4-nitrophthalonitrile (77.6 g, 0.449 mol) was added in one portion and the reaction mixture was heated at 80°C for 6-8 hr. The mixture was allowed to cool to ambient temperature and poured into 1000 mL of distilled water. The mixture was made acidic by the addition of 6 M aqueous HCl and the resin was extracted out of the water layer by toluene (200 mL). The toluene extracts were washed 3 times with 500 mL of distilled water and dried using magnesium sulfate. Removal of the toluene resulted in an amber oil, which was dried at 80°C under vacuum. The 2:1 oligomeric phthalonitrile was isolated as an amber glassy solid (165 g, 95%). ¹H-NMR [CDCl₃]: λ 7.70 (m, aromatic-HR), 7.31 (m, aromatic-HR), 7.11 (m, aromatic-HR), 7.00 (m, aromatic-HR), 6.80 (m, aromatic-HR), 3.92 (m, aliphatic-HR), 1.78 (m, aliphatic-HR), 1.73 (s, aliphatic-HR), 1.67 (s, aliphatic-HR), 1.61 (s, aliphatic-HR), 1.50 (m, aliphatic-HR).

Example 3

Curing of a 2:1 oligomeric phthalonitrile based on bisphenol A and 1,6-dibromohexane with an aromatic amine

Samples containing the 2:1 oligomeric phthalonitrile from Example 2 and 2-5 weight% of bis[4-(4-aminophenoxy)phenyl]sulfone, bis[4-(3-aminophenoxy)phenyl]sulfone, or 1,3-bis(3-aminophenoxy)benzene (*m*-APB) were stirred at 200°C for 2 minutes and cured under nitrogen by heating at 250°C for 12 hr (overnight) and at 300°C for 8 hr to afford thermoset polymers. The polymers exhibited excellent thermal stability up to 400°C before any weight loss was detected. Catastrophic decomposition of the polymers occurred above 375°C in air.

Example 4

Synthesis of 2:1 oligomeric phthalonitrile based on bisphenol AF and 1,6-dibromohexane in one reaction pot

To a 2000 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added bisphenol AF (149 g, 0.442 mol), 1,6-dibromohexane (53.4 g, 0.219 mol), powdered anhydrous K₂CO₃ (150 g, 1.09 mol), and

dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled to 50°C. At this time, 4-nitrophthalonitrile (80.1 g, 0.463 mol) was added in one portion and the reaction mixture was heated at 80°C for 6-8 hr. The mixture was allowed to cool to ambient temperature and poured into 1000 mL of distilled water. The mixture was made acidic by the addition of 6 M aqueous HCl and the resin was extracted out of the water layer by toluene (200 mL). The toluene extracts were washed 3 times with 500 mL of distilled water and dried using magnesium sulfate. Removal of the toluene resulted in an amber oil, which was dried at 80°C under vacuum. The 2:1 oligomeric phthalonitrile was isolated as an amber glassy solid (224 g, 97%). ¹H-NMR [CDCl₃]: λ 7.75 (m, aromatic-HR), 7.32 (m, aromatic-HR), 7.08 (m, aromatic-HR), 6.97 (m, aromatic-HR), 6.81 (m, aromatic-HR), 4.10 (m, aliphatic-HR), 1.80 (m, aliphatic-HR), 1.51 (m, aliphatic-HR).

Example 5

Curing of a 2:1 oligomeric phthalonitrile based on bisphenol AF and 1,6-dibromohexane with an aromatic amine – Samples containing the 2:1 oligomeric phthalonitrile from Example 4 and 2-5 weight% of bis[4-(4-aminophenoxy)phenyl]sulfone, bis[4-(3-aminophenoxy)phenyl]sulfone, or 1,3-bis(3-aminophenoxy)benzene (*m*-APB) were stirred at 200°C for 2 minutes and cured under nitrogen by heating at 250°C for 12 hr (overnight) and at 300°C for 8 hr to afford thermoset polymers. The polymers exhibited excellent thermal stability up to 400°C before any weight loss was detected. Catastrophic decomposition of the polymers occurred above 375°C in air.

Example 6

Synthesis of 2:1 oligomeric hydroxyl compound based on bisphenol A and bis(2-chloroethyl) ether isolated as the dipotassium salt – To a 2000 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added bisphenol A (100 g, 0.298 mol), bis(2-chloroethyl) ether (31.3 g, 0.219 mol), powdered anhydrous K₂CO₃ (150 g, 1.09 mol), and dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled and the dipotassium salt of the 2:1 oligomeric hydroxyl compound was left in solution to use in further reactions.

Example 7

Synthesis of 2:1 oligomeric phthalonitrile based on bisphenol A and bis(2-chloroethyl) ether in one reaction pot

To a 2000 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added bisphenol A (100 g, 0.298 mol), bis(2-chloroethyl) ether (31.3 g, 0.219 mol), powdered anhydrous K₂CO₃ (150 g, 1.09 mol), and dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled to 50°C. At this time, 4-nitrophthalonitrile (77.7 g, 0.449 mol) was added in one portion and the reaction mixture was heated at 80°C for 6-8 hr. The mixture was allowed to cool to ambient temperature and poured into 1000 mL of distilled water. The mixture was made acidic by the addition of 6 M aqueous HCl and the resin was extracted out of the water layer by toluene (200 mL). The toluene extracts were washed 3 times with 500 mL of distilled water and dried using magnesium sulfate. Removal of the toluene resulted in an amber oil, which was dried at 80°C under vacuum. The 2:1 oligomeric phthalonitrile was isolated as an amber glassy solid (164 g, 94%). ¹H-NMR [CDCl₃]: λ 7.68 (m, aromatic-HR), 7.27 (m, aromatic-HR), 7.11 (m, aromatic-HR), 6.97 (m, aromatic-HR), 6.81 (m, aromatic-HR), 4.10 (m, aliphatic-HR), 3.88 (m, aliphatic-HR), 1.73 (s, aliphatic-HR), 1.66 (s, aliphatic-HR), 1.59 (s, aliphatic-HR).

Example 8

Curing of a 2:1 oligomeric phthalonitrile based on bisphenol A and bis(2-chloroethyl) ether with an aromatic amine

Samples containing the 2:1 oligomeric phthalonitrile from Example 7 and 2-5 weight% of bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS), bis[4-(3-aminophenoxy)phenyl]sulfone (*m*-BAPS), or 1,3-bis(3-aminophenoxy)benzene (*m*-APB) were stirred at 200°C for 2 minutes and cured under nitrogen by heating at 250°C for 12 hr (overnight), 300°C for 8 hr to afford thermoset polymers. The polymers exhibited excellent thermal stability up to 400°C before any weight loss was detected. Catastrophic decomposition of the polymers occurred above 375°C in air.

Example 9

Synthesis of 2:1 oligomeric hydroxyl compound based on bisphenol A and bis(chloromethyl)tetramethyl disiloxane isolated as the dipotassium salt

To a 2000 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added bisphenol A (100 g, 0.298 mol), bis(chloromethyl)tetramethyl disiloxane (50.1 g, 0.217 mol), powdered anhydrous

K₂CO₃ (150 g, 1.09 mol), and dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled and the potassium salt of the 2:1 oligomeric hydroxyl compound was left in solution to use in further reactions.

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Example 10

Synthesis of 2:1 oligomeric phthalonitrile based on bisphenol A and

bis(chloromethyl)tetramethyl disiloxane in one reaction pot – To a 2000 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added bisphenol A (100 g, 0.298 mol),
10 bis(chloromethyl)tetramethyl disiloxane (50.1 g, 0.217 mol), powdered anhydrous K₂CO₃ (150 g, 1.09 mol), and dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled to 50°C. At this time, 4-nitrophthalonitrile (77.7 g, 0.449 mol) was added in one portion and the reaction mixture was heated at 80°C for 6-8 hr. The mixture was
15 allowed to cool to ambient temperature and poured into 1000 mL of distilled water. The mixture was made acidic by the addition of 6 M aqueous HCl and the resin was extracted out of the water layer by toluene (200 mL). The toluene extracts were washed 3 times with 500 mL of distilled water and dried using magnesium sulfate. Removal of the toluene resulted in an amber oil, which was dried at 80°C under vacuum. The 2:1 oligomeric phthalonitrile was isolated as an
20 amber glassy solid (179 g, 94%). ¹H-NMR [CDCl₃]: λ 7.72 (m, aromatic-HR), 7.67 (m, aromatic-HR), 7.34 (m, aromatic-HR), 7.08 (m, aromatic-HR), 6.97 (m, aromatic-HR), 6.86 (m, aromatic-HR), 3.76 (m, aliphatic-HR), 3.50 (m, aliphatic-HR), 1.71 (s, aliphatic-HR), 1.64 (s, aliphatic-HR), 1.61 (s, aliphatic-HR), 0.20 (s, Si-CH₃), 0.05 (s, Si-CH₃).

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Example 11

Curing of a 2:1 oligomeric phthalonitrile based on bisphenol A and

bis(chloromethyl)tetramethyl disiloxane with an aromatic amine – Samples containing the 2:1 oligomeric phthalonitrile from Example 10 and 2-5 weight% of bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS), bis[4-(3-aminophenoxy)phenyl]sulfone (*m*-BAPS), or
30 1,3-bis(3-aminophenoxy)benzene (*m*-APB) were stirred at 200°C for 2 minutes and cured under nitrogen by heating at 250°C for 12 hr (overnight) and at 300°C for 8 hr to afford thermoset polymers. The polymers exhibited excellent thermal stability up to 400°C before any weight loss was detected. Catastrophic decomposition of the polymers occurred above 375°C in air.

Example 12

Synthesis of 2:1 oligomeric phthalonitrile based on 1,3-dihydroxybenzene

(resorcinol) and bis(chloromethyl)tetramethyl disiloxane in one reaction pot – To a 2000

5 mL, three-necked flask fitted with a thermometer and a nitrogen inlet were added 1,3-dihydroxybenzene (48.2 g, 0.438 mol), bis(chloromethyl)tetramethyl disiloxane (50.1 g, 0.217 mol), powdered anhydrous K₂CO₃ (150 g, 1.09 mol), and dimethylsulfoxide (DMSO) (1000 mL). The resulting mixture was degassed with nitrogen at ambient temperature and heated at 90°C under a nitrogen atmosphere for 8-16 hr. The mixture was cooled to 50°C. At this time, 4-nitrophthalonitrile (76.1 g, 0.440 mol) was added in one portion and the reaction mixture was heated at 80°C for 6-8 hr. The mixture was allowed to cool to ambient temperature and poured into 1000 mL of distilled water. The mixture was made acidic by the addition of 6 M aqueous HCl and the resin was extracted out of the water layer by toluene (200 mL). The toluene extracts were washed 3 times with 500 mL of distilled water and the toluene extracts were dried using magnesium sulfate. Removal of the toluene resulted in an amber oil, which was dried at 80°C under vacuum. The 2:1 oligomeric phthalonitrile was isolated as an amber glassy solid (131 g, 95%). ¹H-NMR [CDCl₃]: λ 7.70 (m, aromatic-HR), 7.69 (m, aromatic-HR), 7.35 (m, aromatic-HR), 7.10 (m, aromatic-HR), 6.98 (m, aromatic-HR), 6.88 (m, aromatic-HR), 3.73 (m, aliphatic-HR), 3.46 (m, aliphatic-HR), 0.22 (s, Si-CH₃), 0.06 (s, Si-CH₃).

Example 13

Curing of a 2:1 oligomeric phthalonitrile based on 1,3-dihydroxybenzene

(resorcinol) and bis(chloromethyl)tetramethyl disiloxane with an aromatic amine – Samples containing the 2:1 oligomeric phthalonitrile from Example 12 and 2-5 weight% of bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS), bis[4-(3-aminophenoxy)phenyl]sulfone (*m*-BAPS), or 1,3-bis(3-aminophenoxy)benzene (*m*-APB) were stirred at 200°C for 2 minutes and cured under nitrogen by heating at 250°C for 12 hr (overnight) and at 300°C for 8 hr to afford thermoset polymers. The polymers exhibited excellent thermal stability up to 400°C before any weight loss was detected. Catastrophic decomposition of the polymers occurred above 375°C in air.

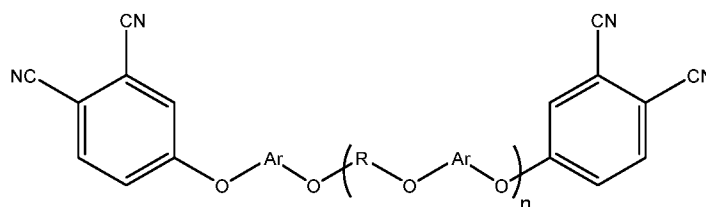
Obviously, many modifications and variations are possible in light of the above teachings. It is therefore to be understood that the claimed subject matter may be practiced otherwise than as specifically described. Any reference to claim elements in the singular, e.g.,

using the articles “a”, “an”, “the”, or “said” is not construed as limiting the element to the singular.

CLAIMS

What is claimed is:

1. A phthalonitrile compound having the formula:



- 5 wherein n is a positive integer;
 wherein each R comprises a hydrocarbon chain optionally comprising $-O-$ or $-SiR'_2-O-$;
 wherein each R' is an aliphatic group; and
 wherein each Ar is an aromatic group with the proviso that Ar comprises at least
 10 two aromatic rings when n is 1 and R is an alkylene group.

2. The phthalonitrile compound of claim 1, wherein each Ar is $-C_6H_4-C(CH_3)_2-C_6H_4-$,
 $-C_6H_4-C(CF_3)_2-C_6H_4-$, or $-C_6H_4-SO_2-C_6H_4-$.

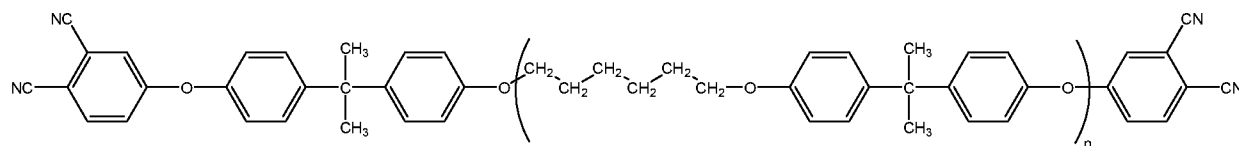
3. The phthalonitrile compound of claim 1, wherein each Ar is *m*-phenylene.

4. The phthalonitrile compound of claim 1, wherein each R is an alkylene group or
 15 hexylene.

5. The phthalonitrile compound of claim 1, wherein each R is $-C_2H_4-O-C_2H_4-$.

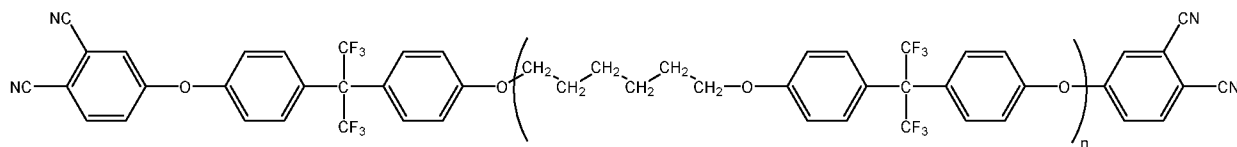
6. The phthalonitrile compound of claim 1, wherein each R is
 $-CH_3-Si(CH_3)_2-O-Si(CH_3)_2-CH_3-$.

7. The phthalonitrile compound of claim 1, wherein the phthalonitrile compound is:

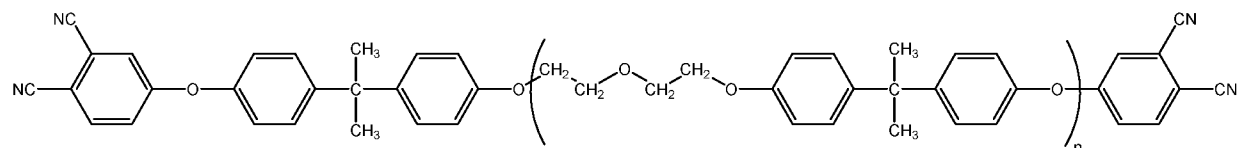


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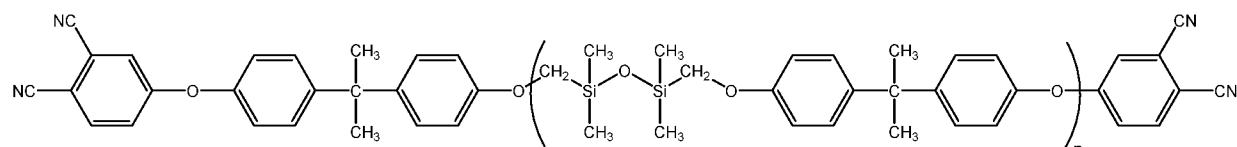
8. The phthalonitrile compound of claim 1, wherein the phthalonitrile compound is:



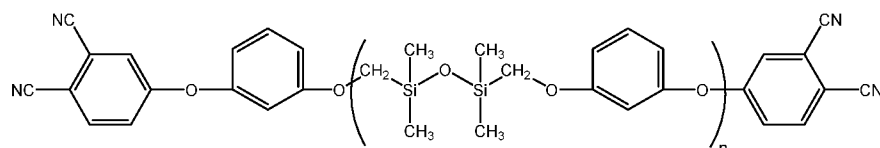
9. The phthalonitrile compound of claim 1, wherein the phthalonitrile compound is:



10. The phthalonitrile compound of claim 1, wherein the phthalonitrile compound is:



11. The phthalonitrile compound of claim 1, wherein the phthalonitrile compound is:



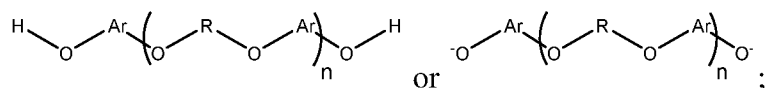
12. A method comprising:

10 curing the phthalonitrile compound of claim 1 with a curing additive to form a thermoset.

13. The method of claim 12, wherein the curing additive is bis(3-[4-aminophenoxy]phenyl)sulfone, bis[4-(4-aminophenoxy)phenyl]sulfone, 1,4-bis(3-aminophenoxy)benzene, or 1,3-bis(3-aminophenoxy)benzene.

14. A method comprising:

reacting an excess of a dihydroxyaromatic compound having the formula HO-Ar-OH
with a dihalocompound having the formula X-R-X to form an oligomer having
the formula



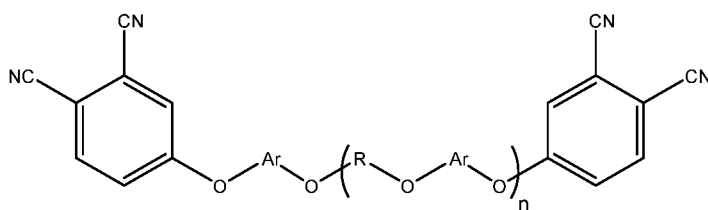
wherein each X is a halide;

wherein each R comprises a hydrocarbon chain optionally comprising -O- or -
SiR'₂-O-;

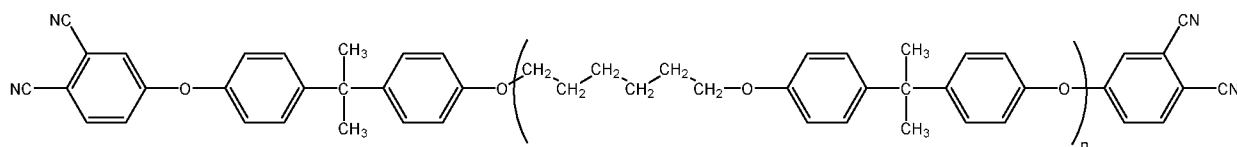
wherein each R' is an aliphatic group; and

wherein each Ar is an aromatic group; and

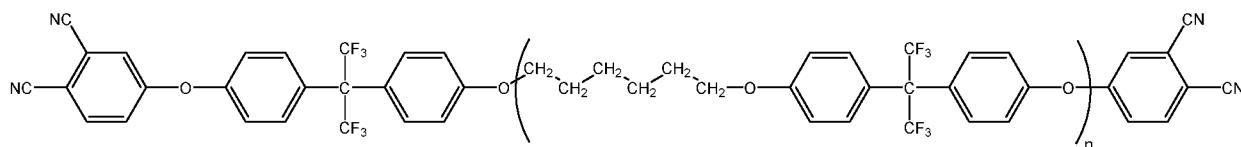
reacting the oligomer with 4-nitrophthalonitrile to form a phthalonitrile compound having
the formula:



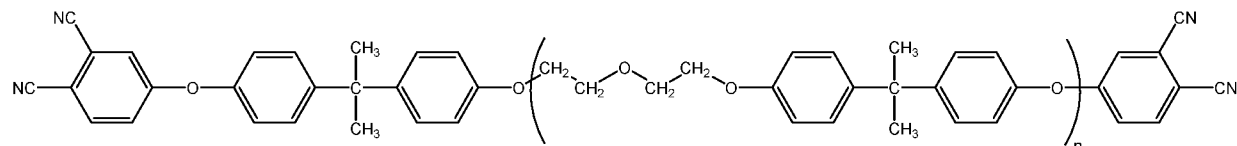
15. The method of claim 14, wherein the phthalonitrile compound is:



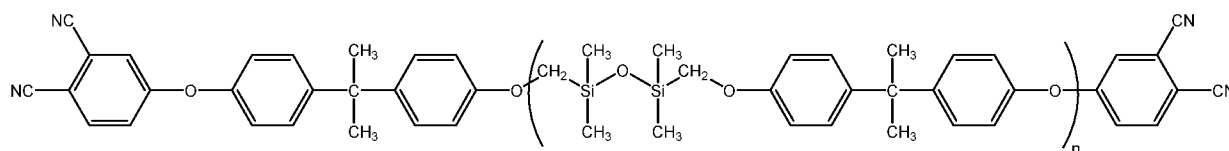
16. The method of claim 14, wherein the phthalonitrile compound is:



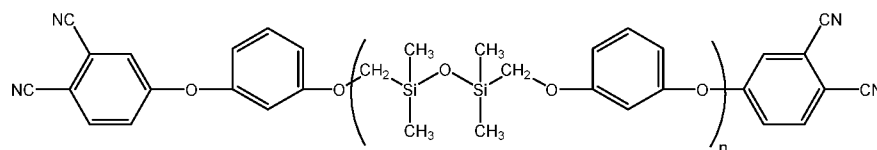
17. The method of claim 14, wherein the phthalonitrile compound is:



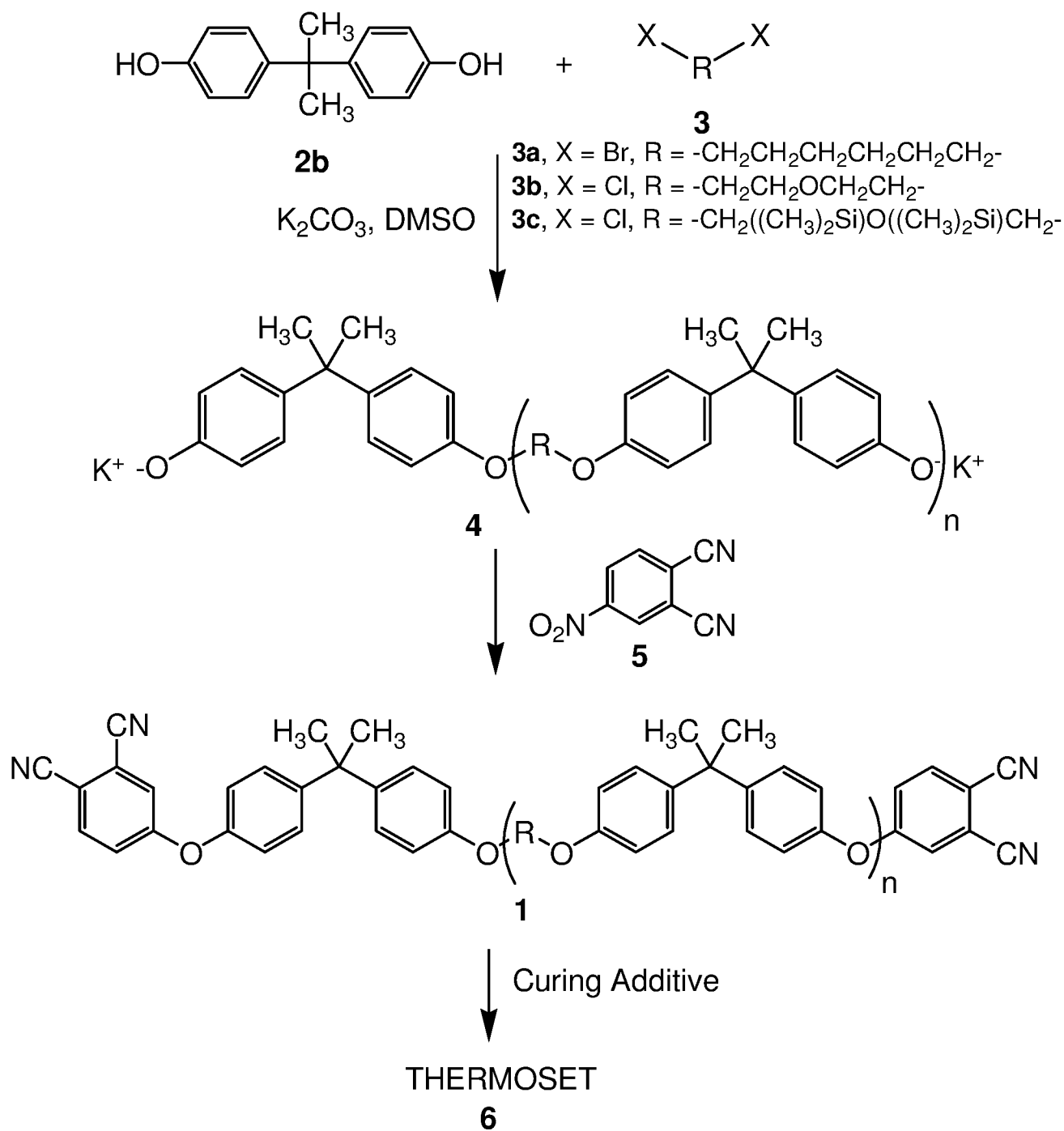
18. The method of claim 14, wherein the phthalonitrile compound is:



19. The method of claim 14, wherein the phthalonitrile compound is:



- 5 20. The method of claim 14, further comprising:
curing the phthalonitrile compound with a curing additive to form a thermoset.

*Fig. 1*

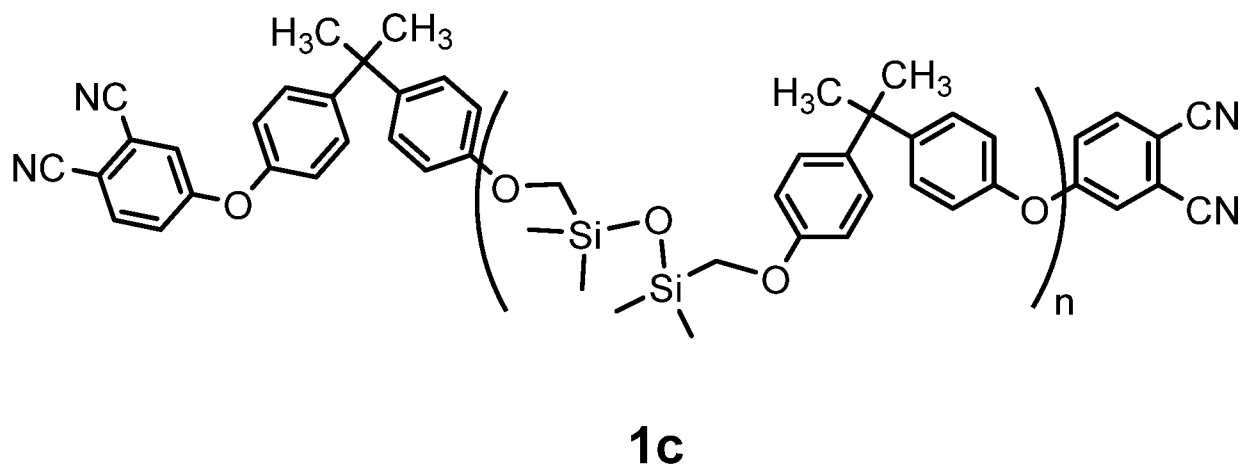
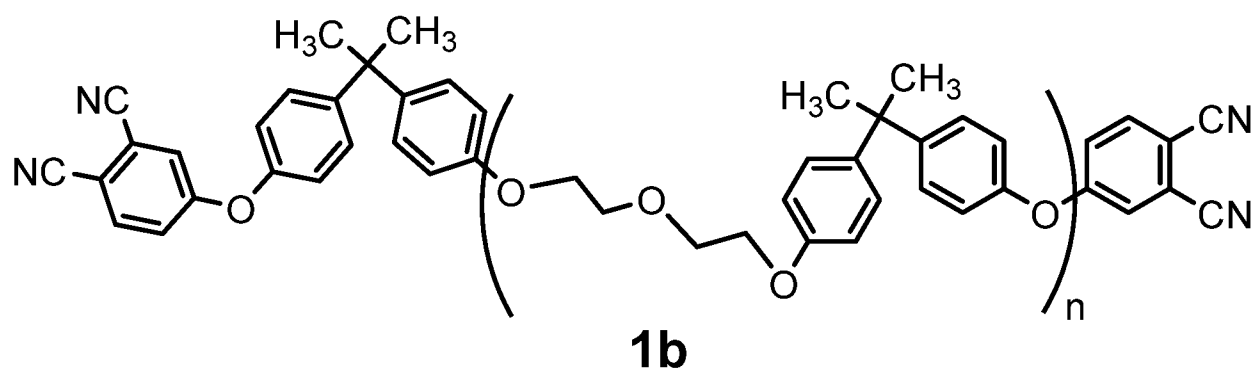
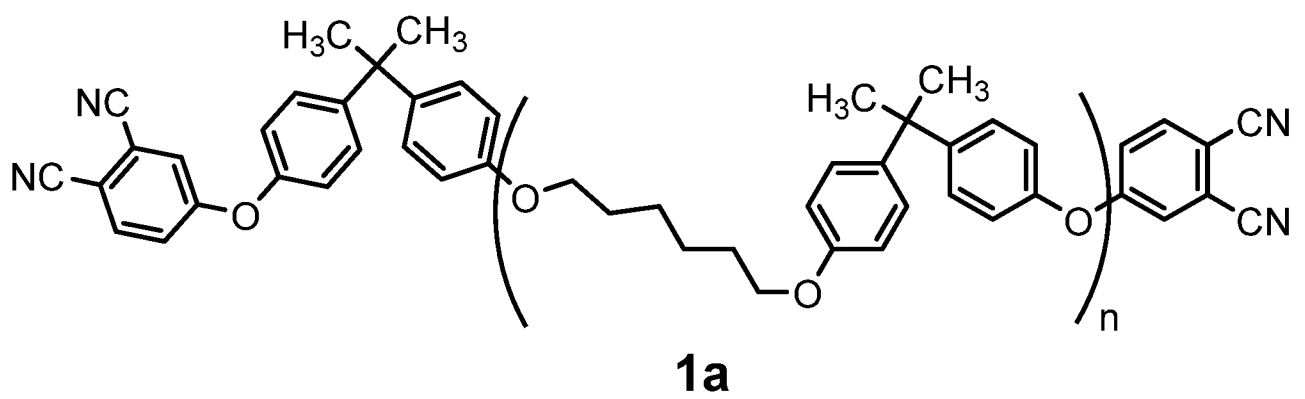
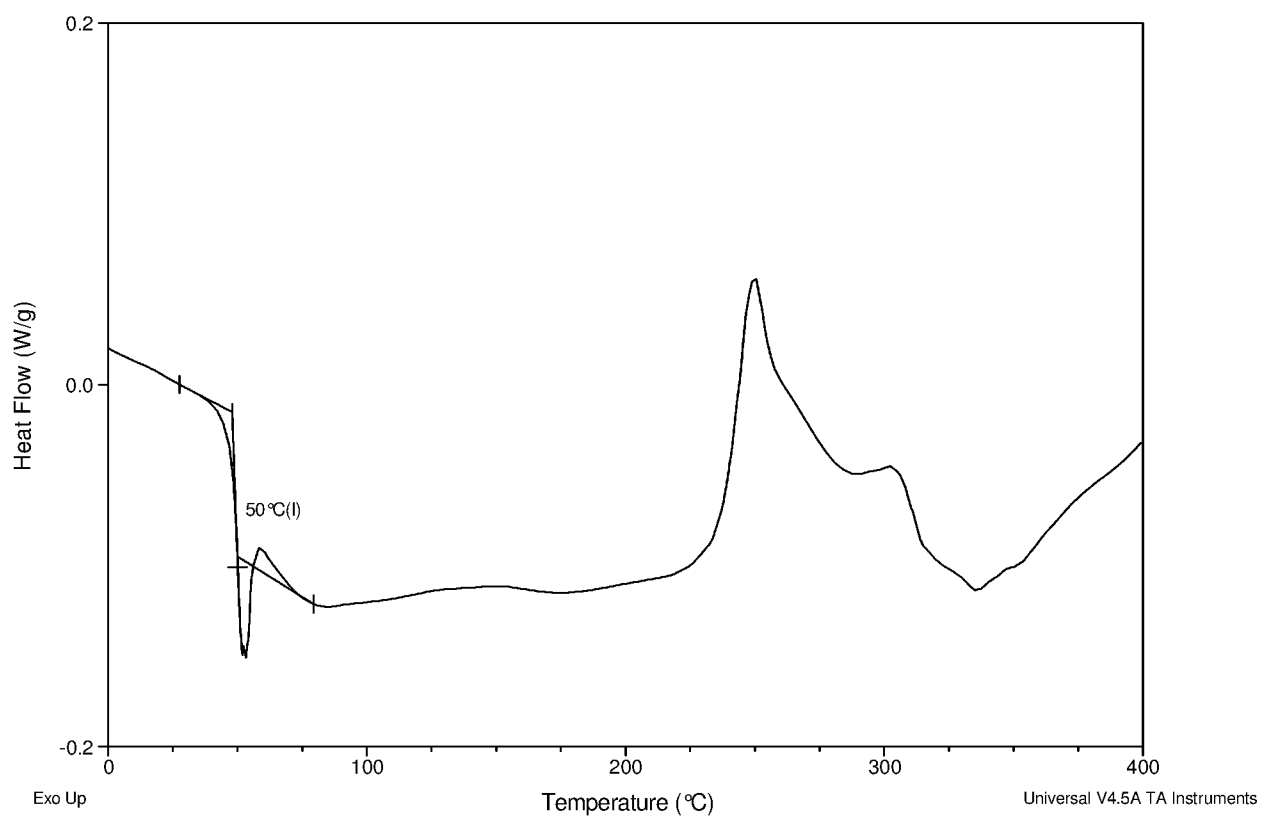


Fig. 2

***Fig. 3***

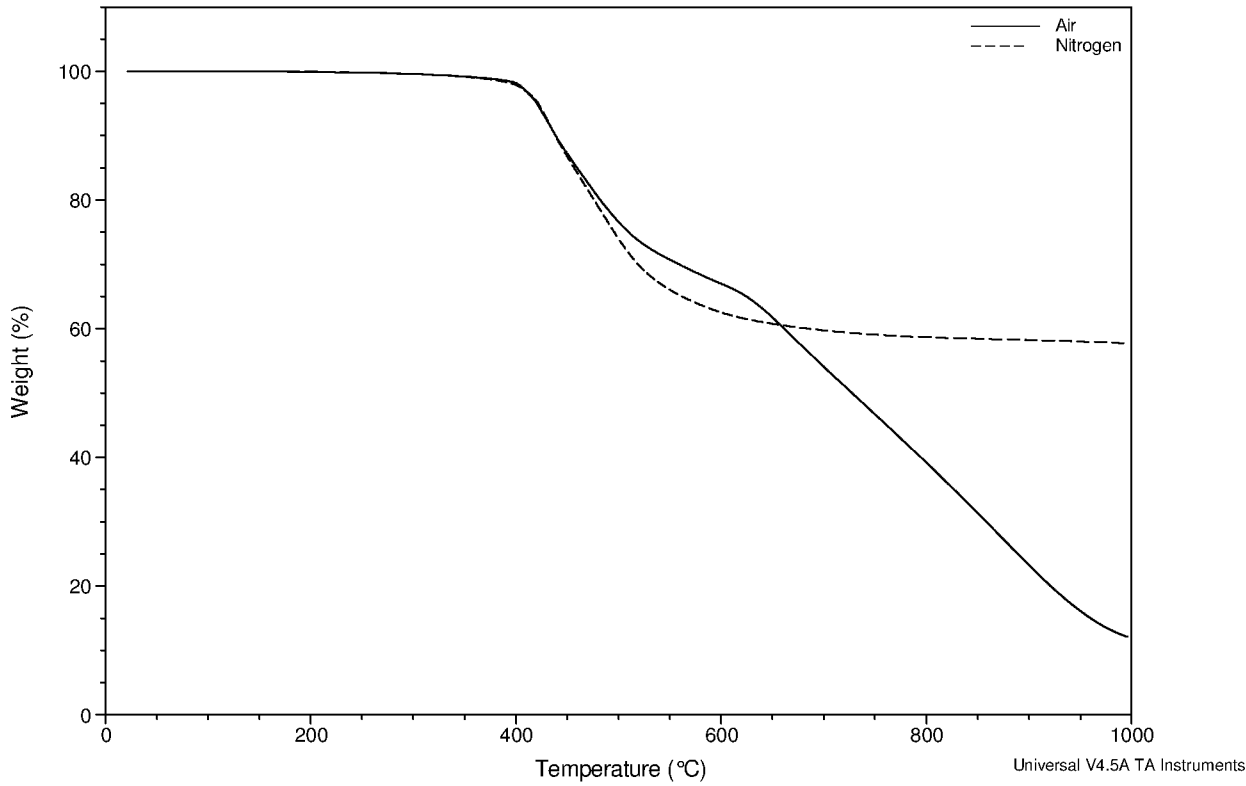


Fig. 4

A. CLASSIFICATION OF SUBJECT MATTER**C07C 255/51(2006.01)i, C07C 255/54(2006.01)i, C08G 69/38(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 255/51; C08G 64/12; C07C 41/00; C10M ; C08G 64/14; C08G 64/42; C07C 255/54; C08G 69/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: phthalonitrile, curing additive, polymer, phthalonitrile monomer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 06-298923 A (MITSUI TOATSU CHEM INC) 25 October 1994 See abstract; claims 1-2; paragraphs [0007]-[0060], [0069]-[0089].	1-20
A	JP 06-128372 A (MITSUI TOATSU CHEM INC) 10 May 1994 See abstract; claims 1-3; paragraphs [0008]-[0027], [0051]-[0074].	1-20
A	JP 06-263864 A (MITSUI TOATSU CHEM INC) 20 September 1994 See abstract; claim 1; paragraphs [0029], [0052]-[0068].	1-20
A	US 05104559 A (PAWLOSKI, CHESTER E. et al.) 14 April 1992 See abstract; page 2, line 31 - page 5, line 9; claims 1-14.	1-20
A	JP 06-256499A (MITSUI TOATSU CHEM INC) 13 September 1994 See abstract; claims 1-2; paragraphs [0009]-[0026], [0056]-[0065].	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

01 April 2016 (01.04.2016)

Date of mailing of the international search report

01 April 2016 (01.04.2016)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

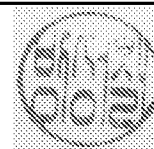
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/065675

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