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PATENT APPLICATION

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3	PHTHALONITRILE PREPOLYMERIZATION COMPOSITION
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5	Background of the Invention
6	1. Field of the Invention
7	The invention relates to polymerizable phthalonitrile compositions, and in particular to
8	storable mixtures of phthalonitrile monomers and curing agents.
9	2. Description of the Related Art
10	Phthalonitrile polymers of various types are described generally in U.S. Patent No.
11	3,730,946, U.S. Patent No. 3,763,210, U.S. Patent No. 3,787,475. U.S. Patent No. 3,869,499, U.S.
12	Patent No. 3,972,902, U.S. Patent No. 4,209,458, U.S. Patent No. 4,223,123, U.S. Patent No.
13	4,226,801, U.S. Patent No. 4,234,712, U.S. Patent No. 4,238,601, U.S. Patent No. 4,259,471, U.S.
14	Patent No. 4,304,896, U.S. Patent No. 4,307,035, U.S. Patent No. 4,315,093, U.S. Patent No.
15	4,351,776, U.S. Patent No. 4,408,035, U.S. Patent No. 4,409,382, U.S. Patent No. 4,410,676, U.S.
16	Patent No. 5,003,039, U.S. Patent No. 5,003,078, U.S. Patent No. 5,004,801, U.S. Patent No.
17	5,132,396, U.S. Patent No. 5,159,054, U.S. Patent No. 5,202,414, U.S. Patent No. 5,208,318, U.S.
18	Patent No. 5,237,045, U.S. Patent No. 5,242,755, U.S. Patent No. 5,247,060, U.S. Patent No.
19	5,292,854, U.S. Patent No. 5,304,625, U.S. Patent No. 5,350,828. U.S. Patent No. 5,352,760, U.S.
20	Patent No. 5,389,441, U.S. Pat. No. 5,464,926, U.S. Patent Application by Satva B. Sastri and Teddy

PATENT APPLICATION

M. Keller for "FIBER-REINFORCED PHTHALONITRILE COMPOSITE CURED WITH LOW REACTIVITY AROMATIC AMINE CURING AGENT" filed October 2, 1997 and U.S. Patent
 Application by Satya B. Sastri and Teddy M. Keller for "PHTHALONITRILE THERMOSET
 POLYMERS AND COMPOSITES CURED WITH HALOGEN-CONTAINING AROMATIC
 AMINE CURING AGENTS" filed October 2, 1997. All of these patents and applications are
 incorporated herein by reference.

7 The above references teach an in situ method of polymerization wherein a phthalonitrile monomer is heated to a temperature above the melting point of the monomer and a curing agent is 8 added to the melt stage to promote polymerization of the phthalonitrile monomer. A method wherein 9 the curing agent is added immediately before the heating step has also been described. These 10 methods of polymerization can be inconvenient in some circumstances, particularly in the fabrication 11 of composites by methods such as resin transfer molding (RTM), filament winding, injection 12 molding, or prepreg formulation, where it may be difficult or cumbersome to mix the monomer and 13 the curing agent on site or to add the curing agent to the melt after the heating step is begun. 14 Alternatively, many of the above references teach that a frangible B-stage polymer can be created 15 by heating the phthalonitrile monomer with a curing agent to initiate the polymerization process and 16 then quenching the reaction before the polymerization goes to completion. The B-stage polymer 17 created by this process can be stored indefinitely at room temperature. However, creation of a B-18 stage prepolymer involves the additional time-consuming and cost-consuming step of partial 19 polymerization of the monomer. 20

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1	In conventional resin systems such as epoxies, polyimides, vinyl esters, cyanate esters, etc.,
2	a mixture of a monomer and a curing agent must be used fairly soon after the mixture is created
3	because the monomer begins to immediately polymerize in the presence of the curing agent. Even
4	under freezer conditions, the mixture has a short shelf life. As the material polymerizes, it becomes
5	highly viscous and unprocessable. Thus, long term storage of a mixture of the monomer and a curing
6	agent in these conventional resin systems is not possible.
7	Summary of the Invention
8	It has now been discovered that phthalonitrile monomers can be combined with curing agents
9	below the melting temperatures of the monomer and curing agent without polymerization taking
10	place, and that the mixture can be maintained in an unreacted state for an indefinite period of time.
11	Accordingly, the present invention is directed to a polymerizable composition suitable for
12	storage prior to polymerization, made by a process comprising the steps of mixing a phthalonitrile
13	monomer and a curing agent under non-reactive conditions below the melting temperatures of the
14	phthalonitrile monomer and the curing agent and in the absence of a solvent to create a
15	homogeneous, unreacted mixture. The invention further relates to an article comprising a dry,
16	homogeneous, unreacted mixture of a phthalonitrile monomer and a curing agent in a storage
17	container. The invention further relates to a stored polymerizable composition made by a process
18	comprising the steps of mixing a phthalonitrile monomer and a curing agent under non-reactive
19	conditions in the absence of a solvent to create a homogeneous, unreacted mixture and storing the
20	unreacted mixture under non-reactive conditions. The invention further relates to a method of

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making a phthalonitrile polymer comprising the steps of mixing a phthalonitrile monomer and a curing agent at a first location under non-reactive conditions to create a homogeneous, unreacted mixture, transporting the mixture to a second location remote from the first location, and polymerizing the phthalonitrile monomer by heating the mixture at the second location to a temperature above the melting point of the mixture.

6 By creating a prepolymer mixture for long-term storage according to the present invention,

7 the extra step of creating a B-stage prepolymer as described in the above-cited references is avoided.

8

Detailed Description of the Preferred Embodiment

9 The present invention relates to a polymerizable composition suitable for storage prior to 10 polymerization, made by a process comprising the step of mixing a phthalonitrile monomer and a 11 curing agent under non-reactive conditions to create a homogeneous, unreacted mixture. The 12 phthalonitrile monomer may be any phthalonitrile monomer described in the above referenced 13 patents. Preferably, the phthalonitrile monomer is a compound of the formula:

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wherein A is any divalent organic radical. More preferably, A is selected from the group consisting
of substituted or unsubstituted phenyl radicals, polyphenyl radicals, polyphenoxy radicals, fused
aromatic poly-ring radicals and radicals of the general form -Ar-Z-Ar- where Ar is a substituted or
unsubstituted aromatic group and Z is

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any alkylene of up to six carbon atoms, any halogenated alkylene of up to six carbon atoms, an
imide-containing group or a connecting bond. By the word "substituted", it is meant that any known
substituent could be attached to the aromatic moiety. Substituents include but are not limited to
halogens, chalcogens, and organic radicals such as phenyl, alcohol, carboxyl, carbonyl, or aliphatic
groups of less than 10 carbon atoms. Phthalonitrile monomers of the above description are dry
solids, typically powders, below their melting temperature.

8 The curing agent may be any curing agent useful in promoting the polymerization of the 9 phthalonitrile monomer under reactive conditions, such as temperatures above the melting point of 10 the monomer. The curing agent should be a dry solid, for example, a powder, and should be stable 11 and nonvolatile under storage conditions, during the heat up to the polymerization temperature and 12 during polymerization of the monomer. Preferably, the curing agent is selected from the group of 13 curing agents consisting of aromatic amines, phenols, inorganic acids, strong organic acids, metals, 14 metallic salts and combinations thereof. Most preferably, the curing agent is an aromatic amine.

According to the invention, the phthalonitrile monomer and the curing agent are mixed and stored under non-reactive conditions, that is, under conditions wherein the phthalonitrile monomer and the curing agent do not react and the phthalonitrile monomer does not polymerize. Generally, this will be at a temperature below the melting temperatures of the phthalonitrile monomer and the curing agent. Preferably, the monomer and the curing agent are mixed and stored at room

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1	temperature or at the ambient temperature depending on the location. For an additional precaution
2	against reactivity, the monomer and the curing agent may be mixed and stored in an inert
3	atmosphere. The monomer and the curing agent may be mixed by any method known in the art for
4	creating a dry, homogeneous mixture in the absence of a solvent.
5	The phthalonitrile monomer and the curing agent are mixed thoroughly to create a
6	homogeneous, unreacted mixture. By the term "homogeneous" as used herein, it is meant that both
7	the phthalonitrile monomer and the curing agent are distributed evenly throughout the mixture. The
8	mixture may thus be made in bulk quantities from which smaller portions can be subdivided. The
9	mixture may be stored in any suitable storage container.
10	With the present invention, it is not necessary to polymerize the mixture at the same location
11	that the mixing is carried out. The homogeneous, unreacted mixture may be created in one location
12	and then may be put into a storage container and transported to a second location for use. At the
13	second location, the phthalonitrile monomer is polymerized by heating the homogeneous, unreacted
14	mixture to a temperature above the melting point of the mixture. If, at the second location, it is
15	desirable to change the ratio of phthalonitrile monomer to curing agent prior to polymerization, for
16	example to speed up or slow down the polymerization for a particular practical application, this can
17	be done by adding and thoroughly mixing an additional amount of the monomer or curing agent to
18	achieve the desired monomer-curing agent ratio.
19	Having described the invention, the following examples are given to illustrate specific

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applications of the invention, including the best mode now known to perform the invention. These

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1	specific examples are not intended to limit the scope of the invention described in this application.
2	Examples
3	
4	Example 1: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy)
5	biphenyl monomer and an amine catalyst, 1,3-bis(3-aminophenoxy)benzene (m-APB) and cure to
6	a thermoset.
7	4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g. 3.4 mmoles) and m-APB (0.026 g,
8	0.087 mmole) were thoroughly mixed at room temperature to obtain a homogeneous mixture. Upon
9	heating of the mixture above the melt temperature, the mixture will cure to a thermoset. A sample
10	of the mixture was placed on a hot plate at 255°C to melt and maintain the mixture in the melt phase
11	with periodic stirring to monitor the increase in viscosity and the time to gelation. The melt was
12	very viscous after 3 hours at 255°C and a vitrified product resulted after about 12 hours at 255°C.
13	
14	Example 2: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy)
15	biphenyl monomer and 1,3-bis(3-aminophenoxy)benzene (m-APB) and cure to a thermoset.
16	4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and m-APB (0.051 g,
17	0.17 mmole) were thoroughly mixed at room temperature to obtain a homogeneous mixture. Upon
18	heating of the mixture above the melt temperature, the mixture will cure to a thermoset. A sample
19	of the mixture was placed on a hot plate at 255°C to melt and maintain the mixture in the melt phase
20	with periodic stirring to monitor the increase in viscosity and the time to gelation. A vitrified product

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1 was obtained after 1 hour at 255°C.

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Example 3: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy) 3 biphenyl monomer and bis[4-(4-aminophenoxy)phenyl]sulfone (p-BAPS) and cure to a thermoset. 4 4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and p-BAPS (0.038 5 g, 0.087 mmole) were thoroughly mixed at room temperature to obtain a homogeneous mixture. 6 Upon heating of the mixture above the melt temperature, the mixture will cure to a thermoset. A 7 sample of the mixture was placed on a hot plate at 255°C to melt and maintain the mixture in the 8 melt phase with periodic stirring to monitor the increase in viscosity and the time to gelation. The 9 melt was very viscous after 6 hours at 255°C and a vitrified product resulted after about 18 hours 10 11 at 255°C. 12 **Example 4:** Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy) 13

biphenyl monomer and bis[4-(4-aminophenoxy)phenyl]sulfone (p-BAPS) and cure to a thermoset.
4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and p-BAPS (0.076
g, 0.17 mmole) were thoroughly mixed at room temperature to obtain a homogeneous mixture. Upon
heating of the mixture above the melt temperature, the mixture will cure to a thermoset. A sample
of the mixture was placed on a hot plate at 255°C to melt and maintain the mixture in the melt phase
with periodic stirring to monitor the increase in viscosity and the time to gelation. The melt was
very viscous after 30 minutes at 255°C and a vitrified product resulted after 1.5 hours at 255°C.

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Example 5: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy)
biphenyl monomer and a phenolic catalyst, 4,4'-biphenol and cure to a thermoset.
4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and 4,4'-biphenol
(0.186 g, 1.0 mmole) were thoroughly mixed at room temperature to obtain a homogeneous mixture.
Upon heating of the mixture above the melt temperature, the mixture will cure to a thermoset. A
sample of the mixture was placed on a hot plate at 255°C to melt and maintain the mixture in the
melt phase with periodic stirring to monitor the increase in viscosity and the time to gelation. The
melt was very viscous after 2 hours at 255°C and a vitrified product resulted after about 4 hours at
255°C.
Example 6: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy)
biphenyl monomer and 4,4'-biphenol and cure to a thermoset.
4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and 4,4'-biphenol
(0.744 g, 4.0 mmole) were thoroughly mixed at room temperature to obtain a homogeneous mixture.
Upon heating of the mixture above the melt temperature, the mixture will cure to a thermoset. A
sample of the mixture was placed on a hot plate at 255°C to melt and maintain the mixture in the
melt phase with periodic stirring to monitor the increase in viscosity and the time to gelation. A
vitrified product was obtained after 45 minutes at 255°C.
Example 7: Formation of prepolymerization composition from 4.4'-bis(3.4-dicyanophenoxy)

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1	biphenyl monomer and an organic acid catalyst, p-toluenesulfonic acid and cure to a thermoset.
2	4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and p-toluenesulfonic
3	acid monohydrate (0.03 g, 0.15 mmole) were thoroughly mixed at room temperature to obtain a
4	homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture will
5	cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
6	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
7	the time to gelation. The melt was very viscous after 3 hours at 255°C and a vitrified product
8	resulted after 8 hours at 255°C.
9	
10	Example 8: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy)
11	biphenyl monomer and p-toluenesulfonic acid and cure to a thermoset.
12	
13	4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and p-toluenesulfonic
14	acid monohydrate (0.12 g, 0.6 mmole) were thoroughly mixed at room temperature to obtain a
15	homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture will
16	cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
17	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
18	the time to gelation. The melt was very viscous after 1 hour at 255°C and a vitrified product
19	resulted after 5 hours at 255°C.
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1	Example 9: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy)
2	biphenyl monomer and a metallic salt, stannous chloride and cure to a thermoset.
3	4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and stannous chloride
4	dihydrate (0.034 g, 0.15 mmole) were thoroughly mixed at room temperature to obtain a
5	homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture will
6	cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
7	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
8	the time to gelation. The melt was very viscous after 2 hours at 255°C and a vitrified product
9	resulted after 6 hours at 255°C.
10	
11	Example 10: Formation of prepolymerization composition from 4,4'-bis(3,4-dicyanophenoxy)
12	biphenyl monomer and a metallic salt, stannous chloride and cure to a thermoset.
13	
14	4,4'-Bis(3,4-dicyanophenoxy) biphenyl monomer (1.5 g, 3.4 mmoles) and stannous chloride
15	dihydrate (0.135 g, 0.6 mmole) were thoroughly mixed at room temperature to obtain a
16	homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture will
17	cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
18	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
19	the time to gelation. The melt was very viscous after 1 hour at 255°C and a vitrified product
20	resulted after 3.5 hours at 255°C.

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1	Example 11: Formation of prepolymer composition from 2,2-bis[4-(3,4-
2	dicyanophenoxy)phenyl]propane and 1,4-bis(4-aminophenoxy)benzene (p-APB)
3	2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]propane monomer (1.5 g, 3.108 mmoles) and p-APB
4	(0.034 g, 0.12 mmole) were thoroughly mixed at room temperature to obtain a homogeneous
5	mixture. Upon heating of the mixture above the melt temperature, the mixture will cure to a
6	thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and maintain the
7	mixture in the melt phase with periodic stirring to monitor the increase in viscosity and the time to
8	gelation. The melt was very viscous after 2 hours and had vitrified after about 4 hours at 255°C.
9	
10	Example 12: Formation of prepolymer composition from 2,2-bis[4-(3,4-
11	dicyanophenoxy)phenyl]hexafluoropropane and 1,4-bis(4-aminophenoxy)benzene (p-APB)
12	
13	2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane monomer (1.5 g, 2.540 mmoles)
14	and p-APB (0.028 g, 0.095 mmole) were thoroughly mixed at room temperature to obtain a
15	homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture will
16	cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
17	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
18	the time to gelation. The melt was very viscous after 2 hours and had vitrified after about 4 hours
19	at 255°C.

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1	Example 13: Formation of prepolymer composition from 2,2-bis[4-(3,4-
2	dicyanophenoxy)phenyl]propane and 4,4'-diaminodiphenyl sulfone (p-DDS)
3	2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]propane monomer (1.5 g, 3.108 mmoles) and p-DDS
4	(0.029 g, 0.117 mmole) were thoroughly mixed at room temperature to obtain a homogeneous
5	mixture. Upon heating of the mixture above the melt temperature, the mixture will cure to a
6	thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and maintain the
7	mixture in the melt phase with periodic stirring to monitor the increase in viscosity and the time to
8	gelation. The melt was very viscous after 4 hours and had vitrified after about 9 hours at 255°C.
9	
10	Example 14: Formation of prepolymer composition from 2,2-bis[4-(3,4-
11	dicyanophenoxy)phenyl]hexafluoropropane and 4,4'-diaminodiphenyl sulfone (p-DDS)
12	
13	2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane monomer (1.5 g, 2.540 mmoles)
14	and p-DDS (0.024 g, 0.095 mmole) were thoroughly mixed at room temperature to obtain a
15	homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture will
16	cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
17	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
18	the time to gelation. The melt was very viscous after 1 hour and had vitrified after about 2.5 hours
19	at 255°C.
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1	Example 15: Formation of prepolymer composition from 2,2-bis[4-(3,4-
2	dicyanophenoxy)phenyl]propane and 4",4"'-(hexafluoroisopropylidene)bis(4-phenoxyaniline)(FA)
3	2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]propane monomer (1.5 g, 3.108 mmoles) and FA
4	(0.061 g, 0.117 mmole) were thoroughly mixed at room temperature to obtain a homogeneous
5	mixture. Upon heating of the mixture above the melt temperature, the mixture will cure to a
6	thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and maintain the
7	mixture in the melt phase with periodic stirring to monitor the increase in viscosity and the time to
8	gelation. The melt was very viscous after 4 hours and had vitrified after about 10 hours at 255°C.
9	
10	Example 16: Formation of prepolymer composition from 2,2-bis[4-(3,4-
11	dicyanophenoxy)phenyl]hexafluoropropane and 4",4"'-(hexafluoroisopropylidene)bis(4-
12	phenoxyaniline) (FA)
13	2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane monomer (1.5 g, 2.540 mmoles)
14	and FA (0.05 g, 0.095 mmole) were thoroughly mixed at room temperature to obtain a homogeneous
15	mixture. Upon heating of the mixture above the melt temperature, the mixture will cure to a
16	thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and maintain the
17	mixture in the melt phase with periodic stirring to monitor the increase in viscosity and the time to
18	gelation. The melt was very viscous after 1 hour and had vitrified after about 2 hours at 255°C.
19	
20	Example 17: Formation of prepolymer composition from bis[4-(3,4-dicyanophenoxy)phenyl]sulfone

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1 and 4,4'-diaminobenzophenone

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2	Bis[4-(3,4-dicyanophenoxy)phenyl]sulfone monomer (1.5 g, 2.974 mmoles) and 4,4'-
3	diaminobenzophenone (2.0 wt.%, 0.142 mmole) thoroughly mixed at room temperature to obtain
4	a homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture will
5	cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
6	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
7	the time to gelation. The melt was very viscous after 3 hours and had vitrified after about 12 hours
8	at 255°C.
9	
10	Example 18: Formation of prepolymerization composition from imide-containing phthalonitrile
11	monomer and an amine catalyst, 1,3-bis(3-aminophenoxy)benzene (m-APB) and cure to a thermoset.
12	An imide-containing monomer (1.5 g, 2.45 mmoles, synthesized from 3,3',4,4'-benzophenone
13	tetracarboxylic dianhydride and 4-(3-aminophenoxy)phthalonitrile), and m-APB (0.214 g, 0.073
14	mmole) were thoroughly mixed at room temperature to obtain a homogeneous mixture. Upon
15	heating of the mixture above the melt temperature, the mixture will cure to a thermoset. A sample
16	of the mixture was placed on a hot plate at 255°C to melt and maintain the mixture in the melt phase
17	with periodic stirring to monitor the increase in viscosity and the time to gelation. The melt was very
18	viscous after 2 hours at 255°C and a vitrified product resulted after about 6 hours at 255°C.
19	
20	Example 19: Formation of prepolymer composition from an oligomeric aromatic ether-containing

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1	phthalonitrile monomer and bis[4-(4-aminophenoxy)phenyl]sulfone (p-BAPS)
2	1.5 g of an oligomeric multiple aromatic ether-containing phthalonitrile monomer prepared
3	from 4,4'-difluorobenzophenone (12.01 g, 551.5 mmoles), 4,4'-dihydroxybiphenyl (20.11 g, 108.1
4	mmoles) and 4-nitrophthalonitrile (19.0 g, 109.8 mmoles) and 2%wt. bis[4-(4-
5	aminophenoxy)phenyl]sulfone (0.069 mmole) were thoroughly mixed at room temperature to
6	obtain a homogeneous mixture. Upon heating of the mixture above the melt temperature, the mixture
7	will cure to a thermoset. A sample of the mixture was placed on a hot plate at 255°C to melt and
8	maintain the mixture in the melt phase with periodic stirring to monitor the increase in viscosity and
9	the time to gelation. The melt was very viscous after 6 hours and had vitrified after about 12 hours
10	at 255°C.
11	
12	Example 20: Thermal stability of cured phthalonitrile resins
13	The thermal stability of the cured phthalonitrile polymers from Example 1-11 were evaluated
14	by thermogravimetric analysis (TGA) on powdered samples under an inert atmosphere of nitrogen.
15	Results indicate that in all cases, samples are stable up to about 400°C and begin to lose weight
16	thereafter. When the powdered samples are postcured to elevated temperatures of 8 hours at 350°C
17	and 8 hours at 375°C in the TGA furnace, all samples show improved thermal stability with weight
18	loss occurring only above 480-500°C. The samples also retain about 60-65% char upon pyrolysis
19	to 1000°C under inert conditions. In an oxidative environment, samples cured to 255°C show rapid
20	weight loss above 400°C, typical of most carbon-based materials. Samples that are postcured to

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1	elevated temperatures of 8h at 350°C and 8 hours at 375°C in the TGA furnace show better thermo-
2	oxidative stability than the 255°C cured resins and are stable to 500°C.
3	
4	Obviously, many modifications and variations of the present invention are possible in light
5	of the above teachings. It is therefore to be understood that
6	the invention may be practiced otherwise than as specifically described

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ABSTRACT

A polymerizable composition suitable for storage prior to polymerization is made by mixing a phthalonitrile monomer and a curing agent under non-reactive conditions below the melting temperatures of the phthalonitrile monomer and the curing agent and in the absence of a solvent to create a homogeneous, unreacted mixture.