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Inventor Teddy M. Keller

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HIGH TEMPERATURE EPOXY-PHTHALONITRILE BLENDS

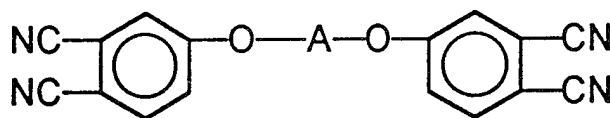
Background of the Invention

1. Field of the Invention

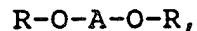
The present invention relates generally to high temperature polymers, and more specifically to high temperature polymer blends including a phthalonitrile resin.

2. Description of the Background Art

In United States Patent No. 4,619,986, issued October 28, 1986, to Teddy M. Keller, the entirety of which is incorporated herein by reference for all purposes, phthalonitrile resins having the formula:



are blended with epoxy monomers having the formula:



where A is selected from the group consisting of $-\phi-C_nH_{2n}-\phi-$, $-\phi-SO_2-\phi-$, $-\phi-$, $-C_nH_{2n}-$ and $-\phi-\phi-$, wherein n ranges from 1-4, the phenyl groups are linked at the para or meta positions, and R is selected from the group consisting of linear epoxies having 3-5 carbon atoms. When polymerized, the blend forms a polymer of

1 greatly improved thermo-oxidative stability relative to the amine-
2 cured epoxy. However, the thermal stability of the polymerized
3 blend is less than that of the amine-cured phthalonitrile polymer.
4
5

6 **Summary of the Invention**
7

8 Accordingly, it is an object of this invention to provide a
9 polymer having a high thermal stability.

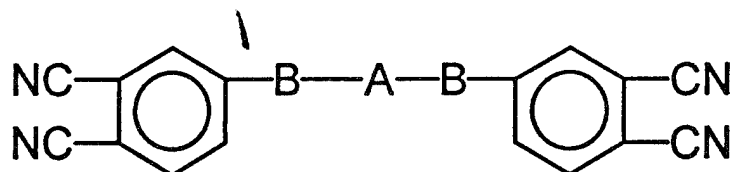
10 Another object of the present invention is to provide a
11 polymer with a low affinity for water, and a low cure temperature
12 compared to the cure temperature of bisphenol-linked
13 phthalonitrile.

14 Another object of the present invention is to provide a
15 phthalonitrile polymer blend having an improved thermo-oxidative
16 stability compared to that of the amine-cured epoxy polymer and at
17 least essentially equivalent thermal stability compared to that of
18 the corresponding phthalonitrile polymer.
19

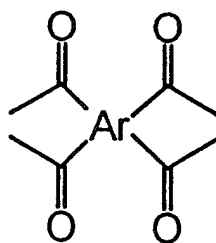
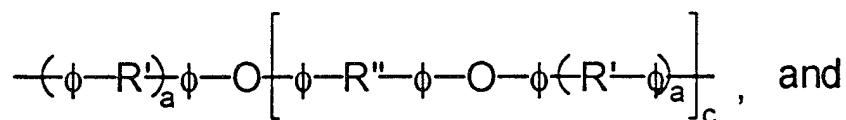
20 These and additional objects of the invention are accomplished
21 by a polymer formed by copolymerizing a phthalonitrile resin with
22 an epoxy resin having at least three epoxy groups. In another
23 embodiment, the present invention is a copolymer formed by the
24 polymerization of a bisphthalonitrile with a bisphenol epoxy resin,
25 at least one of which has a perfluorinated alkylene bridging group.

Description of the Preferred Embodiments

In a typical embodiment, the present invention is obtained by the copolymerization of a phthalonitrile resin having the formula:



where A is any at least divalent group having at least one aromatic or heterocyclic moiety and is typically selected from the group consisting of:



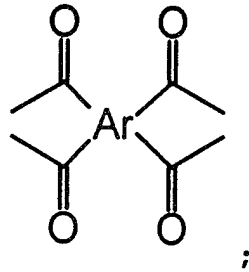
;

Ar is any aromatic or heterocyclic moiety;

B is oxygen, sulfur or nitrogen, and is nitrogen when A is:

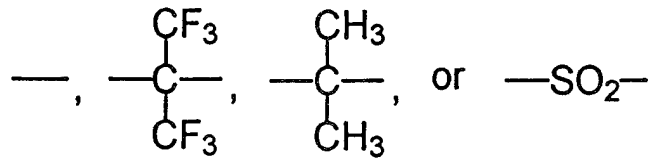
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1
2
3

R' is:

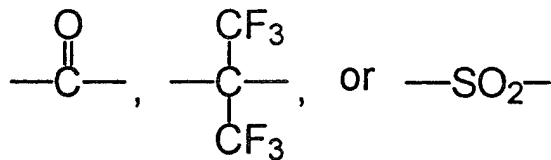


4
5
6

and may be the same or different at each position within A;

7

R'' is:



8
9
10

and may be the same or different at each position within A;

11

a is 0 or 1;

12

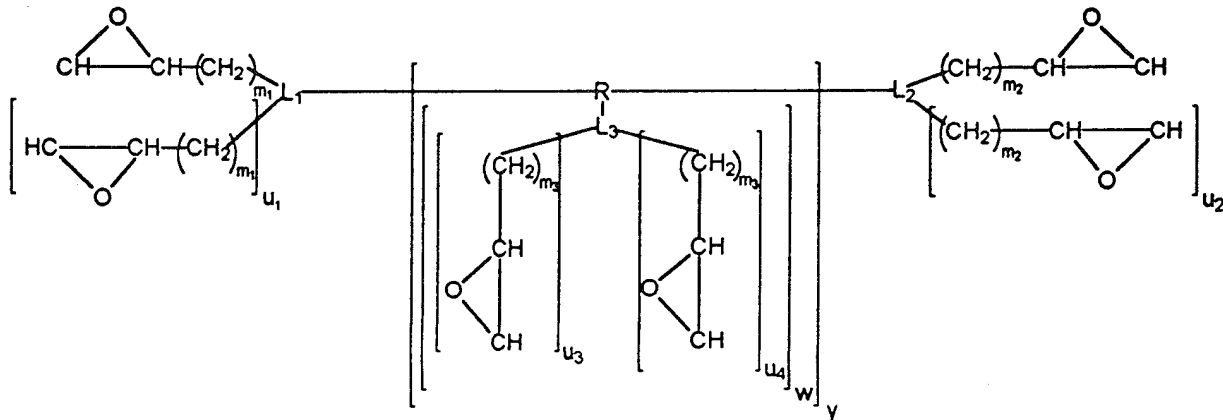
c is equal to or greater than 1; and

13

n is equal to or greater than 1;

14

with an epoxy resin of the formula:



where:

L_1 is CH_2 , oxygen, or sulfur when $u_1=0$ and is nitrogen when $u_1=1$;

L_2 is CH_2 , oxygen, or sulfur when $u_2=0$ and is nitrogen when $u_2=1$;

L_3 is CH_2 , oxygen, or sulfur when $u_4=0$ and is nitrogen when $u_4=1$;

m_3 is an integer having a value of from 1 to 3, inclusive, when L_3 is other than CH_2 , and is 0 to 3 when L_3 is CH_2 ;

m_1 is an integer having a value of from 1 to 3, inclusive when L_1 is other than CH_2 and is 0 to 3 when L_1 is CH_2 ;

m_2 is an integer having a value of from 1 to 3, inclusive when L_2 is other than CH_2 and is 0 to 3 when L_2 is CH_2 ;

u_1 is 0 or 1;

u_2 is 0 or 1;

u_3 is 0 when w is 0 and is 1 when w is at least 1;

u_4 is 0 when w is 0 and is 0 or 1 when w is at least 1;

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1 w is an integer and is typically 0 or 1;
2 at least one of u_1 , u_2 , and u_3 is equal to 1;
3 y is at least one; and

4 R is any at least divalent organic radical having at least one
5 aromatic or heterocyclic moiety.

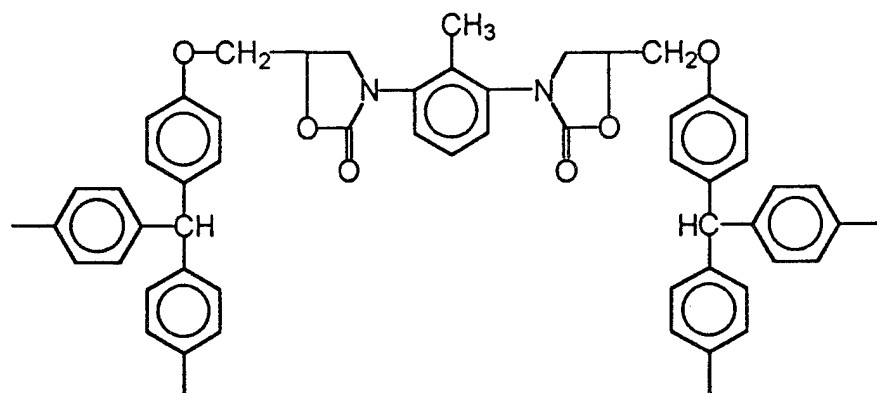
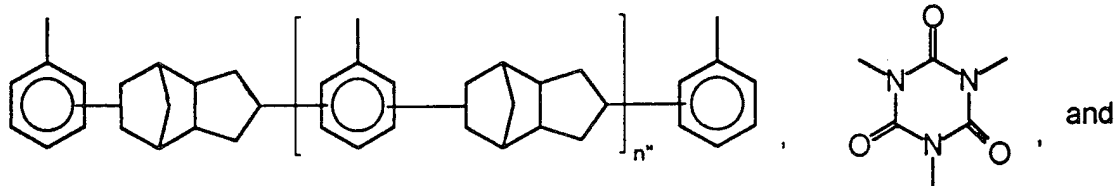
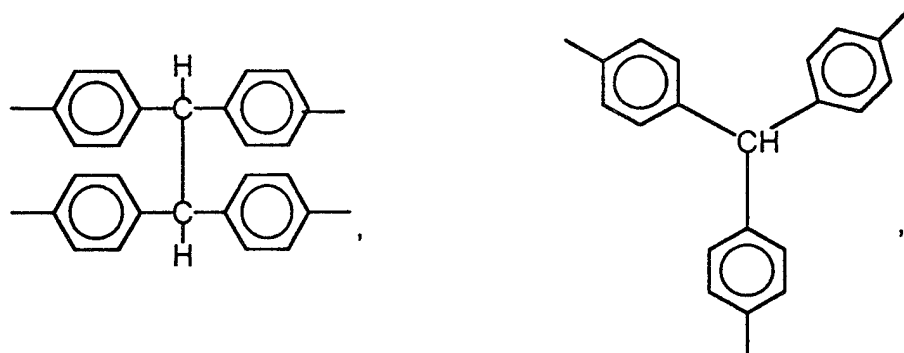
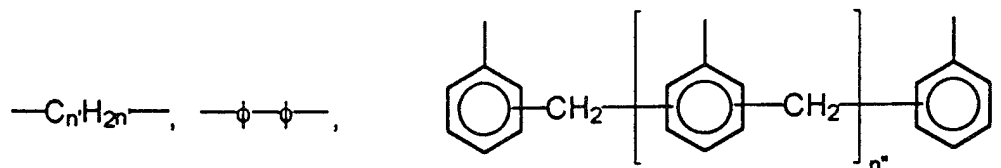
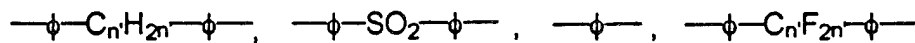
6 m_1 and m_2 may be the same or different and are typically the
7 same. L_1 and L_2 may be the same or different and are typically the
8 same. L_3 , when present, may be the same as or different from any
9 of L_1 and L_2 and is typically the same as L_1 and L_2 . Usually, if u_1
10 equals 1, u_2 will also equal 1.

11 Where w has a value greater than one, then R is at least
12 tetravalent and each $\text{---}L_3\text{---}(\text{CH}_2)_{m_3}\text{---}\text{CH}\text{---}\text{CH}$ is attached to a different carbon
13 along R.

14
15 Typically, R is selected from the group consisting of:

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where n' is an integer equal to or greater than 1, and n'' is an integer equal to or greater than 1.

Usually, y , n , n' , and n'' are sufficiently small that the

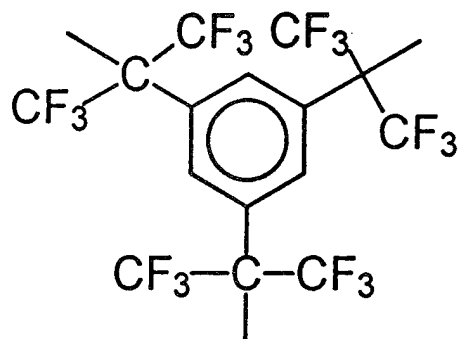
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1 epoxy resin and phthalonitrile are liquids at temperatures below
2 about 270°C. Usually, the phthalonitrile resin and the epoxy resin
3 will be miscible with each other at reaction temperatures, thus
4 permitting intimate mixture and complete reaction. While the
5 reaction between the epoxy and phthalonitrile resins may be
6 performed at any temperature below the decomposition temperature of
7 the least thermally stable resin, much of the advantage in the
8 present invention arises from the low temperatures at which the
9 resins react to form the desired copolymer. Thus, the epoxy and
10 phthalonitrile resins are both typically liquids and miscible with
11 each other, in the unreacted form, at reaction temperatures.

12 Typically, for above compounds having the "n'" or "n"
13 subscript, the compound is available as a mixture of homologous
14 oligomers, of the structure shown for that compound, in which the
15 average value of n' or n", respectively, is from about 0.2 to about
16 3.0, and more often, about 0.2 to about 1.8.

17 Other examples of epoxy resins useful in the present invention
18 include trifunctional fluorinated epoxy resins such as those
19 described in United States Patent No. 4,981,941 to Griffith, filed
20 March 27, 1989 and incorporated herein in its entirety by
21 reference. For example, R in the above formula may be:



1
2
3 The polymerization reaction is accomplished by heating the
4 melt of an epoxy-phthalonitrile mixture either neat, or in the
5 presence of a curing agent, and curing at elevated temperatures
6 (greater than about 150°C and usually greater than about 200°C).
7 The rate of the reaction may be substantially enhanced by the
8 addition of a curing additive. After a short time, which will be
9 dependent on the presence, reactivity, nature, and quantity of
10 curing agent, the melt starts to darken with a resulting viscosity
11 increase. Quantities of 0 to 25 percent molar weight of amine to
12 polymerization mixture are generally preferred. The preferred
13 polymerization temperature is from about 5°C above the melting
14 point of the mixture to about 30°C below the decomposition
15 temperature of the polymer in the polymerization mixture having the
16 lowest decomposition temperature, usually between about 150°C to
17 about 300°C. Polymerization can be performed in several steps over
18 a series of temperatures.

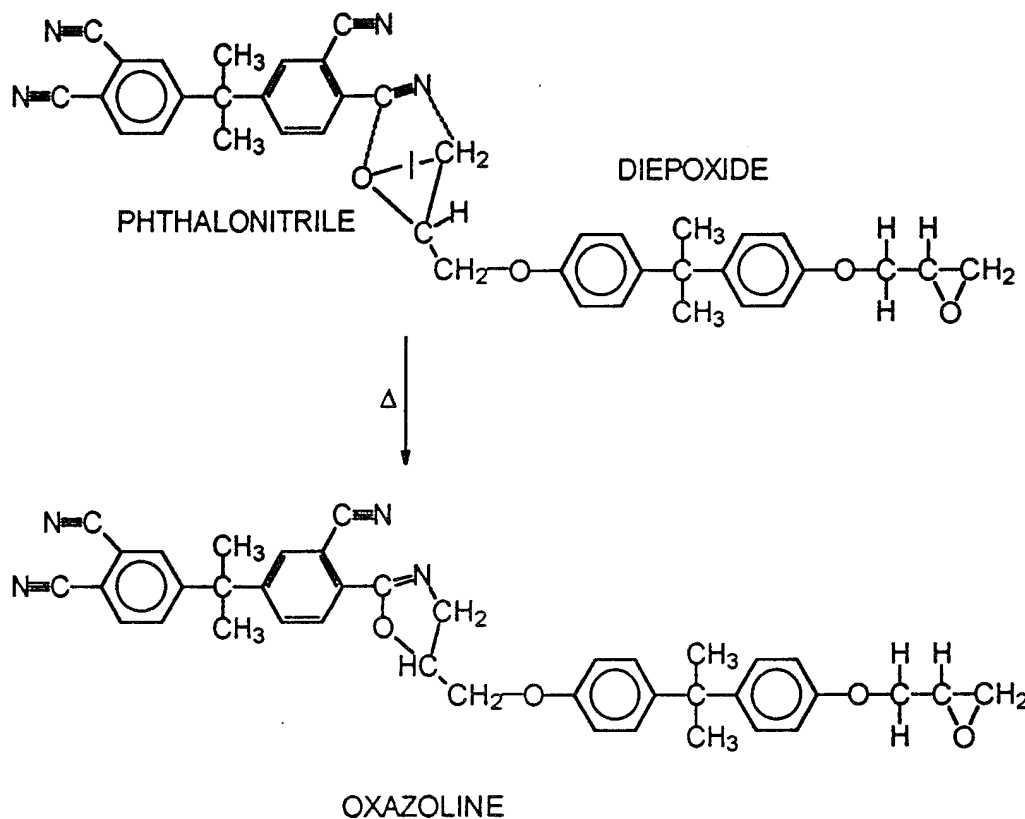
19 The overall physical properties of the new polymer will depend
20 on the relative amounts of epoxy, phthalonitrile, and curing agent

1 (if any) used. Although equimolar amounts of the phthalonitrile
2 and epoxy monomers are most preferred, the physical properties of
3 the resulting polymer can be varied by varying the ratio of
4 phthalonitrile monomer to epoxy monomer. Even a trace amount of
5 one monomer will react with an excess amount of the other monomer
6 to give new characteristic properties to the resulting polymer.
7 Mixtures of mole ratios of 20:1 epoxy/phthalonitrile and
8 phthalonitrile/epoxy diminish the water uptake and enhance the T_g
9 values of the resulting polymer relative to epoxy polymers. Mole
10 ratios of 5:1 epoxy/phthalonitrile and phthalonitrile/epoxy produce
11 dramatic changes in the properties of the polymer as compared to
12 those of the epoxy or phthalonitrile polymer alone. In all cases,
13 the thermo-oxidative stability is enhanced with a resulting higher
14 char yield relative to the epoxy cured with an amine or similar
15 curing agent. Moreover, there is a reduction in the equilibrium
16 water uptake of the epoxy phthalonitrile polymers relative to the
17 epoxy polymer. There is an enhancement in the glass transition
18 temperatures (T_g) relative to the epoxy polymer used whose value is
19 again dependent on the relative amounts of each reactant, with
20 higher ratios of phthalonitrile to epoxy favoring higher T_g 's. The
21 major improvements of the new polymer relative to the
22 phthalonitrile polymer is the processing or polymerization
23 conditions. Lower temperatures are required for the polymerization
24 reaction according to the present invention. This advantage is
25 achieve with little or no significant loss of thermal stability

1 relative to the amine-cured phthalonitrile polymer. In some cases,
2 the epoxy-phthalonitrile copolymer of the present invention may
3 even have improved thermal and oxidative stability over the amine-
4 cured phthalonitrile. This improved stability probably indicates
5 that the extent of polymerization reaction for the blend is higher
6 relative to the amine cured phthalonitrile under similar processing
7 conditions. Moreover, the epoxy-phthalonitrile blend can react
8 without the addition of curing additives. Without a curing
9 additive, pure phthalonitrile upon heat treatment at elevated
10 temperatures is not readily converted to a polymer. Thus, unlike
11 the present invention, pure phthalonitriles, in the absence of a
12 curing agent, require several days of heating above 280°C before
13 the onset of gelation.

14 As stated above, the copolymers of the present invention,
15 unlike the copolymers described in have USP 4,619,986 to Teddy M.
16 Keller, have thermal and oxidative stabilities close to or better
17 than that of the corresponding cured phthalonitrile. This
18 improvement over USP 4,619,986 to Teddy M. Keller may be attributed
19 to the present invention's use of epoxy resins having more than two
20 reactive epoxy groups.

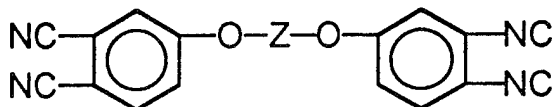
21 Epoxies and phthalonitriles appear to react via the mechanism
22 shown below, using the reaction of one end of a typical
23 phthalonitrile with one end of typical diepoxide as an example:



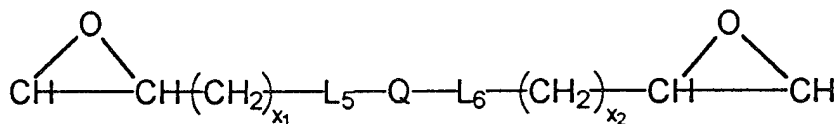
1
2
3 The oxazoline ring formed by this reaction is a highly stable
4 cross-linking center. As is apparent from the above example, a
5 diepoxy can form only two cross linking centers per molecule of
6 diepoxy. Higher epoxides, such as those used in the present
7 invention, can form a greater number of cross-linking centers.
8 Thus, a copolymer formed from a phthalonitriles and a higher
9 epoxide (more than two epoxide groups) will obtain a greater cross-
10 linking density and a higher stability than a copolymer formed from
11 the same phthalonitrile and the same molar quantity of the
12 analogous diepoxy.

13 In an alternative embodiment, the present invention is a

1 copolymer of a bisphthalonitrile with a difunctional bisphenol
2 epoxy, at least one of the components having at least one
3 fluorinated carbon. For example, either or both components may
4 have a perfluorinated alkylene bridging group. Typical useful
5 fluorinated phthalonitrile components useful in making this
6 embodiment of the invention include compounds of the formula:



9 in which Z is $-C_nF_n-$ or $-C(CF_3)_n-$. Some typical fluorinated
10 difunctional epoxy components useful in making this embodiment of
11 the invention are described in the aforementioned United States
12 Patent No. 4,981,941, to Griffith. Generally, useful fluorinated
13 difunctional epoxy components useful in making the present
14 invention include compounds of the formula:



where:

18 L_5 and L_6 are $-CH_2-$, oxygen, or sulfur and may be the same or
19 different; and

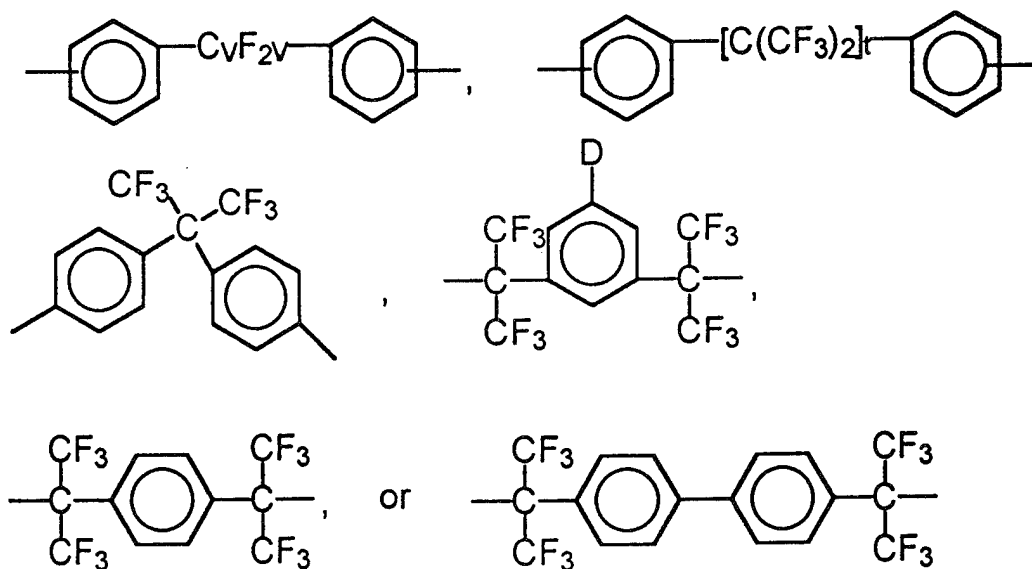
20 x_1 is an integer having a value of from 1 to 3 when L_5 is
21 oxygen or sulfur and has a value of from 0 to 3 when L_5 is $-CH_2-$;

22 x_2 is an integer having a value of from 1 to 3 when L_6 is
23 oxygen or sulfur and has a value of from 0 to 3 when L_6 is $-CH_2-$;

1 Q is any at least divalent organic radical having at least
2 one aromatic moiety and at least one perfluorinated carbon.

3 x_1 and x_2 may be the same or different.

4 Possible structures for Q are many too numerous to list and
5 include, for example:



where:

v is an integer having a value of from 1 to 20, inclusive;

t is an integer having a value of from 1 to 4 and is typically 1 to 2 and is most often 1;

D is hydrogen or $(CF_2)_jCF_3$; and

j is an integer having a value of from 0 through 15, inclusive.

The reaction between the phthalonitrile and epoxy components according to this embodiment is performed in essentially the same manner as described herein for the first

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1 disclosed embodiment.

2 Generally, for all embodiments, the more curing agent that
3 is used, the quicker is polymerization. Unfortunately, the
4 presence of large amounts of unreacted curing agent in the cured
5 polymer can degrade properties. Typically, the weight percent of
6 the curing agent relative to the monomer is 0.1-40 weight
7 percent, preferably 1-20 weight percent and more preferably about
8 5-10 weight percent.

9 As a more specific example, when the curing agent is an
10 amine, the amount of curing agent employed is usually in about
11 0.1 to about 20 weight percent of the polymer mixture.
12 Preferably, this amount is about 1 to about 15 weight percent.
13 Most preferably this amount is about 5 to about 10 weight
14 percent.

15 Any organic amine, phenol, strong organic acid, mineral
16 acid, Lewis acid or salt of any of the above which polymerizes
17 bisphthalonitrile monomers may be used as a curing agent in the
18 present invention. A mixture of curing agents may also be
19 employed.

20 Amine curing agents are useful in the present invention are
21 described, for example, in the above-mentioned United States
22 Patent Nos. 5,003,078; 4,408,035; 5,159,054, all of which are
23 incorporated herein by reference, for all purposes, in their
24 entirety. Typically, the preferred amine curing agents are of
25 the general formula H_2NYNH_2 where Y is an aromatic group.

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1 Amidines, especially diamidines, are particularly useful.

2 Mixtures of amine curing agents may be used.

3 Specific examples of amine curing agents useful in this
4 invention are given below:

5 o-phenylenediamine

6 m-phenylenediamine

7 p-phenylenediamine

8 4,4'-diaminodiphenylpropane

9 4,4'-diaminodiphenylmethane (commonly named 4,4'-
10 methylenedianiline)

11 4,4'-diaminodiphenyl sulfide (commonly named 4,4'-
12 thiodianiline)

13 4,4'-diaminodiphenyl ether (commonly named 4,4'-
14 oxydianiline)

15 1,5-diaminonaphthalene

16 3,3'-dimethylbenzidine

17 3,3'-dimethoxybenzidine

18 2,4-bis(β -amino-t-butyl)toluene

19 bis(p- β -amino-t-butyl)ether

20 bis(p- β -methyl-o-aminopentyl)benzene

21 1,3-diamino-4-isopropylbenzene

22 1,2-bis(3-aminopropoxy)ethane

23 benzidine

24 m-xylylenediamine

25 p-xylylenediamine

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- 1 2,4-diaminotoluene
- 2 2,6-diaminotoluene
- 3 1,3-bis(3-aminophenoxy)benzene
- 4 1,3-bis(4-aminophenoxy)benzene
- 5 1,4-bis(3-aminophenoxy)benzene
- 6 1,4-bis(4-aminophenoxy)benzene
- 7 bis[4-(3-aminophenoxy)phenyl]sulfone
- 8 bis[4-(4-aminophenoxy)phenyl]sulfone
- 9 4,4'-bis(3-aminophenoxy)biphenyl
- 10 4,4'-bis(4-aminophenoxy)biphenyl
- 11 2,2-bis[4-(3-aminophenoxy)phenyl]propane
- 12 2,2-bis[4-(4-aminophenoxy)phenyl]propane
- 13 4,4'-[1,4-phenylene(1-
- 14 methylethylidene]bis(benzeneamine)
- 15 4,4'-[1,4-phenylene(1-methylethylidene]bis(2,6-
- 16 dimethylbenzeneamine)
- 17 hexakis (4-aminophenoxy)cyclotriphosphazene.

18 The curing of phthalonitriles with organic and inorganic
19 acids, which also serve as useful curing agents in the present
20 invention, is described, for example, in USSN 07/818,575, filed
21 January 9, 1992, to Keller et al., entitled "CURING
22 PHTHALONITRILE RESINS.", which is incorporated herein by
23 reference in its entirety. Any strong organic acid, or mixture
24 of organic acids, may be used as a curing agent in the present
25 invention. Typically, a strong organic acid will exhibit a pK_a

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1 in water of less than about 1.0. More preferably, a strong
2 organic acid exhibits a pK_a in water of less than about 0.80.
3 Strong organic acids include, for example, aromatic acids
4 containing inorganic acidic substituents, such as the sulfonic
5 group $-SO_3H$. Specific examples of such aromatic acids include p-
6 toluenesulfonic acid, phenylsulfonic acid, 1-naphthalenesulfonic
7 acid, 2-naphthalenesulfonic acid, 1,5-naphthalenedisulfonic acid,
8 2,6-naphthalenedisulfonic acid, 2,7-naphthalenedisulfonic acid,
9 phenylphosphonic acid, phenylphosphinic acid, and phenylboric
10 acid.

11 While any strong inorganic acid may be used, typical strong
12 inorganic acids useful in the present invention include mineral
13 acids such as hydrochloric acid, phosphoric acid, sulfuric acid,
14 sulfonic acid and nitric acid, and mixtures thereof. Nitric
15 acid, a strong inorganic acid, may be used as a curing agent in
16 the present invention, but is not preferred because of its high
17 oxidation strength.

18 The curing agent may also be a salt of any of the amines,
19 acids or phenols discussed above. Exemplary curing salts for use
20 according to the present invention include bis(3-aminophenoxy)-
21 1,3-benzene p-toluene sulfonate, p-phenylenediamine p-
22 toluenesulfonate, bis(4-aminophenyl)methane hydrochloride, and N-
23 phenylbenzamidine p-toluene sulfonate.

24
25 Having described the invention, the following examples are

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1 given to illustrate specific applications of the invention
2 including the best mode now known to perform the invention.
3 These specific examples are not intended to limit the scope of
4 the invention described in this application.

6 EXAMPLES

7 **Example 1**

8 Dow epoxy novolac (D.E.N. 431) resin (0.51 g. ~1.45 mmol)
9 and 4,4'-bis(3,4-dicyanophenyl)biphenyl (0.63 g, 1.45 mmol) were
10 weighed into an aluminum planchet, melted and mixed at 240-250°C,
11 and degassed at reduced pressure for 1 hour. A small sample was
12 removed for thermal analysis studies. A sample (3.9 mg) of the
13 mixture was placed in a DSC pan and scanned at 10°C/min to 300°C.
14 The DSC thermogram exhibit a small endotherm at ~50°C, a
15 crystallization peak at ~100°C, and an endotherm peaking at
16 ~220°C attributed to the melting point of 4,4'-bis(3,4-
17 dicyanophenyl)biphenyl. After the melting occurred, the sample
18 commenced to exotherm indicating reaction of the 4,4'-bis(3,4-
19 dicyanophenyl)biphenyl and novolac epoxy resin to afford the new
20 high temperature polymer. Upon cooling and rescanning to 275°C,
21 no characteristic T_g was observed.

22
23 **Example 2**

24 Dow epoxy novolac (D.E.N. 431) resin (0.51 g. ~1.45 mmol)
25 and 4,4'-bis(3,4-dicyanophenyl)biphenyl (0.63 g, 1.45 mmol) were

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1 weighed into an aluminum planchet, melted and mixed at 240-250°C,
2 and degassed at reduced pressure for 1 hour. To the degassed
3 blend was added 1,3-(3-aminophenoxy)benzene (APB, 0.02 g) at 240-
4 250°C with stirring. After 30 seconds, a small sample was removed
5 for DSC analysis. The remaining (main) sample started to increase
6 in viscosity almost immediately. After 30 minutes, the main
7 sample had solidified. The solidified sample was then heated at
8 260°C for 3 hours to totally cure. A DSC thermogram was obtained
9 on the uncured sample by scanning at 10°C/min from 25 to 275°C
10 under a flow of nitrogen at 50 cc/min. The sample exhibited an
11 endotherm at ~60°C, an exotherm peaking at ~140°C, and an
12 endotherm peaking at ~220°C attributed to the melting point of
13 the 4,4'-bis(3,4-dicyanophenyl)biphenyl resin. As soon as the
14 melting occurred, the sample immediately started to exotherm.
15 Upon heating at 275°C for 3 hours, the cured copolymer did not
16 exhibit a glass transition (T_g) or softening temperature. A TGA
17 thermogram from 75 to 750°C showed oxidative stability in air to
18 above 300°C before degradation started to slowly occurred.
19 Between 475 and 600°C catastrophic decomposition occurred. When
20 the sample that had been cured to 260°C was postcured at 300°C
21 for 1 hour, improvements in the oxidative stability was observed.

22 23 Example 3

24 Dow Tactix 742 resin, tri(hydroxyphenyl) methane-based epoxy
25 resin, (0.53 g, 1.14 mmol) and 4,4'-bis(3,4-

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1 dicyanophenyl)biphenyl (0.50 g, 1.14 mmol) were weighed into an
2 aluminum planchet, heated to melt at 240-250°C, and degassed at
3 reduced pressure for 1 hour to remove volatiles. A small sample
4 was removed for DSC analysis. A DSC thermogram showed an
5 endotherm peaking at ~50°C, an exotherm peaking at ~110°C, and an
6 endotherm peaking at ~215°C. This latter endotherm is attributed
7 to the melting point of 4,4'-bis(3,4-dicyanophenyl)biphenyl.
8 Almost immediately after the melt of 4,4'-bis(3,4-
9 dicyanophenyl)biphenyl, the sample started to exotherm attributed
10 to reaction of 4,4'-bis(3,4-dicyanophenyl)biphenyl and the Dow
11 Tactix 742 resin to form the copolymer or novel polymeric
12 mixture. After heating of the sample at 250°C for 3 hours, the
13 resulting polymeric mixture did not exhibit a glass transition as
14 determined by heating the sample at 10°C/min to 275°C.

15
16 **Example 4**

17 Dow Tactix 742 resin, tri(hydroxyphenyl) methane-based epoxy
18 resin, (0.53 g, 1.14 mmol) and 4,4'-bis(3,4-
19 dicyanophenyl)biphenyl (0.50 g, 1.14 mmol) were weighed into an
20 aluminum planchet, heated to melt at 240-250°C, and degassed at
21 reduced pressure for 1 hour to remove volatiles. At this time
22 1,3-bis(3-aminophenoxy)benzene (APB, 0.02 g) was added with
23 stirring. After 30 seconds, a sample was removed for DSC
24 analysis. A DSC thermogram showed an endotherm peaking at ~60°C,
25 an exotherm peaking at ~125°C, and an endotherm peaking at ~210°C.

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1 Almost immediately after the melting peak, the main sample
2 started to increase in viscosity. The sample was then heated at
3 260°C for 3 hours. After 30 minutes at 260°C, the sample had
4 solidified. A TGA thermogram in air of a powdered sample of the
5 cured polymer cured at 260°C showed thermo-oxidative stability to
6 300°C before any weight loss was detected. A small amount of the
7 cured polymer was further heated at 300°C for 1 hour in air
8 resulting in a slight improvement in the thermo-oxidative
9 stability.

10
11 **Example 5**

12 Dow epoxy novolac (D.E.N. 431) resin (0.79 g, ~2.29 mmol)
13 and 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane (1.1 g, 2.29
14 mmol) were weighed into an aluminum planchet, mixed at 220°C with
15 stirring, and degassed for 1 hour at reduced pressure. To the
16 melt was added 4,4'-bis (4-aminophenyl)sulfone (0.019 g, 0.076
17 mmol). After mixing thoroughly, the mixture was cured under a
18 nitrogen atmosphere by heating at 150°C for 30 minutes, at 225°C
19 for 2 hours, and at 260°C for 1 hour. The cured sample showed
20 outstanding thermal and oxidative stability relative to the cured
21 Dow epoxy novolac (D.E.N. 431) resin and a slight improvement in
22 the thermal properties when compared to the corresponding amine
23 cured 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane
24 (phthalonitrile) resin (Fig. 1, line A).

1 **Example 6**

2 Dow epoxy novolac (D.E.N. 431) resin (1.10 g, ~3.19 mmol)
3 and 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane (0.76 g, 1.60
4 mmol) were mixed with stirring at 220°C and degassed for 1 hour
5 under reduced pressure. At this time the sample was placed in an
6 over and heated at 220°C for 6 hours resulting in solidification.
7 The polymeric mixture appeared to be fairly tough.

8
9 **Example 7**

10 Dow epoxy novolac (D.E.N. 431) resin (1.50 g, ~4.35 mmol)
11 and 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane (0.42 g, 0.87
12 mmol) were mixed stirring at 220°C and degassed for 1 hour under
13 reduced pressure. To the melt was added 4,4'-bis (4-
14 aminophenyl)sulfone (0.019 g, 0.077 mmol). After stirring for 30
15 seconds, a sample was removed for DSC analysis. A DSC thermogram
16 from 30 to 260°C did not show an endotherm for the melting point
17 of 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane indicating that
18 the resin had been converted from the crystalline phase into the
19 amorphous phase. Upon cooling and rescanning to 260°C, the
20 polymeric mixture did not exhibit a glass transition temperature
21 (T_g).

22
23 **Example 8**

24 Dow epoxy novolac (D.E.N. 431) resin (1.01g, ~2.90 mmol) and
25 a multiple oligomeric aromatic ether-containing phthalonitrile

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1 (1.0 g, ~ 0.93 mmol), prepared from reaction of 4,4'-
2 difluorobenzophenone (1M), 4,4'-
3 (hexafluoroisopropylidene)bisphenol (2M), 4-nitrophthalonitrile
4 (1M), and excess potassium carbonate in N-methylpyrrolidinone as
5 solvent yielding a repeat unit of $-N=1$, were weighed into an
6 aluminum planchet, mixed at 240-250°C, and degassed for 1 hour
7 under reduced pressure. The epoxy-phthalonitrile mixture was
8 cured by heating at 260°C for 6 hours. During the heat treatment,
9 the mixture solidified into a dark polymer. The polymer appeared
10 to be tough.

11

12 **Example 9**

13 Shell Epon 828 (0.5 g, ~1.47 mmol) and a multiple oligomeric
14 aromatic ether-containing phthalonitrile (1.0 g, ~ 0.87 mmol),
15 prepared from reaction of 4,4'-difluorobenzophenone (2M), 4,4'-
16 dihydroxybiphenyl (3M), 4-nitrophthalonitrile (1.5M), and excess
17 potassium carbonate in N-methylpyrrolidinone as solvent yielding
18 a repeat unit of $-N=2$, were weighed into an aluminum planchet,
19 mixed at 240-250°C, and degassed for 1 hour under reduced
20 pressure. The epoxy-phthalonitrile mixture was cured by heating
21 at 260°C for 6 hours. During the heat treatment, the mixture
22 solidified into a dark polymer. The polymer appeared to be tough.

23

1 **Example 10**

2 Dow epoxy novolac (D.E.N. 431) resin (2.01g, 5.80 mmol) and
3 4,4'-bis (4-aminophenyl)sulfone (DADS, 0.30g, 1.21 mmol) were
4 weighed into an aluminum planchet. The mixture was heated with
5 stirring to 150°C to dissolve the curing agent (DADS). After the
6 DADS had dissolved, a small sample was removed for thermal
7 analysis studies and the remaining sample was quenched back to
8 room temperature.

9 Thermal analysis was performed using TGA and DSC. A sample
10 (41.14 mg) of the mixture was placed into in a TGA platinum pan
11 and cured in nitrogen by heating at 150°C and 225°C for 1 and 3
12 hours, respectively. This was the curing procedure recommended by
13 Dow. During the heat treatment, the sample lost about 10% weight.
14 After cooling to room temperature, the cured epoxy novolac resin
15 was heated at 10°C/min in a flow of air (50 cc/min) to 750°C. The
16 sample was stable to approximately 280°C whereupon a slow weigh
17 loss commenced. Between 370°C and 670°C, catastrophic degradation
18 occurred. A DSC thermogram of the mixture shows an exothermic
19 reaction commencing at ~150°C (Fig 1, line B). After curing at
20 150°C and 225°C for 1 and 3 hours, respectively, the cured sample
21 exhibited a T_g of ~160°C. Above 160°C, the sample started to
22 slowly exotherm indicating further reaction.

1 **Example 11**

2 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane (1.50 g, 3.15
3 mmol) was weighed into an aluminum planchet. To the melt at
4 225°C was added 4,4'-bis (4-aminophenyl)sulfone (0.06 g, 0.242
5 mmol) with stirring. After 30 seconds of stirring, a sample of
6 the mixture was removed for thermal analysis studies. A sample
7 (17.446 mg) was weighed into a platinum TGA pan and cured by
8 heating at 225°C for 1 hour, at 260°C for 2 hours, and at 300°C
9 for 4 hours. During the heat treatment, the sample lost ~5.5%
10 weight. Upon cooling the cured sample was scanned at 10°C/min in
11 a flow of air (50 cc/min) to 800°C (Fig. 1, line C). The polymer
12 commenced to slowly loss weight at ~360°C. The sample showed
13 similar oxidative stability relative to the novolac epoxy-
14 phthalonitrile copolymer of Example 5 (Fig. 1, line A).

15
16 Obviously, many modifications and variations of the present
17 invention are possible in light of the above teachings. It is
18 therefore to be understood that,

19 the invention may be practiced otherwise than as
20 specifically described.

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ABSTRACT

A copolymer is formed from reacting, within a melt, a phthalonitrile resin with an epoxy resin having at least three epoxy groups. In an alternative embodiment, a copolymer is formed by reacting a phthalonitrile resin with an epoxy resin, at least one of the epoxy and phthalonitrile resins having a perfluorinated carbon. The copolymers of the present invention have exceptional thermal stability and a low affinity for water.

Figure 1

