Polyphenylquinoxalines are prepared by the nucleophilic displacement reaction of di(hydroxyphenyl)quinoxaline monomers with activated aromatic dihalides or dinitro compounds. The reactions are carried out in polar aprotic solvents during alkali metal bases at elevated temperatures under nitrogen. The di(hydroxyphenyl)quinoxaline monomers are prepared either by reacting stoichiometric quantities of aromatic bis(o-diamines) with a hydroxybenzil or by reacting o-phenylenediamine with a dihydroxybenzil or bis(hydroxyphenylglyoxylyl)benzene.

3 Claims, No Drawings
POLYPHENYLQUINOXALINES VIA AROMATIC 
NUCLEOPHILIC DISPLACEMENT

This is a division of application Ser. No. 07/250,661, 
filed Sept. 28, 1988 now abandoned.

ORIGIN OF INVENTION

The invention described herein was made by employ-
ees of the U.S. Government and may be manufactured 
and used by or for the Government for governmental 
purposes without payment of any royalties thereon or 
therefor.

BACKGROUND OF INVENTION

Polyphenylquinoxalines are high temperature thermo-
plastics which exhibit excellent performance as 
adhesives, coatings, films and composite matrices. 
These materials are heterocyclic polymers synthesized 
by the condensation reaction of a bis(phenyl-a-dike-
tone) with an aromatic bis(o-diamine).

Schematically, this may be represented in Equation I:

\[
\text{H}_2\text{N} \quad \text{NH}_2
\]

\[
\text{Ar} \quad \text{H}_2\text{N} \quad \text{NH}_2
\]

where Ar is 1,2,4,5-tetrasubstituted benzene, 3,3', 4,4'-
tetrasubstituted; biphenyl, diphenylether, diphenyl-
methane, diphenylketone, diphenylsulfone, diphenyl-
thioether or any appropriate bis(o-diamine) and mix-
tures thereof. The catenation of the hydroxy group may 
be Alternatively, meta-meta, para-para, the di(hydroxypheny1) or para-meta.

As a direct result of the use of the condensation reac-
tion to synthesize polyphenylquinoxalines, there are 
several limitations.

First, because the polyphenylquinoxalines are not 
configurationally ordered, their mechanical properties 
(as evidenced for example by tensile modulus) and 
strength are limited, and the resultant lack of crystallin-
ity renders them subject to attack by chlorinated or-
ganic solvents.

Second, the bis(phenyl-a-diketones) required for 
polyphenylquinoxaline formation are relatively difficult 
to prepare and expensive.

Third, the structure of polyphenylquinoxaline is diffi-
cult to vary.

Thus, it is an object of this invention to prepare con-
figurationally ordered polyphenylquinoxalines, in order 
to improve strength and resistance to attack by organic 
solvents.

It is a further object to devise a means of preparing 
polyphenylquinoxaline, either configurationally or-

SUMMARY OF INVENTION

The objects of this invention are obtained by (1) 
forming di(hydroxyphenyl) quinoxaline monomers (a) 
by the condensation of 2 moles of a hydroxybenzil with 
an aromatic bis(o-diamine) as represented in Equation II:

\[
\text{HO} + \text{H}_2\text{N} \quad \text{Ar} \quad \text{NH}_2
\]

where Ar is 1,2,4,5-tetrasubstituted benzene, 3,3', 4,4'-
tetrasubstituted; biphenyl, diphenylether, diphenyl-
methane, diphenylketone, diphenylsulfone, diphenyl-
thioether or any appropriate bis(o-diamine) and mix-
tures thereof. The catenation of the hydroxy group may 
be meta-meta, para-para, or para-meta.

Alternatively, the di(hydroxyphenyl) quinoxaline 
monomers are formed (b) by the condensation of a 
dihydroxybenzil with an aromatic o-diamine, which 
may be a substituted o-diamine, as represented in Equation III:

\[
\text{HO} + \text{H}_2\text{N} \quad \text{Z}
\]
where Z = H, Cl, Br, OCH₃, CH₃, CH₂CH₃, or Ph. The catenation of the hydroxy group may be meta-meta, para-para, or para-meta.

More complex dihydroxybenzils may be used, producing correspondingly more complex phenylquinoxaline monomers, as represented in Equation IV:

![Equation IV](image)

In the case where Z is H, there are no configurational isomers.

(2) polyphenylquinoxalines are produced by the aromatic nucleophilic displacement reaction of a phenyl quinoxaline monomer (described above) with an activated aromatic compound of the following structure:

![Equation V](image)

where X is selected from the group in Equations V and VI:

where Ar is:
EXAMPLES

Example 1

Where: The following Example illustrates the reaction sequence for the synthesis of the polyphenylquinoxaline where \( Y = F \), \( R = \text{nil} \) and \( X \) is:

\[
\begin{align*}
Y & \text{ is } F, \text{Cl}, \text{or NO}_2, \\
R & \text{ is nil, SO}_2, \text{CO}, \text{O}, \text{S(CH}_3)_2, \text{C(CF}_3)_2, \text{or CH}_2 \\
X & \text{ is: } \text{C}=\text{O}, \text{SO}_2,
\end{align*}
\]

Where the di(hydroxyphenyl)quinoxaline monomers have structural isomers, the resultant polyphenyl-
quinoxaline is not configurationally ordered, but the polyphenyl-quinoxalines are new and have excellent properties.

Where the di(hydroxyphenyl)quinoxaline monomers have no structural isomers, the resultant polyphenyl-
quinoxaline is configurationally ordered; certain of these polyphenyl-quinoxalines are semi-crystalline.

The configurationally ordered polyphenylquinoxalines are insoluble in polar aprotic solvents such as N,N-
dimethylacetamide, N-methylpyrrolidone, and dimethylsulfoxide, and are insoluble in chlorinated hydrocar-
bons such as methane chloride, chloroform and tetrachloroethane. Thin films of representative configuration-
ally ordered polyphenylquinoxalines were immersed in hydraulic fluid for 24 hours and chloroform for one hour, after which no noticeable swelling or crazing was observed.

DETAILED DESCRIPTION OF INVENTION

Having generally described the invention, a more complete understanding thereof can be obtained by reference to the following specific examples which are provided herein for purposes of illustration only and do not limit the invention.

Polyphenylquinoxaline Synthesis

Into a 250 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap, and reflux condenser was placed 4-hydroxybenzil (6.23 g, 0.0274 mol), 3,3'-diaminobenzidine (2.94 g, 0.0137 mol), absolute ethanol (30 ml) and benzene (30 ml). The mixture was stirred at room temperature for one hour, then refluxed overnight. The solution was cooled and the yellow solid was filtered, washed with water and dried at 100°C for three hours. Yield 7.94 g (98%), m.p. > 360°C. Anal. Calcd. for CdHjN4O2: C, 80.79%; H, 4.41%; N, 9.42%. Found: C, 80.56%; H, 4.22%; N, 9.48%.

Polyphenylquinoxaline Synthesis

Into a 250 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap, and reflux condenser was placed 1,3-bis(4-fluorobenzyloxy)benzene (1.9339 g, 0.006 mol), 6,6'-bis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] and isomers (3.5678 g, 0.006 mol) powdered anhydrous potassium carbonate (1.90 g, 0.0138 mol), N,N-dime-
thylacetamide (40 ml) and toluene (25 ml). The mixture was heated to 135°C for three to four hours to remove water, toluene was removed from the system and the temperature was increased to 135°C overnight. The
polymer was isolated by precipitation into water/acetic acid mixture, washed successively with water and methanol and dried. Yield 5.1 g (97%) of off-white polymer with an inherent viscosity of 1.09 dL/g and a glass transition temperature of 240°C. Thin films cast from m-cresol solution gave tensile strength, tensile modulus and elongation at 25°C of 11,500 psi, 353,000 psi and 7.7% and at 177°C of 6550 psi, 250,000 psi and 65 percent respectively.

Example 2

The following Example illustrates the reaction sequence for the synthesis of a semi-crystalline polyphenylquinoxaline where Y is F, X is

and Ar is

and Z is H. See Equation V.

Monomer Synthesis

2,3-bis[4-hydroxyphenyl]quinoxaline: Into a 250 ml round bottom flask equipped with a magnetic stirrer and reflux condenser was placed 1,2-diaminobenzene (2.3275 g, 0.0215 mol), 4,4'-dihydroxybenzil (5.2135 g, 0.0215 mol) and absolute ethanol (30 ml). The solution was stirred for one-half hour at room temperature, and a yellow precipitate formed. The mixture was heated to reflux overnight. The solvent was removed by vacuum distillation and the solid dried at 100°C for two hours to give 6.5 g (97%) of yellow powder. The material was recrystallized from 1,4-dioxane/water mixture. Yield 6.0 g (89%) m.p. 336°C–338°C. Anal. Calcd for C_{20}H_{14}N_{2}O_{3}: C, 76.42%; H, 4.49%; N, 8.91%. Found: C, 76.54%; H, 4.44%; N, 8.96%.

Polyphenylquinoxaline Synthesis

Into a 250 ml round bottom flask equipped with a magnetic stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed 1,2-diaminobenzene (2.3275 g, 0.0215 mol), 4,4'-dihydroxybenzil (5.2135 g, 0.0215 mol) and absolute ethanol (30 ml). The solution was stirred for one-half hour at room temperature, and a yellow precipitate formed. The mixture was heated to reflux overnight. The solvent was removed by vacuum distillation and the solid dried at 100°C for two hours to give 6.5 g (97%) of yellow powder. The material was recrystallized from 1,4-dioxane/water mixture. Yield 6.0 g (89%) m.p. 336°C–338°C. Anal. Calcd for C_{20}H_{14}N_{2}O_{3}: C, 76.42%; H, 4.49%; N, 8.91%. Found: C, 76.54%; H, 4.44%; N, 8.96%.

Polyphenylquinoxaline Synthesis

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed 1,3-bis(4-hydroxyphenyl)benzene (2.5927 g, 0.005 mol), 1,2-diaminobenzene (2.9705 g, 0.0274 mol) and absolute ethanol (45 ml). The solids dissolved rapidly to give an orange solution, and after 15 minutes a yellow precipitate formed. The mixture was diluted with absolute ethanol (125 ml) and refluxed overnight. The mixture was poured into water, collected and dried to give 7.0 g (98%) of yellow solid. The solid was recrystallized from ethanol/water (5:1) mixture to give yellow needles, m.p. 339°C–343°C.

Polyphenylquinoxaline Synthesis

1,3-bis[2-quinoxalyl-3-(4-hydroxy-phenyl)]benzene. Into a 250 ml round bottom flask equipped with a magnetic stirrer and reflux condenser was placed 1,3-bis(4-hydroxyphenyl)benzene (5.1412 g, 0.005 mol), powdered anhydrous potassium carbonate (1.6 g, 0.0137 mol), 1,2-diaminobenzene (2.9705 g, 0.0274 mol) and absolute ethanol (45 ml). The solids dissolved rapidly to give an orange solution, and after 15 minutes a yellow precipitate formed. The mixture was diluted with absolute ethanol (125 ml) and refluxed overnight. The mixture was poured into water, collected and dried to give 7.0 g (98%) of yellow solid. The solid was recrystallized from ethanol/water (5:1) mixture to give yellow needles, m.p. 339°C–343°C.

Polyphenylquinoxaline Synthesis

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed 1,3-bis(4-hydroxyphenyl)benzene (2.5927 g, 0.005 mol), 1,3-bis(2-quinoxalyl-3-(4-hydroxyphenyl)] benzene (2.5927 g, 0.005 mol), powdered anhydrous potassium carbonate (1.6 g, 0.0115 mol), N,N-dimethylacetamide (20 ml) and toluene (35 ml). The mixture was heated to 135°C for three to four hours to remove water, then increased to 155°C overnight. The polymer had precipitated from solution overnight during the synthesis. The mixture was poured into acetic acid/water to give an off-white powder which was subsequently washed with water and then methanol and dried at 100°C. Yield 3.55 g (99%) of polymer with a glass transition temperature of 235°C and a crystalline melt temperature of 388°C. The inherent viscosity of a 0.5 percent solution in m-cresol measured at 25°C was 0.24 dL/g. Polymer characterization is presented in Tables 1 and 2 below.
TABLE 1

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>( \eta_{inh} \text{dL/g}^* )</th>
<th>( T_g, ^\circ \text{C}.^** )</th>
</tr>
</thead>
<tbody>
<tr>
<td>nil</td>
<td>SO₂</td>
<td>0.90</td>
<td>283</td>
</tr>
<tr>
<td>nil</td>
<td>CO</td>
<td>0.80</td>
<td>252</td>
</tr>
<tr>
<td>nil</td>
<td>isophthaloyl</td>
<td>1.09</td>
<td>240</td>
</tr>
<tr>
<td>CO</td>
<td>SO₂</td>
<td>0.69</td>
<td>253</td>
</tr>
<tr>
<td>CO</td>
<td>CO</td>
<td>1.30</td>
<td>255</td>
</tr>
<tr>
<td>CO</td>
<td>isophthaloyl</td>
<td>0.61</td>
<td>235</td>
</tr>
<tr>
<td>O</td>
<td>SO₂</td>
<td>0.34</td>
<td>240</td>
</tr>
<tr>
<td>O</td>
<td>terephthaloyl</td>
<td>0.45</td>
<td>226</td>
</tr>
<tr>
<td>O</td>
<td>isophthaloyl</td>
<td>0.46</td>
<td>213</td>
</tr>
</tbody>
</table>

*Inherent viscosities in m-cresol at 0.5% concentration (w/v) at 25\(^\circ\)C.
**Determined by differential scanning calorimetry at 20\(^\circ\)C/min.

TABLE 2

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>( \eta_{inh} \text{dL/g}^* )</th>
<th>( T_g, ^\circ \text{C}.^** )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td></td>
<td>0.54</td>
<td>240</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>0.58</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.83</td>
<td>208 (( T_m = 365 ))</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>0.50</td>
<td>179</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>0.52</td>
<td>179 (( T_m = 377 ))</td>
</tr>
</tbody>
</table>
**TABLE 2-continued**

<table>
<thead>
<tr>
<th>X</th>
<th>( \eta_{inh} ) dL/g*</th>
<th>Tg, °C**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Inherent viscosities in m-cresol at 0.5% concentration (w/v) at 25°C.
**Determined by differential scanning calorimetry at 20°C/min.

**What is claimed as new and desired to be secured by Letters Patent of the U.S. is:**

1. A di(hydroxyphenyl)quinoxaline having the general structure:

\[
\begin{array}{c}
\text{Ar} \end{array}
\]

wherein \( \text{Ar} \) is a radical selected from the group consisting of: \( \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CH}_3, \text{CH}_2\text{CH}_3, \text{OCH}_3, \text{C}_6\text{H}_5, \text{and C}_6\text{H}_5\text{O}. \)

2. The quinoxaline of claim 1 wherein \( \text{Ar} \) is:

3. The quinoxaline of claim 2 where \( Z \) is H.