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 using 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(hydroxyphenylglyoxyl)benzene.
POLYPHENYLQUINOXALINES VIA AROMATIC NUCLEOPHILIC DISPLACEMENT

ORIGIN OF INVENTION

The invention described herein was made by employees of the United States 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 thermoplastics 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-diketone) with an aromatic bis(o-diamine).

Schematically, this may be represented in Equation I:

Polyphenylquinoxalines prepared from such condensations are configurationally unordered with three possible isomers distributed randomly along the polymer chain; see Hergenrother, Encyclopedia of Polymer Science Technology, Vol. 13, p. 55, (1988).

As a direct result of the use of the condensation reaction 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 crystallinity renders them subject to attack by chlorinated organic solvents.

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

Third, the structure of polyphenylquinoxaline is difficult to vary.

Thus, it is an object of this invention to prepare configurationally 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 ordered or not, by a means other than the bis(phenyl-a-diketone)/bis(o-diamine) condensation, so that the use of expensive bis(phenyl-a-diketones) may be avoided and so that the polyphenylquinoxaline structure can be more readily and conveniently varied.

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:

where Ar is 1,2,4,5-tetrasubstituted benzene, 3,3',4,4'-tetrasubstituted; biphenyl, diphenylether, diphenylmethane, diphenylketone, diphenylsulfone, diphenylthioether or any appropriate bis(o-diamine) and mixtures 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:
where \( Z = \text{H, Cl, Br, OCH}_3, \text{CH}_3, \text{CH}_2\text{CH}_3, \text{or Ph}. \) 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:

\[
\begin{align*}
\text{HOFQPOH} + 2 \text{H}_2\text{N}-\text{Ar}^Z \rightarrow \text{HO} - \\
\text{solvent} \quad \text{heat} \quad \text{OH}
\end{align*}
\]

In the case where \( Z = \text{H} \), 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:

\[
\text{alkali metal base} \quad \text{solvent} \quad \text{heat}
\]

and where \( Y = \text{F, Cl, or NO}_2 \).

The polyphenylquinoxaline synthesis and product structure may be represented below, in its two main variants:

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

\( Y \) is F, Cl, or NO\(_2\),
\( R \) is nil, SO\(_2\), CO, O, S, C(CH\(_3\))\(_2\), C(CF\(_3\))\(_2\), or CH\(_2\)

and

\( X \) is: C\( \equiv \)O, SO\(_2\),

and wherein \( n \) is an integer between 4 and 100.

Where the di(hydroxyphenyl)quinoxaline monomers have structural isomers, the resultant polyphenylquinoxaline is not configurationally ordered, but the polyphenylquinoxalines are new and have excellent properties.
inherent viscosity of 1.09 dL/g and a glass transition at 25°C of 11,500 psi, 35,000 psi and 7.7% and at X-ray diffraction.

Yield 5.1 g (97%) of off-white polymer with drying. Yield 5.1 g (97%) of off-white polymer with drying. Yield 5.1 g (97%) of off-white polymer with drying. Yield 5.1 g (97%) of off-white polymer with drying.

**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.

**EXAMPLES**

**EXAMPLE 1**

The following Example illustrates the reaction sequence for the synthesis of the polyphenylquinoxaline where Y = F, R = nil and X is:

\[
\text{See Equation VI.}
\]

Monomer Synthesis-6,6’-bis[2-(4-hydroxyphenyl)-3-phenylquinoxaline] and isomers: Into a 250 ml round bottom flask equipped with a magnetic stirrer 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), 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. 336°C. Anal. Calcd. for C₂₀H₁₄N₂O₂: 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 mechanical stirrer, thermometer, nitrogen inlet, moisture trap, and reflux condenser was placed 1,3-bis(4-fluorobenzoyl)benzene (1.9339 g, 0.006 mol), 2,3-bis(4-hydroxyphenyl)-3-phenylquinoxaline and isomers (3.5678 g, 0.0274 mol) and absolute ethanol (30 ml). The solution was stirred at room temperature for one-half hour, then refluxed overnight. The mixture was heated to reflux. The solvent was removed by vacuum distillation and the solid was 17°C. of 6550 psi, 250,000 psi and 65 percent respectively.

**EXAMPLE 2**

The following Example illustrated the reaction sequence for the synthesis of a semi-crystalline polyphenylquinoxaline where Y is F, X is and Z is H. See Equation V.

**EXAMPLE 3**

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 was 17°C. of 6550 psi, 250,000 psi and 65 percent respectively.

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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 1,2-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 was 17°C. of 6550 psi, 250,000 psi and 65 percent respectively.

**EXAMPLE 2**

The following Example illustrated the reaction sequence for the synthesis of a semi-crystalline polyphenylquinoxaline where Y is F, X 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 was 17°C. of 6550 psi, 250,000 psi and 65 percent respectively.

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EXAMPLE 3
The following Example illustrates the reaction sequence for the synthesis of a semi-crystalline polyphenylquinoxaline where Y is F, X is SO₂ and Ar is

![Chemical Structure](image)

See Equation V.

Monomer 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-hydroxyphenylglyoxylyl)benzene (5.1412 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 4,4'-difluorodiphenyl sulfone (1.2712 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, T_m ) °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>268</td>
</tr>
<tr>
<td>CO</td>
<td>CO</td>
<td>1.30</td>
<td>253</td>
</tr>
<tr>
<td>CO</td>
<td>terephthaloyl</td>
<td>1.01</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° C.

**Determined by differential scanning calorimetry at 20° C./min.

**TABLE 2**

<table>
<thead>
<tr>
<th>X</th>
<th>( \eta_{inh. \text{ dL/g}} )</th>
<th>( T_g. \text{ °C.} ) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>0.54</td>
<td>240</td>
</tr>
<tr>
<td>CO</td>
<td>0.58</td>
<td>209</td>
</tr>
</tbody>
</table>
TABLE 2-continued

POLYMER CHARACTERIZATION

<table>
<thead>
<tr>
<th>X</th>
<th>(\eta_{in}) dL/g*</th>
<th>(T_g), °C**</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CO}_2)</td>
<td>0.83</td>
<td>208 ((T_m = 365))</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>0.50</td>
<td>179</td>
</tr>
<tr>
<td>(\text{SO}_2)</td>
<td>0.52</td>
<td>179 ((T_m = 377))</td>
</tr>
<tr>
<td>(\text{SO}_2)</td>
<td>0.24</td>
<td>235 ((T_m = 388))</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 United States is:

1. A poly(phenylquinoxaline) consisting of repeating units having the general structural formula

\[
\text{Ar} - \text{C} - \text{N} - \text{Ar}
\]

wherein the substitution of oxygen is selected from the group consisting of meta-meta, para-para, and para-meta;

wherein \(\text{Ar}\) is a radical selected from the group consisting of:
wherein R is a bond or is selected from the group consisting of: O, S, C==O, SO₂, CH₂, C(CH₃)₂, and C(CF₃)₂;

and wherein n is an integer between 4 and 100.

2. The poly(phenylquinoxaline) of claim 1 wherein Ar is a radical represented by:

and R is a bond or is selected from the group consisting of: O, and C==O.

3. The poly(phenylquinoxaline) of claim 2 wherein X is selected from the group consisting of: SO₂, C==O, and

and X is selected from the group consisting of SO₂, C==O, and
5. The polymer of claim 4 wherein Z is H.
6. The poly(phenylquinoxaline) of claim 1 wherein Ar is represented by:

and X is SO₂.
7. The polymer of claim 6 wherein Z is H.
8. A process for synthesizing polyphenylquinoxalines by aromatic nucleophilic displacement, which comprises reacting a di(hydroxyphenyl)quinoxaline having the general structure:

wherein Ar is a radical selected from the group consisting of:

wherein R is a bond or is selected from the group consisting of:
O, S, C=O, SO₂, CH₂, C(CH₃)₂, and C(CF₃)₂;

wherein Z is a substituent selected from the group consisting of:
H, F, Cl, Br, CH₃, CH₂CH₃, OCH₃, C₆H₅, and C₂H₅OH; with an activated aromatic dihalide or dinitro compound having the general structure:

wherein X is a radical selected from the group consisting of:

(A)

(B)
wherein Y is selected from the group consisting of: Cl, F, and NO₂, and wherein said reaction is carried out in a polar aprotic solvent selected from the group consisting of N,N-dimethylacetamide, N-methylpyrrolidinone, sulfolane, diphenylsulfolane, N-cyclohexylpyrrolidinone, and dimethylsulfoxide; wherein said reaction is carried out in the presence of an alkali metal base selected from the group consisting of K₂CO₃, Na₂CO₃, KOH, and NaOH; and wherein said reaction is carried out with the application of heat.

9. The method of claim 8 wherein X is selected from the group consisting of: SO₂, C==O, and

10. The method of claim 8 wherein Y is selected from the group consisting of F and Cl.

11. The process of claim 9 wherein Y is selected from the group consisting of F and Cl.

12. The method of claim 8 where the solvent is N,N-dimethylacetamide.

* * * * *