PHENYLATED POLYAMIDE-QUINOXALINES

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ABSTRACT: A series of new phenylated amide-quinoxalines which have excellent thermal and solubility properties have been synthesized and characterized. The copolymers derived from terephthaloyl and iso-phthaloyl chlorides have decomposition temperatures between 445-495°C while those from phthaloyl chloride are between 325-350°C. High molecular weight polymers were prepared by reacting aromatic bis-o-diamines with bis(benzilyl)amides. These new polymers have potential use as high temperature films, fibers and adhesives.

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PHENYLATED POLYAMIDE-QUINOXALINES

This report contains information concerning the synthesis and characterization of new phenylated amide-quinoxaline copolymers which have excellent thermal and solubility properties. It has been shown that the thermal stabilities of the meta and para copolymers are comparable and superior to those of the ortho copolymers. These new polymers should be useful as adhesives and coating materials in ordnance components. In addition, the para copolymers are potential high strength-high modulus fiber candidates.

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ROBERT WILLIAMSON II
Captain, USN
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ALBERT LIGHTBODY /
By direction
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INTRODUCTION

The Navy has a continuing interest in ordnance materials that are capable of withstanding temperature extremes. There is a need for better high temperature adhesives in aircraft. New materials are required for the protection of sensitive electronic equipment and flight decks from jet aircraft and missile exhausts. High temperature fibers are also needed which are non-melting and non-flammable for use as fire protection in the flight suits of Navy pilots.

Polymers have been developed in recent years like the polybenzimidazoles, polyimides and polyquinoxalines that are thermally stable and resistant to air oxidation. However, these polymers have proved to be intractable and difficult to process. The Naval Ordnance Laboratory has been actively seeking a solution to this problem of processability and has developed in recent years the phenylated polyquinoxalines (PPQ) and phenylated imide-quinoxalines. These polymer systems exhibit excellent solubilities in a variety of solvents and have been used as laminating resins in high temperature composites and also have been fabricated into films and fibers. It should be noted that aromatic polyamide fibers are presently under commercial development by several companies. Their high specific strength and modulus properties combined with their high elongation-to-break values make these fibers attractive in the area of composites as a possible replacement for glass fibers.

The objective of this work was to synthesize and characterize a new series of phenylated amide-quinoxalines which because of their inherent structure should have improved solubility and thermal properties.

BACKGROUND

Aromatic polyamides have been shown\(^\text{1}\) to have outstanding thermal stabilities. Preston\(^\text{2}\) demonstrated that ordered aromatic copolyamides were much more stable than random polymers and that this stability increased as the p-phenylene content was increased. However, the solubility of ordered aromatic polyamide systems is limited to solvents such as dimethylacetamide-lithium chloride, and, once isolated, the p-phenylene copolymers could not be redissolved.\(^\text{2}\)

NOL has been active in the development of high temperature-processable polymer systems such as the phenylated polyquinoxalines\(^\text{3-7}\) and the phenylated imide-quinoxalines.\(^\text{8-9}\) It was felt that if a polymer based on the amide-quinoxaline structure could be
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synthesized that it would have improved solubility properties without any decrease in thermal performance.

EXPERIMENTAL

This paper describes the synthesis, characterization and evaluation of a series of polyamide-quinoxalines made from phthaloyl, isophthaloyl and terephthaloyl chlorides. Polymer characterization included elemental analysis and determination of inherent viscosities and glass transition temperatures. Thermal stability was evaluated by means of thermogravimetric analysis in vacuum and solubilities were determined in a number of solvents.

Monomer Synthesis

4-Aminobenzil. The synthesis of this compound has been described in detail in a previous publication.\(^8\)

\[ \text{N,N'-Bis(4-benzyl)terephthalamide (XIV).} \]

A mixture of 0.400 g (0.00178 mole) of 4-aminobenzil, 0.181 g (0.00089 mole) of terephthaloyl chloride, and 20 ml of dry toluene was heated at reflux with stirring until the evolution of HCl was completed (4-5 hr). The light yellow solid which precipitated upon cooling was filtered and washed with dry toluene. The solid product was purified by refluxing it twice with 100 ml portions of reagent alcohol to give 0.50g (97%) of a grey-yellow solid which had a melting point of 331°C.

\[ \text{N,N'-Bis(4-benzyl)phthalamide (XII) and N,N'-bis(4-benzyl)-isophthalamide (XIII).} \]

These compounds were prepared by the above procedure, and their elemental analyses and melting points are given in Table I.

Aromatic Tetraamines

The following tetraamines were obtained commercially and were purified by recrystallization from water with charcoal and a trace of sodium sulfide: 3,3',4,4'-tetraaminodiphenyl ether, 3,3',4,4'-tetraaminobenzophenone, and 3,3',4,4'-tetraaminodiphenylysulfone.

Model Compound

\[ \text{N,N'-Bis[1,4-2[(3-phenylquinoxaliny)]phenylene]terephthalamide.}\]

This model compound was prepared by reacting o-phenylenediamine with XIV under the same conditions used in the polymerization of these bis(benzyl)amides with bis-o-diamines.

A mixture of 0.108 g (0.001 mole) of o-phenylenediamine and 0.290 g (0.0005 mole) of N,N'-bis(4-benzyl)terephthalamide (XIV) was added to 5 ml of m-cresol. After heating at 120-130°C for 2 hr the reaction was completed by refluxing for an additional hour. The
reaction mixture was added to 50 ml of reagent alcohol and the yellow solid which separated was filtered. The solid was slurried several times in hot alcohol. The yield was 0.35 g (95%).

ANAL. Calcd C, 79.54%; H, 4.56%; N, 11.60%; Found: C, 79.39%; H, 4.56%; N, 11.63%.

Polymer Synthesis

All polymers were prepared under similar reaction conditions. Equimolar quantities of the o-bisdiamines and bis(benzyl) amides were stirred under nitrogen in m-cresol to give 10% polymer solutions. The reactants were heated at 120-130°C for 2 hr followed by an additional 2 hr at reflux to complete the polymerization. The polymers were isolated by precipitation in methanol followed by filtration and drying. The polymer properties are given in Table II.

RESULTS AND DISCUSSION

Synthesis

The synthesis of 4-aminobenzil was carried out according to the reaction sequence (1).

\[
\begin{align*}
\text{O}_2\text{N-} & \quad \text{CH}_2\text{CO-} \quad \text{Fe} \quad \text{H}_2\text{N-} & \quad \text{CH}_2\text{CO-} \quad \text{Ac}_2\text{O} \\
\text{CH}_3\text{CONH-} & \quad \text{CH}_2\text{CO-} \quad \text{SeO}_2 \\
\text{CH}_3\text{CONH-} & \quad \text{COCO-} \quad \text{HCl} \quad \text{H}_2\text{N-} & \quad \text{COCO-} \\
\end{align*}
\]

The overall yield for the preparation is about 25%.

The product, 4-aminobenzil, was then reacted with phthaloyl, isophthaloyl, and terephthaloyl chlorides to produce the following bis(benzyl)amides:
where -Ar- is the o-(XII), m-(XIII), or p-phenylene (XIV) group.

The preparation of the amide-quinoxaline polymers was carried out in m-cresol by condensation of the above bis(benzilyl) amides with various bis-o-diamines according to eq. (2).

\[
\begin{align*}
\text{nH}_2\text{N} & \text{-} \left[ \begin{array}{c}
\text{NHCO-} \text{-} \text{Ar-} \text{-} \text{CONH-} \\
\end{array} \right] \\
\text{nH}_2\text{N} & \text{-} \left[ \begin{array}{c}
\text{NHCO-} \text{-} \text{Ar-} \text{-} \text{CONH-} \\
\end{array} \right] \\
\end{align*}
\]

The polymers obtained are tabulated in Table II.

High molecular weight polymers were obtained from the isophthaloyl- and terephthaloyl diamides which gave strong fibers and films from m-cresol solutions. The inherent viscosities of these polymers ranged from 0.85 to 1.85 dL/g (Table II). The phthaloyl series, on the other hand, were low molecular weight polymers with inherent viscosities in the range 0.02-0.09 dL/g.

Thermal Properties

The relative order of thermal stability of the amide-quinoxaline copolymers as determined by thermal gravimetric analysis in vacuum was para > meta > ortho. In the case of the terephthaloyl polymers, the temperature at which the initial weight loss occurred in para polymers was about 450°C, while the meta polymers began to decompose between 425 and 435°C, and the ortho polymers between 325 and 350°C (Figs. 1, 2, 3). These results agree with Wright's\(^1\) work on the polyamides, in which he found that thermal stability improved as the p-phenylene content of the polymers increased. The low level of thermal stability of the ortho polymers could be a result of their low molecular weights or a consequence of chain scission by imide formation at higher temperatures according to the scheme (3).
The weight losses at 800°C in vacuum for the para and meta polymers were comparable (40-60%), while the ortho polymers lost 80-95% of their original weight.

Within a given series of copolymers the order of weight retention at 800°C based on the bridging of the tetraamine was CO > nil > SO₂ > O. This generalization held whether the diamide was the o-, m-, or p-phenylene isomer.

Glass Transition Temperatures (Tₐ)

The glass transition temperatures were obtained by dielectric loss measurements on thin films as previously described¹⁹ (Table II).

Solubility of Polymers

Qualitative solubilities of polymers were determined on powdered samples in excess solvent (Table III). The samples were allowed to stand overnight at room temperature without agitation before a solubility judgment was made. The polymers had excellent solubility in dimethylacetamide m-cresol and N-methylpyrrolidone but were insoluble in chloroform, which is a solvent for phenylated polyquinoxaline and imide-quinoxaline copolymers. Partial solubility or swelling was noted for certain polymers in formic acid, tetrahydrofuran, and tetrachloroethane. The solubilities of the ortho polymers were not recorded because of the low molecular weight of these polymers.

CONCLUSION

Soluble, phenylated amide-quinoxaline ordered copolymers of high molecular weight can be prepared by condensation of bis(benzi-lyl)amides with various tetraamines. The resulting polymers are nonmelting, thermally stable materials which can be processed from solution.
RECOMMENDATIONS

In addition to their excellent thermal and solubility properties, these phenylated amide-quinoxalines are quite polar in nature and should be evaluated in areas such as high temperature adhesives in supersonic aircraft. The para copolymers have the potential to be fabricated into high modulus crystalline fibers capable of withstanding extreme temperature environments. These fibers could then be used in protective flight suits where fire hazards to personnel exist aboard ships or Navy aircraft.
REFERENCES


TABLE I
Characterization of Monomers

\[
\text{\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{monomers.png}
\caption{Structure of the monomers.}
\end{figure}}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>(-\text{Ar-})</th>
<th>Color</th>
<th>Mp, (^{\circ}\text{C})</th>
<th>Elemental analyses(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>XII</td>
<td></td>
<td>Lemon yellow</td>
<td>213</td>
<td>C, %  (74.37) (74.47)</td>
</tr>
<tr>
<td>XIII</td>
<td></td>
<td>Light yellow</td>
<td>233</td>
<td>C, %  (74.54) (74.47)</td>
</tr>
<tr>
<td>XIV</td>
<td></td>
<td>Grey-yellow</td>
<td>331</td>
<td>C, %  (74.28) (74.47)</td>
</tr>
</tbody>
</table>

\(^{a}\) The calculated values are shown in parentheses.
### TABLE II. Characterization of Phenylated Amide-Quinoxaline Copolymers

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ar</th>
<th>X</th>
<th>Inherent viscosity, dl/g(^a)</th>
<th>Glass transition temperature, (T_g, ^\circ C)</th>
<th>Elemental analyses(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>o-phenylene</td>
<td>nil</td>
<td>0.09</td>
<td>-</td>
<td>78.90, 4.62, 9.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(79.76, 4.18, 11.63)</td>
</tr>
<tr>
<td>II</td>
<td>o-phenylene</td>
<td>CO</td>
<td>0.02</td>
<td>-</td>
<td>77.90, 3.85, 10.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(78.39, 4.03, 11.19)</td>
</tr>
<tr>
<td>III</td>
<td>o-phenylene</td>
<td>O</td>
<td>0.02</td>
<td>-</td>
<td>77.40, 4.28, 10.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(78.04, 4.09, 11.38)</td>
</tr>
<tr>
<td>IV</td>
<td>m-phenylene</td>
<td>nil</td>
<td>1.85</td>
<td>279</td>
<td>78.25, 4.11, 11.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(79.76, 4.18, 11.63)</td>
</tr>
<tr>
<td>V</td>
<td>m-phenylene</td>
<td>CO</td>
<td>1.20</td>
<td>253</td>
<td>76.03, 4.15, 10.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(78.39, 4.03, 11.19)</td>
</tr>
<tr>
<td>VI</td>
<td>m-phenylene</td>
<td>SO(_2)</td>
<td>1.20</td>
<td>278</td>
<td>71.45, 4.02, 10.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(73.27, 3.84, 10.68)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.05 (4.08)</td>
</tr>
<tr>
<td>VII</td>
<td>m-phenylene</td>
<td>O</td>
<td>1.32</td>
<td>298</td>
<td>76.70, 4.24, 10.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(78.04, 4.09, 11.38)</td>
</tr>
<tr>
<td>VIII</td>
<td>p-phenylene</td>
<td>nil</td>
<td>1.65</td>
<td>-</td>
<td>77.73, 4.35, 11.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(79.76, 4.18, 11.63)</td>
</tr>
<tr>
<td>IX</td>
<td>p-phenylene</td>
<td>CO</td>
<td>1.00</td>
<td>247</td>
<td>76.68, 4.09, 10.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(78.39, 4.03, 11.19)</td>
</tr>
<tr>
<td>X</td>
<td>p-phenylene</td>
<td>SO(_2)</td>
<td>0.85</td>
<td>228</td>
<td>71.36, 3.63, 10.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(73.27, 3.84, 10.68)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.00 (4.08)</td>
</tr>
<tr>
<td>XI</td>
<td>p-phenylene</td>
<td>O</td>
<td>1.04</td>
<td>266</td>
<td>77.10, 4.08, 11.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(78.04, 4.09, 11.38)</td>
</tr>
</tbody>
</table>

\(a\) Viscosities were determined in m-cresol at 30 ± 0.1°C.

\(b\) Determined by dielectric loss measurements in vacuum on polymer films.

\(c\) The calculated values are shown in parentheses.
TABLE III
Solubility of Phenylated Amide-Quinoxaline Copolymers

<table>
<thead>
<tr>
<th>Solvent</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
<th>X</th>
<th>XI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>-</td>
<td>±</td>
<td>-</td>
<td>±</td>
<td>-</td>
<td>±</td>
<td>±</td>
<td>±</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>±</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dimethylacetamide</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>N-Methylpyrrolidone</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Pyridine</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Formic acid</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

a Solubility: (+) soluble; (-) insoluble; (±) swelling or limited solubility.
FIG. 1 THERMAL GRAVIMETRIC ANALYSIS OF ortho PHENYLENE AMIDE-QUINOXALINE COPOLYMERS
FIG. 2 THERMAL GRAVIMETRIC ANALYSIS OF META PHENYLENE AMIDE-QUINOXALINE COPOLYMERS
FIG. 3 THERMAL GRAVIMETRIC ANALYSIS OF para PHENYLENE AMIDE-QUINOXALINE COPOLYMERS
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Naval Ship Research and Development Center
Annapolis, Maryland  21404
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A series of new phenylated amide-quinoxalines which have excellent thermal and solubility properties have been synthesized and characterized. The copolymers derived from terephthaloyl and isophthaloyl chlorides have decomposition temperatures between 445-495°C while those from phthaloyl chloride are between 325-350°C. High molecular weight polymers were prepared by reacting aromatic bis-o-diamines with bis(benzyl)amides. These new polymers have potential use as high temperature films, fibers and adhesives.
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