Aromatic polyamide resins having repeating units, each containing at least one m-ethynyl amido subunit:

These resins can be thermally treated to undergo intramolecular cyclization, without evolution of volatiles, into polyimidines containing the following subunit.
ETYNYL-CONTAINING AROMATIC POLYAMIDE RESIN

RIGHTS OF THE GOVERNMENT

The invention described herein may be manufactured and used by or for the Government of the United States for all governmental purposes without the payment of any royalty.

This is a division of application Ser. No. 06/807,426, filed Dec. 10, 1985, now U.S. Pat. No. 4,663,425.

BACKGROUND OF THE INVENTION

This invention relates to novel polymeric compounds and to a method for their synthesis. In particular, this invention relates to novel ethynyl-substituted aromatic polyamides.

Interest in laminates and laminating processes for use in a wide variety of industrial applications has increased considerably in the past few years. Glass fiber laminates, for example, find wide use as structural materials because of their lightweight, high relative strength, and high resistance to corrosion and other damaging effects encountered in an environment subject to extreme fluctuations in temperature and weather. Consequently, a concentrated research effort has evolved in an attempt to develop polymeric materials suitable for use as laminating resins. Such resins must possess a high degree of thermal stability and strength after curing coupled with good solubility characteristics before curing, if they are to be useful for impregnating and bonding the wide variety of laminate materials presently in use.

The research effort referred to above has culminated in the development of several resinous materials that have been found suitable from a stability and strength standpoint. Unfortunately, however, problems have arisen when using such materials due to the evolution of gas during the curing step which occurs after the laminate sheets are impregnated. The curing process which liberates gaseous side products has the deleterious effects of producing voids in the cured laminates which, in turn, substantially weakens the final laminated product.

It is an object of the present invention to provide novel aromatic polyamide resins which can be cured without evolving volatile side products.

Other objects, aspects and advantages of the invention will be readily apparent to those skilled in the art from the following detailed disclosure of the invention.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a novel aromatic polyamide resin having repeating units, each containing at least one o-ethynyl amido subunit:

The resins of this invention which contain the above subunit can be thermally treated to undergo intramolec-ular cyclization, without evolution of volatiles, into polyimides containing the following subunit:

More specifically, in accordance with the present invention there is provided a first aromatic polyamide resin of the general formula:

wherein n is an integer and Ar is a divalent aromatic radical having the general formula:

wherein Z is selected from the following: --CH₂--; --CO--; --S--; --O--; and --SO₂--.

There is also provided a second aromatic polyamide resin represented by either of the following formulas:

wherein n and Ar are as described above and Ar' is a monovalent aromatic radical selected from the group consisting of phenyl and Cl- to C3-substituted phenyl, such as, for example, p-tolyl, p-cumenyl, p-ethylphenyl, and p-propylphenyl.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polymer represented by Formula III is prepared by the polycondensation of tolane-2,4'-dicarbonyl chloride with a diamino compound. The reaction may be represented by the following equation:
on the order of

provide thermoset resins. When heated to temperatures

hours to a stirred solution of 1,3-bis(dibromomethyl)-

terephthaloyl chloride with a diamino compound. The reaction may be represented by the following equation:

\[
\text{Ar}-\text{C}+\text{Cl} \rightarrow \text{Ar}-\text{C} \quad \text{Cl}
\]

The polymer represented by Formula IV is prepared by the polycondensation of a 2,4-bis(arylthynyl)isophthaloyl chloride with a diamino compound. The reaction may be represented by the following equation:

\[
\text{H}_3\text{N}-\text{Ar}-\text{NH}_2 \rightarrow \text{IV}
\]

As shown by the above equations, substantially equi-
molar amounts of reactants are utilized. The reaction is carried out in the presence of a suitable solvent, one which is inert to the reactants and the resulting poly-
mer, and one in which at least one of the monomers is soluble. Examples of suitable solvents include N-methyl-
2-pyrrolidone, N,N-dimethylformamide, tetramethyl urea, MW, and one in which at least one of the monomers is

which is inert to the reactants and the resulting poly-

teraphthaloyl chloride with a diamino compound. The reaction may be represented by the following equation:

\[
\text{Ar}-\text{C}+\text{Cl} \rightarrow \text{Ar}-\text{C} \quad \text{Cl}
\]

The polymer represented by Formula V is prepared by the polycondensation of a 2,4-bis(arylthynyl)iso-

theticoyl chloride with a diamino compound. The reaction may be represented by the following equation:

\[
\text{H}_3\text{N}-\text{Ar}-\text{NH}_2 \rightarrow \text{V}
\]

EXAMPLE I

Tolane-2,4'-dicarboxyl Chloride

2,4'-Tolane dicarboxylic acid (2.40 g, 0.009 moles) was stirred at room temperature for 48 hours in 35 ml of thionyl chloride (redistilled from boiled linseed oil). This suspension was then refluxed for eight hours to give a clear, light red solution. The excess thionyl chloride was then stripped off to give a grey solid, mp 79°-85° C. Recrystallization from hexane afforded 1.38 g (51% yield) of tolane-2,4'-dicarboxylic chloride as a

white, off-solid which after drying at 58° C./0.10

mm Hg exhibited mp 184.5°-185.5° C.

Anal. Calc'd for C_{23}H_{22}ClO_2: C, 63.39; H, 2.66; Cl, 23.39; MW, 266. Found: C, 63.42; H, 2.12; Cl, 23.21; MW, 266 (mass spectrum).

EXAMPLE II

4,6-Bis(phenylethynyl)isophthaloyl Chloride

Bromine (395.5 g, 2.472 mole) (dried over concen-

trated sulfuric acid) was added dropwise to stirred 4,6-
dibromo-1,3-xylene (150 g, 0.568 mole) in an ultraviolet irradiation apparatus. Approximately 90 ml of bromide was added over 2.5 hour with the temperature being maintained at 120°-130° C. An additional 20 ml was added over two hours at 130°-150° C. and the final 17 ml was added over two hours at 150°-160° C. After the bromine was completely taken up, the yellow reaction mixture was distilled in portions to give a 1,3-bis(di-
bromomethyl)-4,6-dibromobenzene as a white solid bp 178°-182° C./0.02 mm Hg. Recrystallization from absolute ethanol yielded a total of 259 g (79% yield) of white crystals, mp 115°-118° C.

Anal. Calc'd for C_{23}H_{16}Br_2: C, 66.58; H, 0.69; MW, 580, Found: C, 64.95; H, 0.67; MW, 580 (mass spectrum).

An aqueous solution of silver nitrate (71.0 g, 0.418 mole) in 544 ml of water added dropwise over three hours to a stirred solution of 1,3-bis(dibromomethyl)-

4,6-dibromobenzene (40.0 g, 0.069 mole) in 300 ml cello-
solve at 80°-85° C. The green reaction mixture was stirred at temperature for an additional 3.5 hours and filtered while hot. The collected precipitate was washed thoroughly with water and suction dried on the frit. Water added to the filtrate produced a white product that was recrystallized from cyclohexane to yield 6.1 g of white crystals. The dried green precipitate was extracted with hot benzene and the resulting material recrystallized from cyclohexane to yield 7.1 g of white crystals. Combined yield of 4,6-dibromoisophthalaldehyde was 13.6 g (66% yield). mp 188°-191° C.

Anal. Calc'd for C_{12}H_8Br_2O_2: C, 38.73; H, 3.25; Br, 36.41; MW, 436 (mass spectrum).

EXAMPLE III

2,5-Bis(phenylethynyl)terephthaloyl Chloride (Method I)

2,5-Dibromo-1,4-xylene (43.0 g, 0.163 mole) was dissolved in 350 ml of glacial acetic acid and 550 ml of acetic anhydride. To the vigorously stirred solution at 0°-5° C. was cautiously added 90 ml of concentrated sulfuric acid. With the temperature being maintained at 5° C., chromium trioxide (93.0 g, 0.530 mole) was gradually added over a period of 1.5 hours, care being taken to keep the reaction temperature below 5° C. The red reaction mixture gradually became very viscous and took on a deep green coloration. After being stirred for four more hours, it was then brought to room temperature and poured with stirring into five liters of cold water. The white precipitate was filtered and washed on the frit with water until no green color appeared in the washings. The white solid was stirred in two liters of 2% sodium carbonate solution for one hour, isolated by filtration, and washed well on the frit with water. Air drying overnight afforded 45.3 g (56% yield) of unpurified 2,5-dibromo a,a',a'-tetraacetoxy-1,4-xylene, mp 200°-210° C. Recrystallization of an analytical sample from isopropanol gave mp 219°-221° C.

Anal. Calc'd for C_{16}H_{16}O_4Br_2: C, 39.23; H, 3.32; Br, 54.75; MW, 550 (mass spectrum).

A solution of diphenyl(a-chlorobenzyl)phosphonate (28.70 g, 0.080 mole) in 150 ml of dry dimethylsulfoxide was cooled to 0°-5° C. Sodium hydride (3.84 g, 0.016 mole) (as a 50% suspension in mineral oil) was added to the rapidly stirred solution. With the temperature being maintained at 0°-5° C., 2,5-dibromoterephthalaldehyde (11.64 g, 0.04 mole) slurried in 50 ml of dry dimethylsulfoxide was added over a five minute period. Considerable foaming took place during the addition. After being allowed to continue at room temperature overnight, the reaction mixture was added to 250 ml of ice water. The resultant beige precipitate was filtered and washed on the frit with water. Drying at 60° C./1.0 min Hg for two hours yielded 16.63 g of beige product, mp 203°-235° C. The crude product was extracted with 400 ml of heptane for two hours in an extraction apparatus. The heptane solution upon cooling gave 8.45 g (48% yield) of 1,4-bis(phenylethynyl)-2,5-dibromobenzene in light yellow crystals, mp 155°-158° C. An additional 3.5 g of slightly lower melting material was recovered from the mother liquor.

Anal. Calc'd for C_{24}H_{14}Cl_2O_2: C, 60.58; H, 2.77; Br, 36.65; MW, 436. Found: C, 60.85; H, 2.52; Br, 36.41; MW, 436 (mass spectrum).

n-Butyl lithium (2.11 g, 0.033 mole) (14.25 ml of a 2.32M solution in hexane) was added over five minutes.
to a vigorously stirred solution of 1,4-bis(phenylethynyl)2,5-dibromobenzene (6.54 g, 0.015 mole) in 500 ml of ether at 0° C. The initial yellow slurry took on a brown color for several minutes before a dull yellow precipitate was formed. After being allowed to stir for three hours at 0° C. under a nitrogen blanket, the reaction mixture was added to a slurry of dry ice in 300 ml of ether. This slurry was stirred for five hours and the excess dry ice was then allowed to evaporate. The ether solution was then extracted with 500 ml of a very dilute aqueous potassium hydroxide solution which was in turn extracted with 50 ml of ether. The cooled aqueous layer was acidified with dilute sulfuric acid to give a yellow precipitate which was isolated by filtration. Drying for three hours at 60° C./1.0 mm Hg yielded 5.10 g of crude product, mp >360° C. with slight shriveling at 190°-200° C. Recrystallization from isopropanol afforded 2.90 g (53% yield) of 2,5-bis(phenylethynyl)-terephthaloyl chloride as a powdery yellow solid, mp >360° C. with shrinking at 270°-275° C.

**Anal. Calc'd for C_{34}H_{22}N_{2}O_{4}:**

- C: 78.15;
- H: 3.00;
- N: 3.00;
- MW, 403. Found: C: 71.30; H: 2.91; MW, 403 (mass spectrum).

**EXAMPLE IV**

2,5-Bis(phenylethynyl)terephthalaldehyde (Method 2)

2,5-Dibromoterephthalaldehyde (29.2 g, 0.100 mole) and phenylacetylene (25.3 g, 0.250 mole) were dissolved at 80° C. under nitrogen in a mixture of freshly distilled triethylamine (200 ml) and pyridine (200 ml). Palladium acetate (0.54 g, 0.0024 mole) and triphenylphosphine (1.26 g, 0.0048 mole) were added to the vigorously stirred red solution. The resultant exotherm did not subside for fifteen minutes and a voluminous white precipitate was formed. After an additional hour at reflux, the red slurry was added with vigorous stirring to a sulfuric acid mixture. The slightly gummy brown precipitate was washed several times with water in a blender and isolated by filtration. It was dried overnight over phosphorus pentoxide at 80° C./1.0 mm Hg to yield 39.5 g of light brown solid, mp 145°-162° C. The crude product was recrystallized from ethyl acetate gave 14.6 g (44% yield) of 2,5-bis(phenylethynyl)terephthalaldehyde, mp 179°-181° C.

**Anal. Calc'd for C_{34}H_{22}N_{2}O_{4}:**

- C: 86.42; H: 4.42; MW 334 (mass spectrum).
- 2,5-Bis(phenylethynyl)terephthalaldehyde (5.01 g, 0.015 mole) was stirred under nitrogen in 300 ml of redistilled acetone at 0° C. Then a chromim trioxide/sulfuric acid solution was added and the reaction was allowed to proceed at 0° C. for an additional two hours. The resultant slurry was poured into 600 ml of ice water and the yellow precipitate was isolated by filtration. After being washed well on the filter with water, the yellow solid was allowed to dry on the filter. Drying for one hour at 50° C./1.0 mm Hg over phosphorus pentoxide afforded 5.40 g (98% yield) of 2,5-bis(phenylethynyl)terephthaloyl chloride, mp >360° C. with slight shrinking at 260°-270° C.

**EXAMPLE V**

Polycondensation of Tolane-2,4'-dicarboxylic Chloride with 4,4'- (m-Phenylenedioxy)dianiline

4,4'-(m-Phenylenedioxy)dianiline (0.6724 g, 0.0023 mole) was dissolved in 5 ml of N-methyl-2-pyrrolidone (distilled from calcium hydride) and the resultant water-white solution was cooled to 0° C. Tolane-2,4'-dicarboxylic chloride (0.6972 g, 0.0023 mole) followed by eight ml of N-methyl-2-pyrrolidone was added to the vigorously stirred solution. The resultant pale green solution was stirred at 0° C. for an hour and at room temperature for 36 hours. The polymer was precipitated from methanol and was washed several times with methanol in a continuous extraction apparatus for 36 hours. Drying at 58° C./0.10 mm Hg for 16 hours gave 1.0 g (83% yield) of cream colored polymer: η_inch = 0.31 dl/g (N,N-dimethylacetamide, 25° C., 0.2 dl/g).

**EXAMPLE VI**

Polycondensation of 2,5-Bis(phenylethynyl)terephthaloyl Chloride with 4,4'- (m-Phenylenedioxy)dianiline

4,4'-(m-Phenylenedioxy)dianiline (0.5847 g, 0.0020 mole) was dissolved in 10 ml of N,N-dimethylacetamide (distilled from calcium hydride). The resultant water-white solution was cooled under nitrogen to 0° C. 2,5-Bis(phenylethynyl)terephthaloyl chloride (0.8065 g, 0.0020 mole) was added as a solid to the vigorously stirred solution over a five minute period. Three ml of N,N-dimethylacetamide were used to wash the residual dicarboxylic chloride into the reaction flask. The resultant yellow slurry gradually became a clear pale green solution over the course of thirty minutes. After being stirred for three hours at 0° C. and sixteen hours at room temperature, the slightly viscous solution was a pale yellow color. The polymer was isolated by precipitation from methanol and washed several times with methanol in a blender. Drying at 58° C./0.10 mm Hg for eight hours and at 100° C./0.10 mm Hg for four hours gave 1.20 g (96% yield) of fluffy yellow polymer: η_inch = 0.51 dl/g (MeSO_3)H, 25° C., 0.2 g/dl).
EXAMPLE VII
Polycondensation of 2,5-Bis(phenylethynyl)terephthaloyl Chloride with 4,4'-Oxydianiline

4.4'-Oxydianiline (0.2880 g, 0.0014 mole) was dissolved in 5 ml of N-methyl-2-pyrrolidone (distilled from calcium hydride) and the resultant water-white solution was cooled under nitrogen to 0-5° C. 2,5-Bis(phenylethylnyl)terephthaloyl chloride (0.5800 g, 0.0014 mole) was added to the vigorously stirred solution with four ml of solvent being used to wash residual monomer into the reaction flask. The reaction temperature was maintained at 0-5° C. for several hours and at room temperature for several days. The resultant clear yellow solution was added to 100 ml of methanol and the precipitated polymer was isolated by filtration. It was washed with methanol in a blender and extracted for several days with hot methanol in an extraction apparatus. Drying at 100° C.0.10 mm Hg for six hours yielded 0.68 g (92% yield) of pale yellow polymer: η = 0.67 dl/g (MeSO₃H, 25° C., 0.2 g/dl).

TABLE

<table>
<thead>
<tr>
<th>Polymer No.</th>
<th>Monomer</th>
<th>Visc. (g)</th>
<th>Tg-init (°C)</th>
<th>Tg-final (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Toluene-2,4'-dicarboxylic acid chloride</td>
<td>4,4'-Oxydianiline</td>
<td>0.29 (b)</td>
<td>170</td>
</tr>
<tr>
<td>II</td>
<td>Toluene-2,4'-dicarboxylic acid chloride</td>
<td>4,4'-oxydianiline</td>
<td>0.31</td>
<td>182</td>
</tr>
<tr>
<td>III</td>
<td>2,5-Bis(phenylethynyl)terephthaloyl chloride</td>
<td>4,4'-Oxydianiline</td>
<td>0.30 (b)</td>
<td>200</td>
</tr>
<tr>
<td>IV</td>
<td>2,5-Bis(phenylethynyl)terephthaloyl chloride</td>
<td>4,4'-oxydianiline</td>
<td>0.31</td>
<td>189</td>
</tr>
<tr>
<td>V</td>
<td>4,6-Bis(phenylethynyl)terephthaloyl chloride</td>
<td>4,4'-Oxydianiline</td>
<td>0.20 (b)</td>
<td>185</td>
</tr>
<tr>
<td>VI</td>
<td>4,6-Bis(phenylethynyl)terephthaloyl chloride</td>
<td>4,4'-oxydianiline</td>
<td>0.26</td>
<td>174</td>
</tr>
</tbody>
</table>

TABLE IX

The polymer listed as polymer no. IV in the preceding table was heated in an oven under nitrogen at 255° C. for 16 hours. The resulting polyphthalimidine had a Tg-init of 278° C. Differential scanning calorimetry and thermomechanical analysis revealed an exotherm at 367° C., indicating incomplete cyclization. Additionally, the IR spectrum exhibited bands indicative of the uncyclized polyamide structure as well as the polyphthalimidine structure.

Various modifications may be made in the present invention without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. An aromatic polyamide resin capable of intramolecular cyclization into a polyimine containing repeating units of the formula:

wherein Ar is a divalent aromatic radical having the general formula:

wherein Z is selected from the group consisting of -H₂-, -CO-, -SO-, -O-, and -SO₂-.

2. The resin of claim 1 wherein Ar is
3. The resin of claim 1 wherein Ar is
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,752,642
DATED : June 21, 1988
INVENTOR(S) : Robert C. Evers et al

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col 3, lines 16-20, the structure should appear as follows:

\[
\begin{align*}
\text{Ar}^\prime - \text{C} & \equiv \text{C} \quad \text{COCl} \\
\text{ClOC} & \quad \text{C} \equiv \text{C} - \text{Ar}^\prime
\end{align*}
\]

Col 3, lines 30-34, the structure should appear as follows:

\[
\begin{align*}
\text{ClOC} & \quad \text{COCl} \\
\text{Ar}^\prime - \text{C} & \equiv \text{C} \quad \text{C} \equiv \text{C} - \text{Ar}^\prime
\end{align*}
\]

Col 4, line 52, "bromide" should read "bromine".
Col 4, line 63, "MV" should read "MW".
Col 5, line 52, "c, 78.68;" should read "C, 78.68;".
Claim 1, last line, "-SO-" should read "-S-".

Signed and Sealed this Tenth Day of January, 1989

Attest:

DONALD J. QUIGG

Attesting Officer

Commissioner of Patents and Trademarks