Novel polyimides containing pendant siloxane groups (PISOX) were prepared by the reaction of functionalized siloxane compounds with hydroxy containing polyimides (PIOH). The pendant siloxane groups on the polyimide backbone offer distinct advantages such as lowering the dielectric constant and moisture resistance and enhanced atomic oxygen resistance. The siloxane containing polyimides are potentially useful as protective silicon oxide coatings and are useful for a variety of applications where atomic oxygen resistance is needed.
POLYIMIDES CONTAINING PENDENT SILOXANE GROUPS

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 the payment of any royalties thereon or thereof.

BACKGROUND OF THE INVENTION
1. Field of the Invention
The present invention relates generally to polyimides. In particular, it relates to polyimides containing siloxane groups, especially pendent siloxane groups.

2. Description of the Related Art
Polyimides (PI) comprise a large family of heterocyclic polymers which were first prepared in the late 1950s. Since then a large volume of information has been generated concerning the synthesis, characterization, use, physical and mechanical properties of these polymers. There are a number of reports concerning polyimides containing siloxane groups in the main-chain (i.e., polymer backbone). A patent describing polyimides containing siloxane groups in the backbone dates back to 1961, (D. L. Bailey and M. Pike, U.S. Pat. No. 2,998,406 to Union Carbide Corporation). These polymers were first described in the open literature in 1966, [V. H. Kuckertz, Die Makromolekular Chemie, 98, 101 (1966)], and they were prepared from 1,3-bis(3-aminophenyl)-1,1,3,3-tetramethyldisiloxane and pyromellitic dianhydride. Another paper involved the preparation of silicon containing dianhydrides and their subsequent reaction with aromatic diamines to form polyimides, [J. K. Gilliam and H. C. Gilliam, Polymer Engineering and Science, 13(6), 447 (1973)]. Other papers that followed include: I. Yilgor, E. Yilgor, B. C. Johnson, J. Eberle, G. L. Wilkes and J. E. McGrath, Polymer Preprints, 24(2), 78 (1983); S. Maudal and T. L. St. Clair, International Journal of Adhesion and Adhesives, 4(2), 87 (1984); B. C. Johnson, I. Yilgor and J. E. McGrath, Polymer Preprints, 25(2), 54 (1984); A. Berger, Society for the Advancement of Material and Process Engineering Series, 30, 64 (1985); and C. J. Lee, Ibid., 30, 52 (1984).


All of the above-mentioned related art pertain to polyimides containing siloxanes in the polymer backbone.

SUMMARY OF THE INVENTION
A primary object of the present invention is to provide what is not available in the prior art, viz., novel polyimides containing pendent siloxane groups, which polyimides are resistant to atomic oxygen, have low dielectric constants and low moisture absorption characteristics along with unique separation characteristics, and which polyimides are useful as coatings, adhesives, films, membranes, moldings, and composite matrices.

According to the present invention, this primary object and other objects and benefits were achieved by providing novel polyimides containing pendent siloxane groups, which were prepared by the reaction of a hydroxy containing polyimide with either hydrogen terminated siloxane compounds or oligomers, or by the reaction of chloro terminated silicon compounds or oligomers. The resulting solutions were cast into thin films and the solvent subsequently removed by heating under vacuum. In some cases the films were translucent with the color varying from light tan to dark brown. The glass transition temperatures of the polyimides containing pendent siloxane groups ranged from 167° to 235° C. Thermogravimetric analysis showed a 5% weight loss occurring around 380° C. in both air and nitrogen. Thin film tensile properties determined at 23° C. gave tensile strengths and moduli from 8.2-15.6 ksi and 248-453 ksi, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS
Synthesis of the polyimides containing pendent siloxane groups (PISOX) involved the initial preparation of hydroxy containing polyimides (PIOH). The PIOH were prepared as depicted in equation 1 below from the reaction of a diamino-benzyhydrol compound and an aromatic dianhydride in at 23° C. to yield a poly(amide-acid). The poly(amide-acid) was added to a refluxing solution of DMAc, NMP or m-cresol.

\[
\text{Ar} \quad \text{O} \quad \text{O} \quad \text{H} \quad \text{N} \quad \text{OH} \\
\text{O} \quad \text{O} \\
\text{DMAc} \rightarrow \text{PIOH} \quad \text{23° C.} \\
\text{X} \quad \text{X} \quad \text{NH}_2
\]

(Equation 1)
The PIOH must remain soluble in order to prepare the PISOX. The PISOX was prepared as shown in equation 2 from the PIOH and a hydrogen terminated siloxane compound or oligomer or a chloro terminated silicon compound or oligomer. A commercially available PIOH [Cemota Syntorg IP 605 or IP 608 (U.S. Pat. No. 3,609,123)] was also used to prepare PISOX as shown in equation 3.
Random copolymers which contained various amounts of pendent siloxane groups and hydroxy groups were also prepared. These copolymers were synthesized as depicted in equations 4 and 5 by reacting less than 100% of the stoichiometric amount of the appropriate silicon or siloxane compound with the Cemota Syntorg IP 608 PIOH. The polymer solutions were cast into thin films, dried under vacuum and characterized.
Where \( p \) = fraction (percentage) of hydroxy containing repeat unit and \( q = 1 - p \) fraction (percentage) of siloxane containing repeat unit.
In one aspect the invention is a polyimide containing
siloxane groups and having repeating units selected
from the group consisting of

\[
\begin{align*}
\left\{ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \right. \\
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{O}
\end{array}
\right\}
\]

and

\[
\begin{align*}
\left\{ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \right. \\
\begin{array}{c}
\text{Ar} \\
\text{H} \\
\text{C}
\end{array}
\right\}
\]

wherein the catenation of the nitrogen group is selected
from the group consisting of: (A) meta and para, (B)
meta-meta, para-para, and meta-para and (C) as shown;
and wherein Ar is a radical selected from the group
consisting of:

\[
\begin{align*}
\left\{ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \right. \\
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{O}
\end{array}
\right\}
\]

wherein Y is a bond or is a substituent selected from the
group consisting of:

\[
\begin{align*}
\text{O, S, SO}_2, \text{CH}_2, \text{O=C, C(CH}_3}_2, \text{C(CF}_3}_2, \text{Si(CH}_3}_2, \\
\text{Si(CH}_2}_2\text{CF}_2\text{CF}_3)
\]

wherein X is a bond or is a substituent selected from the
group consisting of:
wherein Z is a substituent selected from the group of:

- CH$_3$
- CH$_3$
- CH$_3$
- CH$_3$
- Si-CH$_3$
- Si-CH$_3$
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- Si-CH$_3$
- Si-CH$_3$
wherein \( n \) is an integer between 1 and 1000; and wherein \( m \) is an integer between 1 and 1000.

In another aspect the invention is a copolyimide containing a random mixture of pendent hydroxy and siloxane groups and having repeating units selected from the group consisting of:

\[
\begin{align*}
\text{A)} & \\
\text{B)} & \\
\text{C)} &
\end{align*}
\]
wherein $Y$ is a bond or is a substituent selected from the group consisting of:

- $O$, $S$, $SO_2$, $CH_2$, $O=CH$, $O=C$, $C(CH_3)_2$, $Si(CH_3)_2$
- $Si(CH_2CF_2CF_3)_2$

wherein $X$ is a bond or is a substituent selected from the group consisting of:

- $OCH_3$
- $Cl$ (chlorine)

wherein $Z$ is a substituent selected from the group consisting of:

- $Si(CH_3)_2$
- $Cl$ (chlorine)
CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)

5,304,627

---continued

CH₃

---Si-CH₃

\((\text{CH}_2\text{CH}_3)_3\text{OSi(CH}_3\text{)}_3\)
This text contains a series of reactions and processes related to the synthesis of polyimides containing pendant siloxane groups. The text describes the addition of various reagents, the stirring of solutions, and the precipitation of polyimides into water. There is also a mention of tensile strength and modulus of thin film specimens. The text provides examples of how to synthesize polyimides with specific properties, including the use of hydride and diamines in the reaction medium. The text concludes with an example of a synthesis method for polyimides containing pendant siloxane groups.
mixture was stirred at 23°C under nitrogen until all of the polymer had dissolved (about one hour) and platinic acid (105 mg) was subsequently added. Into the pressure equalizing addition funnel was placed 1,1,2,2,3,3,3-hexamethytrisiloxane (9.86 g, 44.3 mmol) and toluene (25 ml). The siloxane solution was added to the PIOH solution dropwise over a one hour period. The solution was stirred at 23°C under nitrogen for 16 hours and subsequently filtered through a 5.0 micron filter under pressure (about 20 psi). A thin film was cast from the solution onto plate glass. The film was dried to a tack-free state in a dust-proof chamber and stage-dried to 225°C and held at 225°C for one hour under vacuum. The translucent yellow/green film exhibited a Tg of 167°C. Tensile strength and modulus of thin film specimens at 23°C of 16.9 and 404 ksi, respectively were obtained.

Polymer characterization is presented in the following Tables 1 and 2, and thin film properties are presented in Tables 3 and 4.

### Table 1

<table>
<thead>
<tr>
<th>Glass Transition Temperature, °C</th>
<th>Film Appearance, Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>235</td>
<td>orange, translucent, tough, creasable</td>
</tr>
<tr>
<td>239</td>
<td>brown, translucent, tough, creasable</td>
</tr>
<tr>
<td>211</td>
<td>light tan, translucent, tough, creasable</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Glass Transition Temperature, °C</th>
<th>Film Appearance, Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>167</td>
<td>yellow/green, semi-translucent, tough, creasable</td>
</tr>
<tr>
<td>210</td>
<td>orange, clear, tough, creasable</td>
</tr>
<tr>
<td>250</td>
<td>orange, clear,</td>
</tr>
</tbody>
</table>

The following example illustrates the reaction sequence for the synthesis of the polyimide containing 20 pendant siloxane groups from the Cemota Syntorg IP 608 PIOH as depicted in equation 3 above where the pendant group was trimethyl silyl.

**Polyimide Containing Pendant Siloxane Groups**

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and pressure equalizing addition funnel was placed Cemota Syntorg IP 608 PIOH (5.3 g, 21.1 mmol based on hydroxy group content, assuming a molecular weight of 36,000 g/mole) and DMAc (31 ml, 15% solids). The mixture was stirred at 23°C under nitrogen until all of the polymer dissolved (about one hour). Into the pressure equalizing addition funnel was placed the chlorotrimethyisilane (2.65 g, 24.3 mmol) and toluene (10 ml). The toluene/silane solution was added dropwise to the PIOH solution over a 30 minute period. The solution was stirred at 23°C for about 16 hours and subsequently filtered through a 5.0 micron filter under pressure (about 20 psi). The solution was used to cast a thin film on plate glass which was air dried to a tack-free state. The film was stage-dried to 240°C and held at 240°C for one hour under vacuum. The clear orange film exhibited a Tg of 210°C by differential scanning calorimetry. Tensile strength and modulus of thin film specimens at 23°C of 16.9 and 404 ksi, respectively were obtained.
<table>
<thead>
<tr>
<th>Z</th>
<th>Temperature, °C</th>
<th>Glass Transition</th>
<th>Film Appearance, Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP 608 Polyimide</td>
<td>275, 295</td>
<td>tough, creasable</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2-continued

**POLYMER CHARACTERIZATION**

<table>
<thead>
<tr>
<th>CH3-Si-CH3</th>
<th>CH3-Si-CH3</th>
<th>CH3-Si-CH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>N</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 3**

**THIN FILM PROPERTIES**

<table>
<thead>
<tr>
<th>Ar</th>
<th>Tensile Strength, ksi</th>
<th>Modulus, ksi</th>
<th>Elong., %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12.5</td>
<td>390.6</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>453.3</td>
<td>4.1</td>
</tr>
</tbody>
</table>

*Tensile properties determined at 23° C.*

<table>
<thead>
<tr>
<th>CF3</th>
<th>Tensile Strength, ksi</th>
<th>Modulus, ksi</th>
<th>Elong., %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.2</td>
<td>360.6</td>
<td>12.0</td>
</tr>
</tbody>
</table>

**TABLE 4**

**THIN FILM PROPERTIES**

<table>
<thead>
<tr>
<th>Z</th>
<th>Tensile Strength, ksi</th>
<th>Modulus, ksi</th>
<th>Elong., %</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3</td>
<td>16.9</td>
<td>404.1</td>
<td>28.8</td>
<td></td>
</tr>
<tr>
<td>CH3-Si-CH3</td>
<td>10.9</td>
<td>250.0</td>
<td>34.3</td>
<td>2.8</td>
</tr>
<tr>
<td>CH3-Si-O-Si-O-Si</td>
<td>18.1</td>
<td>442.3</td>
<td>10.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

*H (Cemota Syntorg IP 608 Polyimide)*

*Tensile properties determined at 23° C.*
The translucent dark yellow/green film exhibited a Tg of 216° C. by differential scanning calorimetry. Tensile strength, modulus and elongation of thin film specimens at 23° C. of 15.6, 378.9 ksi and 21.0%, respectively were obtained.

**EXAMPLE 7**

The following example illustrates the synthesis of a copolyimide containing pendant siloxane groups from the Cemota Syntorg IP 608 PIOH as depicted in equation 4 above where the pendant siloxane group was 1,1,2,2,3,3,3-heptamethyltrisiloxane.

**Synthesis of Copolyimide Containing Pendant Siloxane Groups**

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, pressure equalizing addition funnel and drying tube filled with calcium carbonate was placed Cemota Syntorg IP 608 PIOH solution (25.5% solids in NMP) (8.79 g solution = 2.24 g polymer, 8.9 mmol based on hydroxyl group content, assuming a molecular weight of 36,000 g/mol) and DMAc (6 ml, 15% solids). The mixture was stirred at 23° C. until all of the polymer had dissolved (about one hour), and platinic acid (45 mg) was subsequently added. Into the pressure equalizing addition funnel was placed 1,1,2,2,3,3,3-heptamethyltrisiloxane (0.50 g, 2.2 mmol, 25% of theoretical hydroxyl content) and toluene (3 ml). The siloxane solution was added dropwise over a 10 minute period. The solution was stirred at room temperature under nitrogen for about 16 hours. The solution was centrifuged, and a thin film was cast onto plate glass. The film was dried to a tack-free state in a dust-proof chamber and subsequently stage-dried to 225° C. and held at 225° C. for one hour under vacuum. The translucent dark yellow/orange film exhibited a Tg of 231° C. by differential scanning calorimetry. Tensile strength, modulus and elongation of thin film specimens at 23° C. of 15.6, 378.9 ksi and 21.0%, respectively, were obtained.

**EXAMPLE 8**

The following example illustrates the reaction sequence for the synthesis of a random copolyimide containing pendant siloxane groups from the Cemota Syntorg IP 608 PIOH as depicted in equation 5 above where the pendant group was trimethylsilyl.

**Copolyimide Containing Pendant Siloxane Groups**

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, pressure equalizing addition funnel and drying tube filled with calcium carbonate was placed Cemota Syntorg IP 608 PIOH solution (25.5% solids in NMP) (9.61 g solution = 2.45 g polymer, 9.75 mmol based on hydroxyl group content, assuming a molecular weight of 36,000 g/mol) and DMAc (7 ml, 15% solids). The mixture was stirred at 23° C. until all of the polymer had dissolved (about one hour), and platinic acid (75 mg) was subsequently added. Into the pressure equalizing addition funnel was placed 1,1,2,2,3,3,3-heptamethyltrisiloxane (1.63 g, 7.31 mmol, 75% of theoretical hydroxyl group content) and toluene (5 ml). The siloxane was added dropwise to the PIOH solution over a 10 minute period. The solution was stirred at 23° C. under nitrogen for about 16 hours. The solution was centrifuged, and a thin film was cast onto plate glass. The film was dried to a tack-free state in a dust-proof chamber and subsequently stage-dried to 225° C. and held at 225° C. for one hour under vacuum. The translucent yellow/orange film exhibited a Tg of 186° C. by differential scanning calorimetry. Tensile strength, modulus and elongation of thin film specimens at 23° C. of 11.5, 281.3 and 34.3%, respectively, were obtained.
EXAMPLE 9

The following example illustrates the reaction sequence for the synthesis of a random copolyimide containing pendent siloxane groups from the Cemota Syn-torg IP 608 PIOH as depicted in equation 5 above where the pendent siloxane group was trimethylsilyl, p=0.50 and q=0.50.

Synthesis of Copolyimide Containing Pendent Siloxane Groups

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, pressure equalizing addition funnel and drying tube filled with calcium carbonate was placed Cemota Syntorg IP 608 PIOH solution (25.5% solids in NMP) (8.52 g solution=2.13 g polymer, 8.47 mmol based on hydroxy group content, assuming a molecular weight of 36,000 g/mol) and DMAc (6 ml, 15% solids). The mixture was stirred at 23°C until it was homogeneous (about one hour). Into the addition funnel was placed the chlorotrimethylsilane (0.46 g, 4.24 mmol, 50% of theoretical hydroxy content) and toluene (5 ml). The toluene solution was added dropwise to the PIOH solution over a 10 minute period, and the solution was stirred at 23°C under nitrogen for about 16 hours. The solution was centrifuged, and a thin film was cast onto plate glass. The film was dried to a tack-free state in a dust-proof chamber and subsequently stage-dried to 240°C and held at 240°C for one hour under vacuum. The transparent orange film exhibited a Tg of 225°C. Tensile strength, modulus and elongation of thin film specimens at 23°C of 21.3, 538 ksi and 11.8%, respectively were obtained.
TABLE 5

COPOLYMER CHARACTERIZATION

<table>
<thead>
<tr>
<th>P</th>
<th>q</th>
<th>Tg, °C</th>
<th>Tensile* Strength, ksi</th>
<th>Tensile* Modulus, ksi</th>
<th>Elong., %</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>75%</td>
<td>25%</td>
<td>231</td>
<td>15.6</td>
<td>378.9</td>
<td>21.0</td>
<td>3.1</td>
</tr>
<tr>
<td>50%</td>
<td>50%</td>
<td>216</td>
<td>13.3</td>
<td>330.9</td>
<td>25.1</td>
<td>3.0</td>
</tr>
<tr>
<td>25%</td>
<td>75%</td>
<td>186</td>
<td>11.5</td>
<td>281.3</td>
<td>34.3</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*Thin film tensile properties determined at 23° C.

**Dielectric Constant determined at 23° C.

TABLE 6

COPOLYMER CHARACTERIZATION

<table>
<thead>
<tr>
<th>P</th>
<th>q</th>
<th>Tg, °C</th>
<th>Tensile* Strength, ksi</th>
<th>Tensile* Modulus, ksi</th>
<th>Elong., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>75%</td>
<td>25%</td>
<td>235</td>
<td>19.0</td>
<td>498.7</td>
<td>9.9</td>
</tr>
<tr>
<td>50%</td>
<td>50%</td>
<td>225</td>
<td>21.3</td>
<td>538.0</td>
<td>11.8</td>
</tr>
<tr>
<td>25%</td>
<td>75%</td>
<td>215</td>
<td>18.7</td>
<td>482.9</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Thin film tensile properties determined at 23° C.

We claim:

1. A polyimide containing siloxane groups and having repeating units selected from the group consisting of:  

   ![Diagram](image1)

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

   ![Diagram](image2)

   wherein the catenation of the nitrogen group is selected from the group consisting of: (A) meta and para, (B) meta-meta, para-para, and meta-para and (C) as shown;
wherein Y is a band or is a substituent selected from the group consisting of:

- $\mathrm{O}$,
- $\mathrm{S}$,
- $\mathrm{SO}_2$,
- $\mathrm{CH}_2$,
- $\mathrm{O}=-\mathrm{C}$,
- $\mathrm{C}($($\mathrm{CH}_3$)$_2$),
- $\mathrm{Si}($($\mathrm{CH}_3$)$_2$),

wherein X is a bond or is a substituent selected from the group consisting of:

- $\mathrm{OCH}_3$,
- $\mathrm{CH}_2\mathrm{Cl}$,
- $\mathrm{CHCl}_2$,
- $\mathrm{CCl}_3$,
- $\mathrm{OCOC}_3$,
- $\mathrm{OSi}($($\mathrm{CH}_2\mathrm{CF}_2\mathrm{CF}_3$)$_2$),

wherein Z is a substituent selected from the group consisting of:

- $\mathrm{CH}_3$,
- $\mathrm{Si}(-\mathrm{CH}_3)$,
- $\mathrm{Si}(-\mathrm{CH}_2\mathrm{CH}_3)$,
- $\mathrm{Si}(-\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_3)$,
- $\mathrm{Si}(-\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_3)$,
- $\mathrm{Si}(-\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_3)$.

- $\mathrm{Si}(-\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}_3)$,
wherein \( R \) is a substituent selected from the group consisting of:

\[
\text{CH}_3, \text{CH}_2\text{CH}_3, (\text{CH}_2)_2\text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{CF}_3, (\text{CH}_2)_2\text{CF}_3
\]

wherein \( \text{Ar}' \) is a substitute selected from the group consisting of:

\[
\text{OCH}_2\text{CH}_3, (\text{CH}_2)_2\text{CH}_3, \text{CH}_2\text{Cl}
\]

wherein \( n \) is an integer between 1 and 1000; and wherein \( m \) is an integer between 1 and 1000.

2. A copolyimide containing a random mixture of pendant hydroxy and siloxane groups and having repeating units selected from the group consisting of:

\[
\text{CH}_3, \text{CH}_2\text{CH}_3, (\text{CH}_2)_2\text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{CF}_3,(\text{CH}_2)_2\text{CF}_3
\]

wherein \( n \) is an integer between 1 and 1000; and wherein \( m \) is an integer between 1 and 1000.
wherein the catenation of the nitrogen group is selected from the group consisting of:

(A) meta and para and (B) meta-meta, para-para, and meta-para; wherein Ar is a radical selected from the group consisting of:

wherein Y is a bond or is a substituent selected from the group consisting of:

O, S, SO$_2$, CH$_2$, O=CH(CH$_3$)$_2$, C(CF$_3$)$_2$, Si(CH$_3$)$_2$, Si(CH$_2$CF$_3$)$_2$;

wherein X is a bond or is a substituent selected from the group consisting of:

wherein Z is a substituent selected from the group consisting of:

```latex
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 & \quad \text{Si=CH}_3 \\
\end{align*}
```
41
-continued

5,304,627

42
-continued
The polyimide containing pendent siloxane groups of claim 5, wherein Ar is selected from the group consisting of:

\[
CH_3, CH_3CH_3, (CH_2)_2CH_3, CH(CH_3)_2, C_6H_5, (CH_2)_2CF_2;
\]

wherein \( R' \) is a substituent selected from the group consisting of:

\[
CH_2, CH_2CH_2, OCH_2O, CF_2, CF_2CF_2, OCF_2O;
\]

wherein \( p \) is a fraction (percentage) between 0.01 and 0.99;
wherein \( q \) is a fraction (percentage) equal to 1 minus \( p \);
wherein \( n \) is an integer between 1 and 1000; and
wherein \( m \) is an integer between 1 and 1000.

3. The polyimide containing pendent siloxane groups of claim 1, wherein the repeating unit is (A) and \( Z \) is selected from the group consisting of:

\[
\text{CH}_3, \text{CH}_3 \text{CH}_3, \text{CH}_3 \text{CH}_3 \\
\text{Si-CH}_3 \text{ and } \text{Si-O-Si-O-Si-CH}_3
\]

4. The random copolyimide containing pendent siloxane groups of claim 2, wherein the repeating unit is (A) and \( Z \) is selected from the group consisting of:

\[
\text{CH}_3, \text{CH}_3 \text{CH}_3, \text{CH}_3 \text{CH}_3 \\
\text{Si-CH}_3 \text{ and } \text{Si-O-Si-O-Si-CH}_3
\]

5. The polyimide containing pendent siloxane groups of claim 1, wherein the repeating unit is (B) and \( Z \) is:

\[
\text{CH}_3, \text{CH}_3 \text{CH}_3, \text{CH}_3 \text{CH}_3 \\
\text{Si-CH}_3 \text{ and } \text{Si-O-Si-O-Si-CH}_3
\]

6. The polyimide containing pendent siloxane groups of claim 5, wherein Ar is selected from the group consisting of:

\[
\begin{array}{c}
\text{CH}_3, \text{CH}_3 \text{CH}_3, \text{CH}_3 \text{CH}_3, \text{CH}_3 \text{CH}_3 \text{CH}_3, \text{CH}_3 \text{CH}_3 \text{CH}_3; \\
\text{Si-CH}_3 \text{ and } \text{Si-O-Si-O-Si-CH}_3
\end{array}
\]

7. The polyimide containing pendent siloxane groups of claim 6, where \( X \) is a bond.

8. The random copolyimide containing pendent siloxane groups of claim 2, wherein the repeating unit is (B) and \( Z \) is selected from the group consisting of:

\[
\text{CH}_3, \text{CH}_3 \text{CH}_3, \text{CH}_3 \text{CH}_3 \\
\text{Si-CH}_3 \text{ and } \text{Si-O-Si-O-Si-CH}_3
\]

9. A process for synthesizing polyimides and random copolyimides containing pendent siloxane groups, which process comprises reacting a member selected from the group consisting of a chloroterminated silicon compound, a chloroterminated silicon oligomer, a hydrogen terminated compound, and a hydrogen terminated oligomer with a polyimide containing hydroxy groups in the presence of a platinic acid catalyst under ambient reaction conditions in a solvent selected from the group consisting of:

\[
\text{N,N-dimethylacetamide, N-methylpyrrolidinone, sulfolane, N-cyclohexylpyrrolidinone, dimethylsulfoxide, toluene, and bis(2-methoxyethyl)ether.}
\]

10. A polyimide containing pendent siloxane groups and having a structure selected from the group consisting of:
11. A random copolyimide containing pendent siloxane groups and having a structure selected from the group consisting of:

```
- N  
  O  
  O  
  C  
  H  
  O  
  O  
  N  
  =N
```

and

```
- N  
  O  
  O  
  C  
  H  
  O  
  O  
  N  
  =N
```