Preparation of Benzophenone Modified Poly (dimethysiloxane) Thermosets

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Preparation of Benzophenone Modified Poly(dimethylsiloxane) Thermosets

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Best Available Copy DISTRIBUTION A. Approved for public release; distribution unlimited.
While the **Ru** catalyzed incorporation of aromatic ketones into siloxane polymer backbones adds various properties to the polymers, the characteristic properties of poly(dimethyl-siloxane) (PDMS), such as low glass transition temperature ($T_g$), are lost.

The **Ru** catalyzed chemical modification of a PDMS copolymer may allow the addition of the properties of the ketones, while retaining the properties of PDMS.
Poly(dimethylsiloxane) (PDMS)

\[
\left( \text{Si-O} \right)_n
\]

- Water repellent/Hydrolysis resistant
- Thermal and electrical insulator
- Oxidative resistant
- Biocompatible
- Low $T_g$ of approximately -125 °C
- Thermally degrades at approximately 300 °C

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Murai Reaction

\[
\text{O} \quad \text{O} \\
\text{CH}_2 \quad \text{CH}_2 \\
\text{Si(OEt)}_3 \\
\longrightarrow \\
\text{Ru} \\
\text{O} \quad \text{O} \\
\text{CH}_2 \quad \text{CH}_2 \\
\text{Si(OEt)}_3 \\
\]

Murai has shown that \( \text{RuH}_{2}(\text{CO})(\text{PPh}_3)_3 \) (\( \text{Ru} \)) catalyzes the addition of vinylsilanes to aromatic ketones in high yield.


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The catalyst, dihydridocarbonyltris(triphenylphosphine) ruthenium (Ru), prepared from RuCl₃₄ is activated with a stoichiometric amount of styrene. Hydrogen is lost from the ruthenium center and ethyl benzene is produced. This activates the catalyst by creating a site of coordinate unsaturation.⁵

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Catalytic Cycle

\[ R = \text{phenyl or mesityl} \]

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This poster reports the Ru-catalyzed addition of benzophenone to 1% vinylmethyl PDMS.
Addition ofrough methylbenzophenone

TMS-\text{O-Si-O-Si-O-Si-O-TMS}
## Glass Transition Temperature

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting Polymer</th>
<th>Benzophenone</th>
<th>2,4,6-Trimethylbenzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w/M_n$</td>
<td>33,300/20,700</td>
<td>34,200/19,800</td>
<td>39,300/22,500</td>
</tr>
<tr>
<td>$T_g$</td>
<td>$-125 , ^\circ C$</td>
<td>$-123 , ^\circ C$</td>
<td>$-123 , ^\circ C$</td>
</tr>
</tbody>
</table>

While thermal stability is increased, low $T_g$ values are retained.
Both copolymers are stable in nitrogen to 350 °C.
Both copolymers are stable in air to 350 °C.
Polymer sample is heated in TGA analyzer at 300 °C for one hour.

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Molecular Weight Increase

<table>
<thead>
<tr>
<th></th>
<th>Benzophenone</th>
<th>2,4,6-Trimethylbenzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting $M_w/M_n$</td>
<td>34,200/19,800</td>
<td>39,300/22,500</td>
</tr>
<tr>
<td>$M_w/M_n$ after heating</td>
<td>157,900/75,500</td>
<td>119,100/57,700</td>
</tr>
</tbody>
</table>

- $M_w$ triples or better upon heating at 300 °C for one hour
- Polymer remains soluble
- Structural changes not visible in NMR spectra.

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**α,ω-Substituted PDMS**

![Chemical structure of α,ω-substituted PDMS]

<table>
<thead>
<tr>
<th></th>
<th>100 cSt</th>
<th>200 cSt</th>
<th>1000 cSt</th>
<th>20,000 cSt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting Material</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starting $M_w/M_n$</td>
<td>9,200/5,400</td>
<td>13,000/6,800</td>
<td>29,900/18,200</td>
<td>87,600/44,800</td>
</tr>
<tr>
<td>Starting $T_g$</td>
<td>-125 °C</td>
<td>-124 °C</td>
<td>-125 °C</td>
<td>-125 °C</td>
</tr>
<tr>
<td><strong>Product</strong> $M_w/M_n$</td>
<td>10,300/7,000</td>
<td>18,200/13,300</td>
<td>34,300/21,400</td>
<td>96,300/59,700</td>
</tr>
<tr>
<td>Product $T_g$</td>
<td>-125 °C</td>
<td>-123 °C</td>
<td>-124 °C</td>
<td>-125 °C</td>
</tr>
</tbody>
</table>

Low $T_g$s are also retained in α,ω-substituted polymers.

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## TGA Experiment

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>100 cSt</th>
<th>200 cSt</th>
<th>1000 cSt</th>
<th>20,000 cSt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting $M_w/M_n$</td>
<td>10,300/7,000</td>
<td>18,200/13,300</td>
<td>34,300/21,400</td>
<td>96,300/59,700</td>
</tr>
<tr>
<td>Product $M_w/M_n$</td>
<td>12,500/7,800</td>
<td>19,600/13,900</td>
<td>44,900/28,500</td>
<td>127,200/70,200</td>
</tr>
</tbody>
</table>

- $M_w$ increases by up to 32% after heating at 300 °C
- Polymer remains soluble
- Structural changes not visible in NMR spectra.

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The Elbs Reaction

Pyrolysis of 2-methylbenzophenone results in the formation of anthracene and fluorene.

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Pyrocondensation of Anthracene

Pyrolysis of anthracene results in the formation of bianthracenyls.
Model Compound

Model compound was prepared and pyrolyzed
Conversion to anthracene was confirmed by UV
Higher molecular weight products were observed

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Polymer Crosslinking

\[ TMS-O\left(\text{Si}-\text{O}\right)_{n}\left(\text{Si}-\text{O}\right)_{m}\text{TMS} \]

\[ \xrightarrow{\Delta} \]

\[ TMS-O\left(\text{Si}-\text{O}\right)_{n}\left(\text{Si}-\text{O}\right)_{m}\text{TMS} \]

\[ \xrightarrow{\Delta} \]

\[ TMS-O\left(\text{Si}-\text{O}\right)_{n}\left(\text{Si}-\text{O}\right)_{m}\text{TMS} \]

• Crosslinks may interfere with reversion reaction

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Summary

• Low $T_g$s are retained with the addition of benzophenones
• Thermal stability is increased in both nitrogen and air
• Molecular weight increases upon heating to 300 °C
• Conversion to anthracene was confirmed by UV
• Pyrocondensation of anthracene may form cross links
• Cross links may interfere with reversion reaction
• Typical characteristics of PDMS (low \( T_g \) and thermal stability) were successfully retained.
• Characteristics of aromatic diketones (electrochemical and photochemical) were successfully added.
• Poly(dimethylsiloxane) containing 0.8% vinylmethyl units was purchased from Gelest.
• Virtually all vinyl groups were substituted with aromatic units when analyzed by NMR.
Acknowledgement

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References