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Preparation of Benzophenone Modified Poly(dimethylsiloxane) Thermosets

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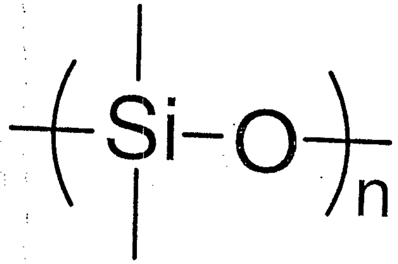
Objective

While the **Ru** catalyzed incorporation of aromatic ketones into siloxane polymer backbones adds various properties to the polymers, the characteristic properties of poly(dimethylsiloxane) (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.

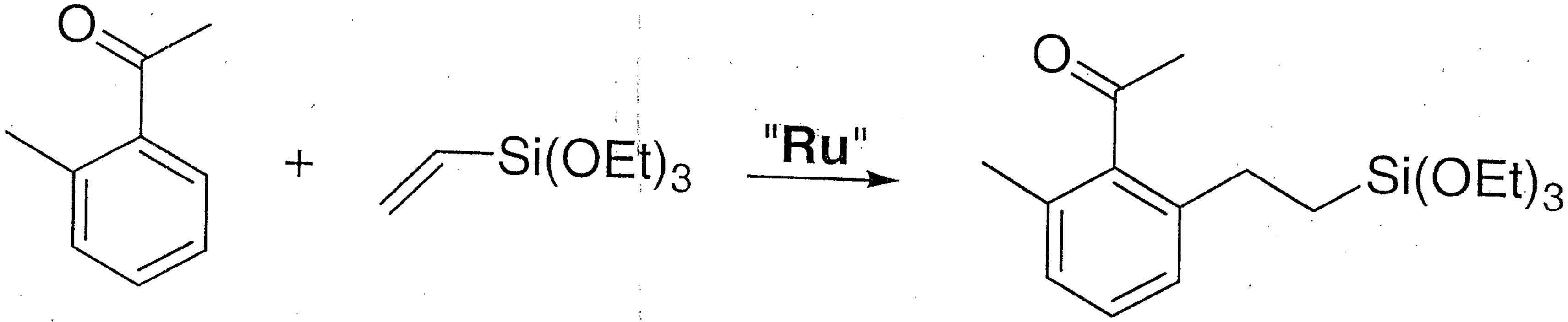
Poly(dimethylsiloxane) (PDMS)



$-(Si-O)_n-$

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

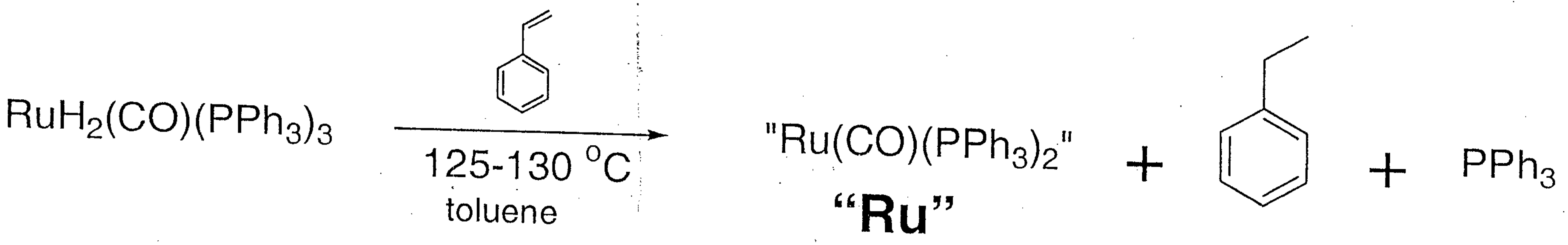
Murai Reaction



Murai has shown that $RuH_2(CO)(PPh_3)_3$ **(Ru)** catalyzes the addition of vinylsilanes to aromatic ketones in high yield.

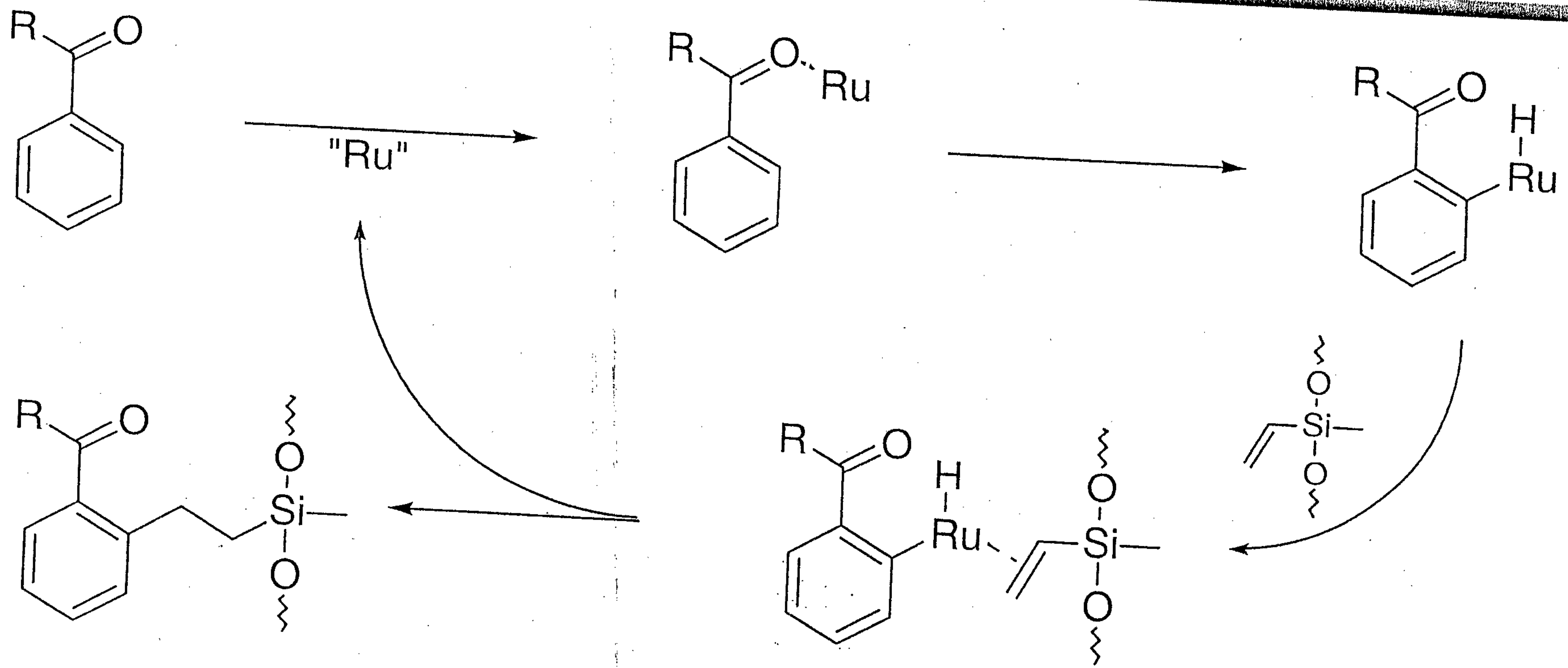
Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, M.; Murai, S. *Bull. Chem. Soc. Jpn.*, **195**, *68*, 62.

Catalyst Activation



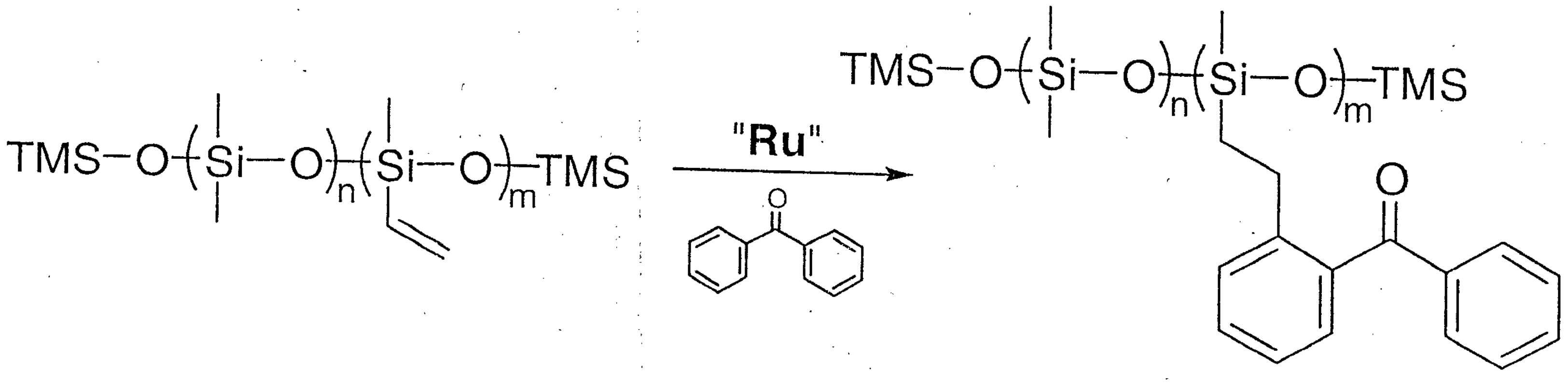
The catalyst, dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru), prepared from $RuCl_3$,[4] is activated with a stoichiometric amount of styrene. Hydrogen is lost from the ruthenium center and ethyl benzene is produced. This activates the catalyst by creating a site of coordinate unsaturation.[5]

Catalytic Cycle



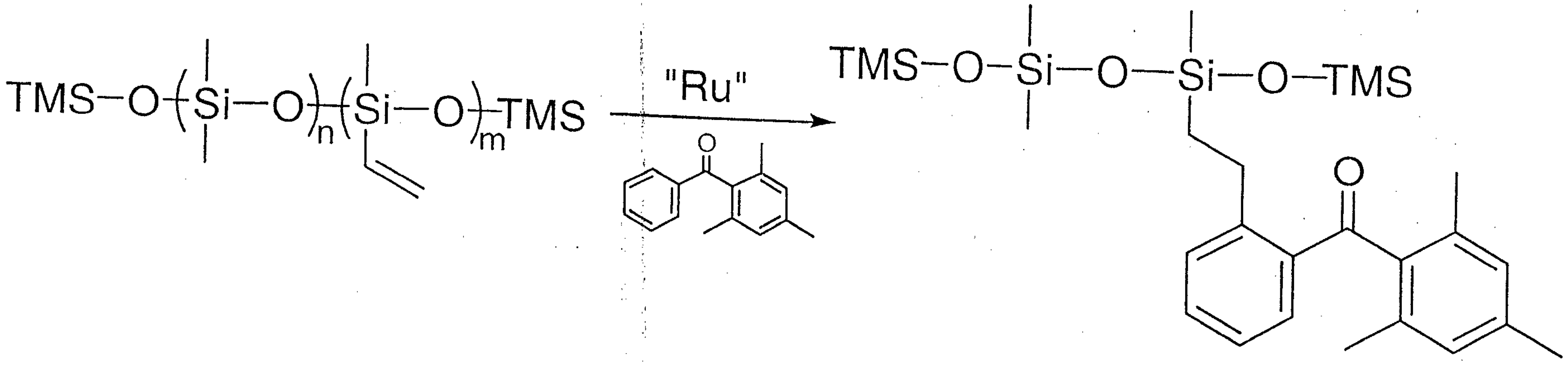
(R = phenyl or mesityl)

Chemical Modification



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

Addition of 2,4,6-Trimethylbenzophenone

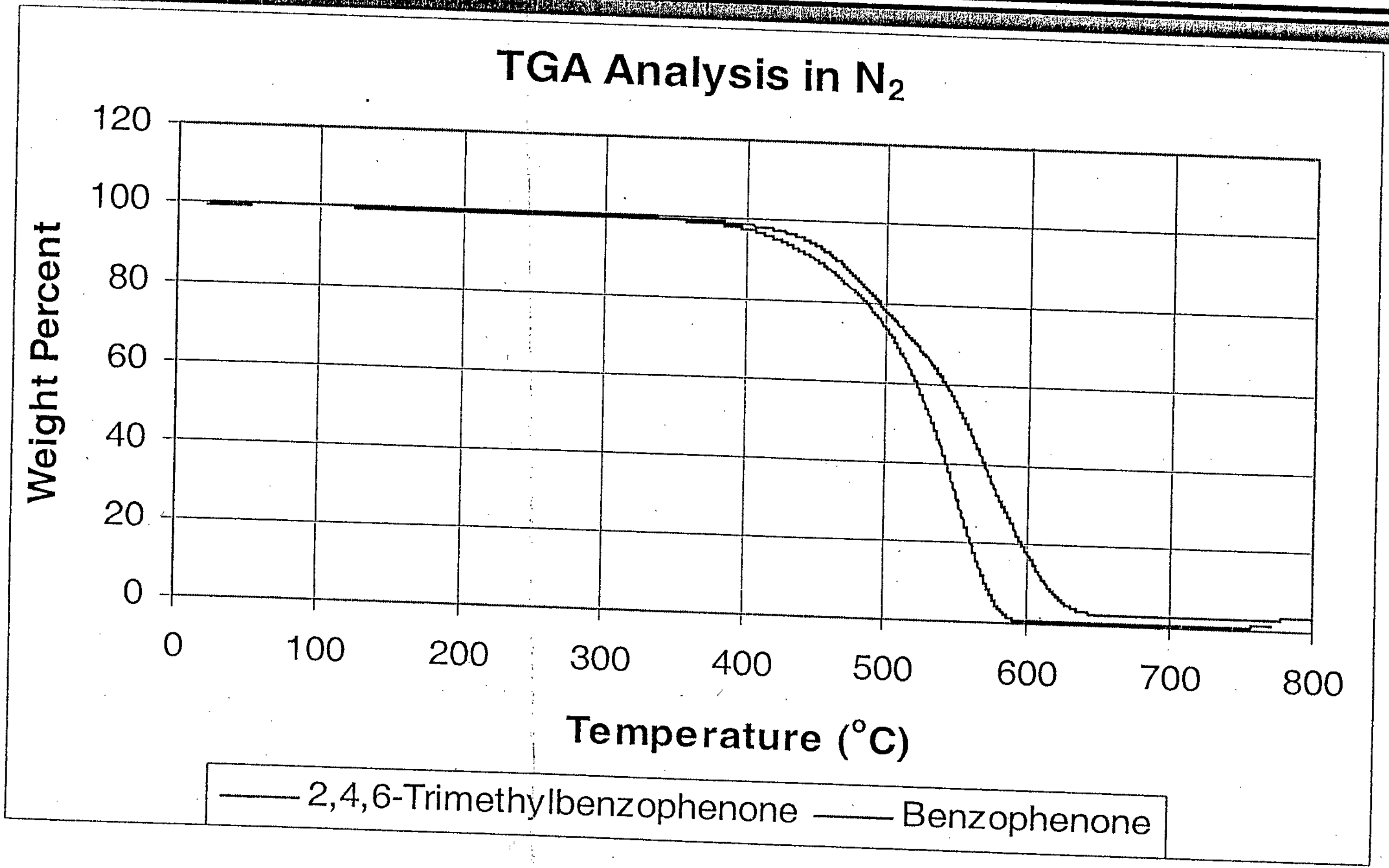


Glass Transition Temperature

Compound	Starting Polymer	Benzophenone	2,4,6-Trimethylbenzophenone
M_w/M_n	33,300/20,700	34,200/19,800	39,300/22,500
T_g	-125 °C	-123 °C	-123 °C

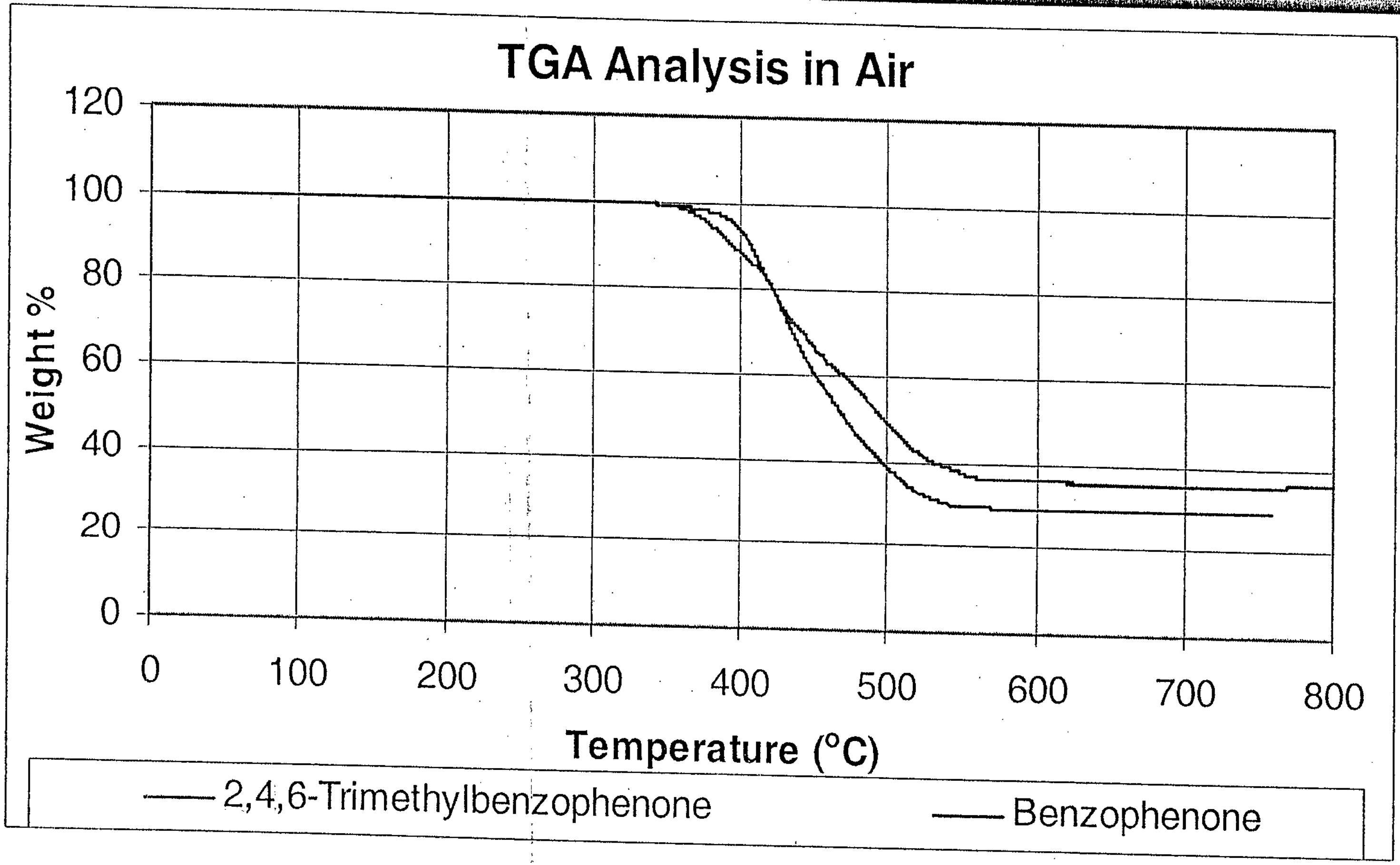
While thermal stability is increased, low T_gs are retained.

Thermal Stability



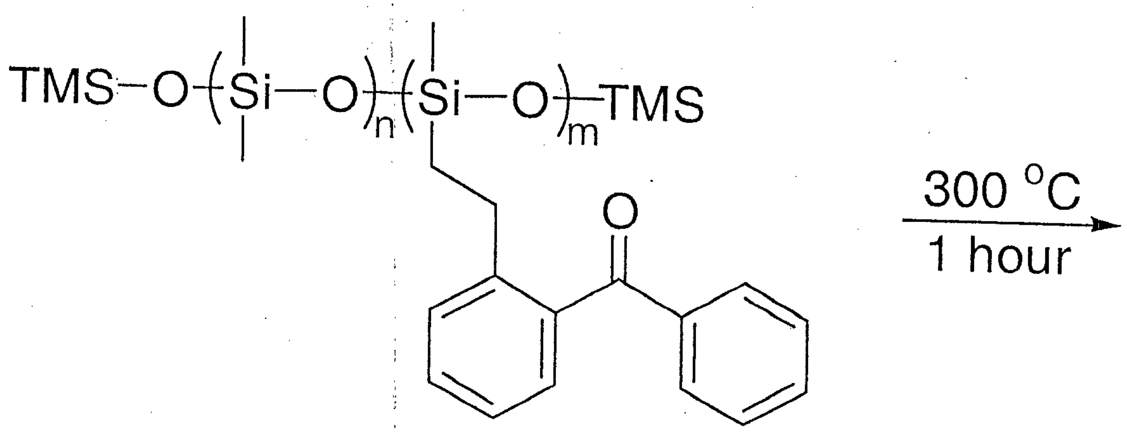
Both copolymers are stable in nitrogen to 350 °C.

Thermal Stability



Both copolymers are stable in air to 350 °C.

TGA Experiment



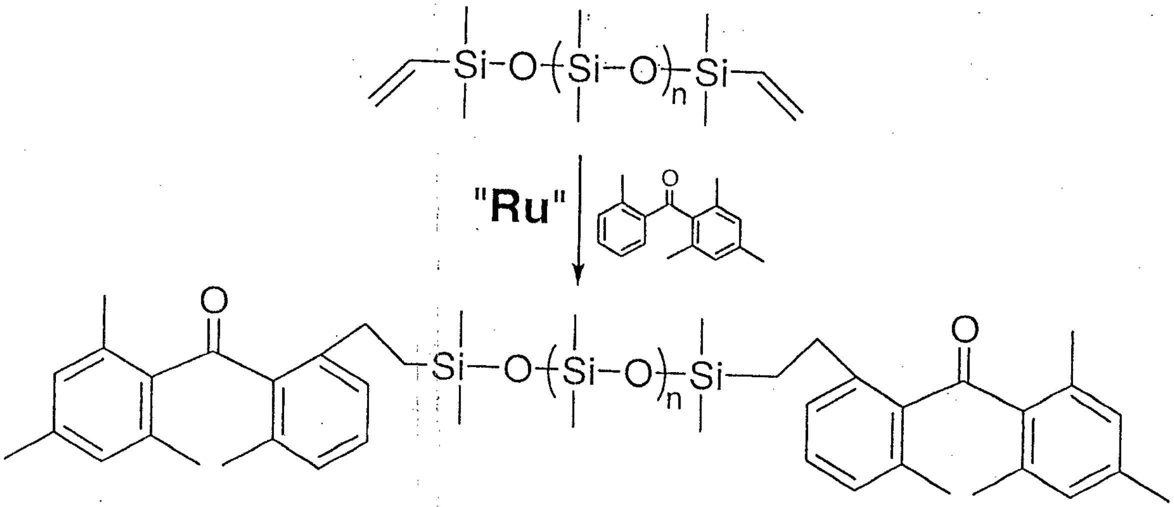
Polymer sample is heated in TGA analyzer at 300 °C for one hour.

Molecular Weight Increase

	Benzophenone	2,4,6-Trimethylbenzophenone
Starting M_w/M_n	34,200/19,800	39,300/22,500
M_w/M_n after heating	157,900/75,500	119,100/57,700

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

α,ω-Substituted PDMS



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

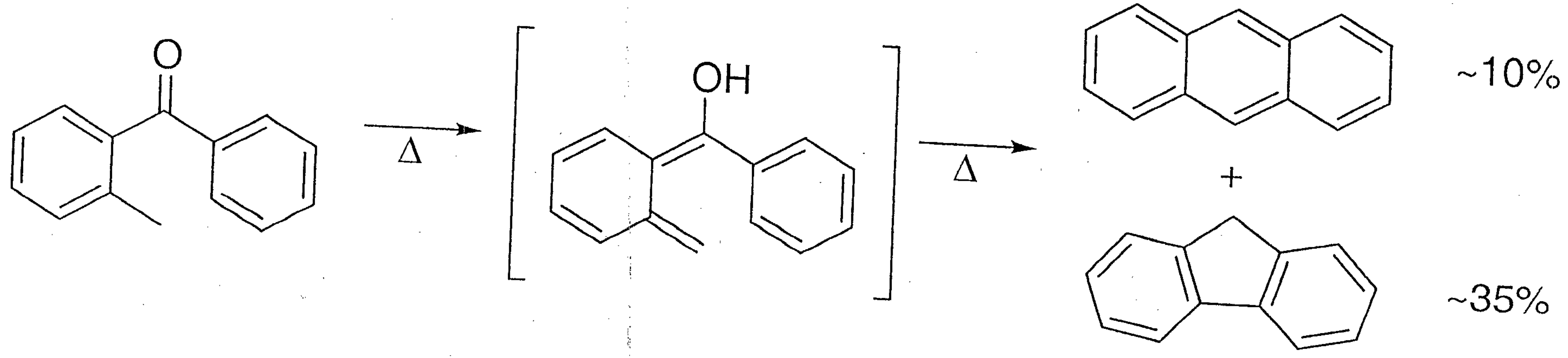
Low T_gs are also retained in α,ω-substituted polymers.

TGA Experiment

Starting Material	100 cSt	200 cSt	1000 cSt	20,000 cSt
Starting M_w/M_n	10,300/7,000	18,200/13,300	34,300/21,400	96,300/59,700
Product M_w/M_n	12,500/7,800	19,600/13,900	44,900/28,500	127,200/70,200

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

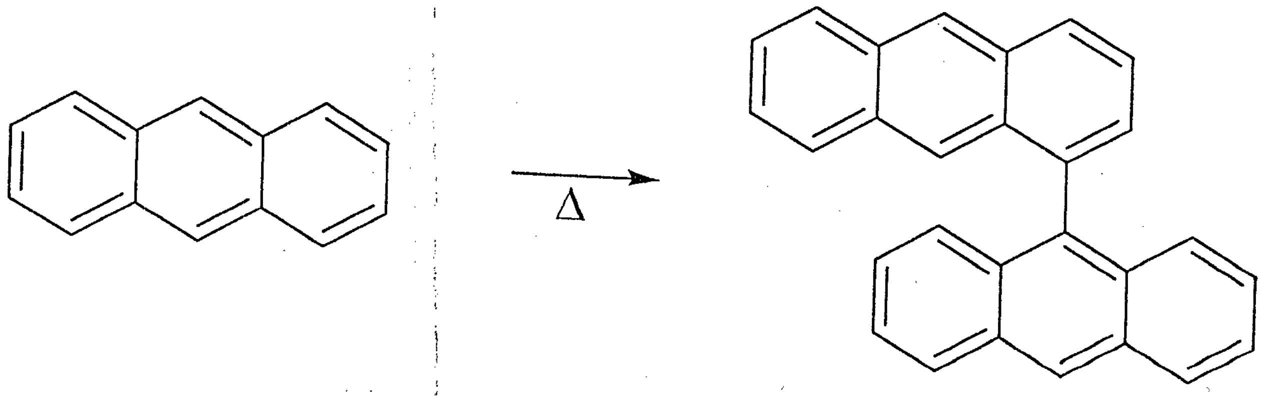
The Elbs Reaction



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

Gu, T. Y.; Weber, W. P. *J. Org. Chem.* **1980**, *45*, 2541.

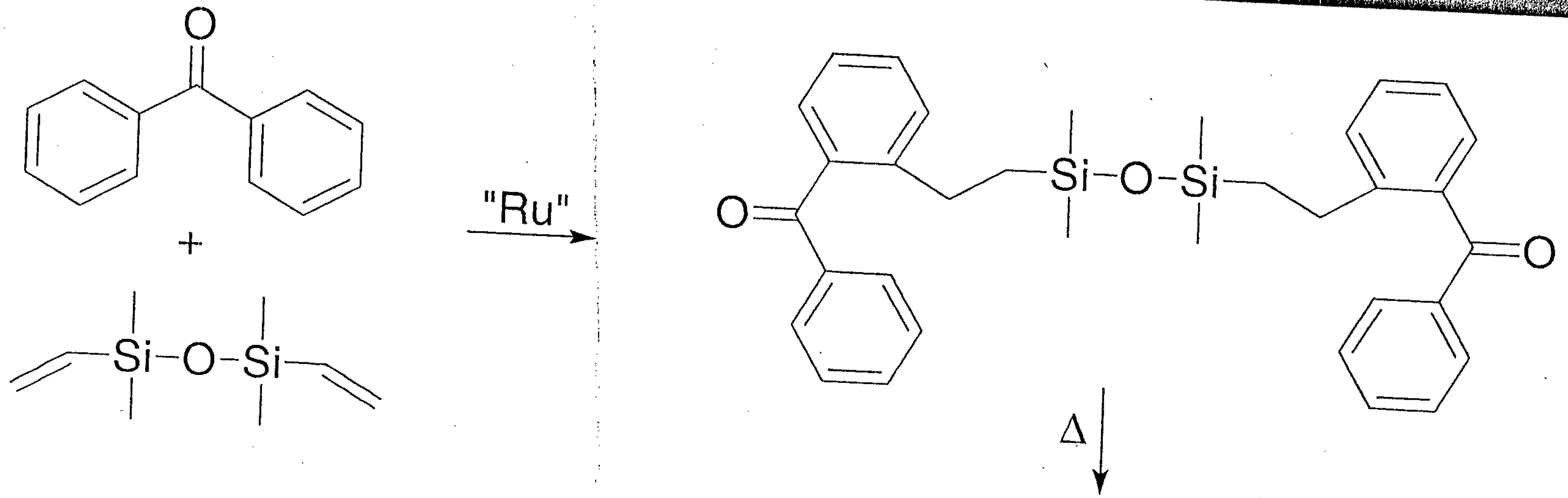
Pyrocondensation of Anthracene



(1,9-Bianthracenyl)

Pyrolysis of anthracene results in the formation of bianthracenyls.

Model Compound



Higher Molecular Weight Products

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

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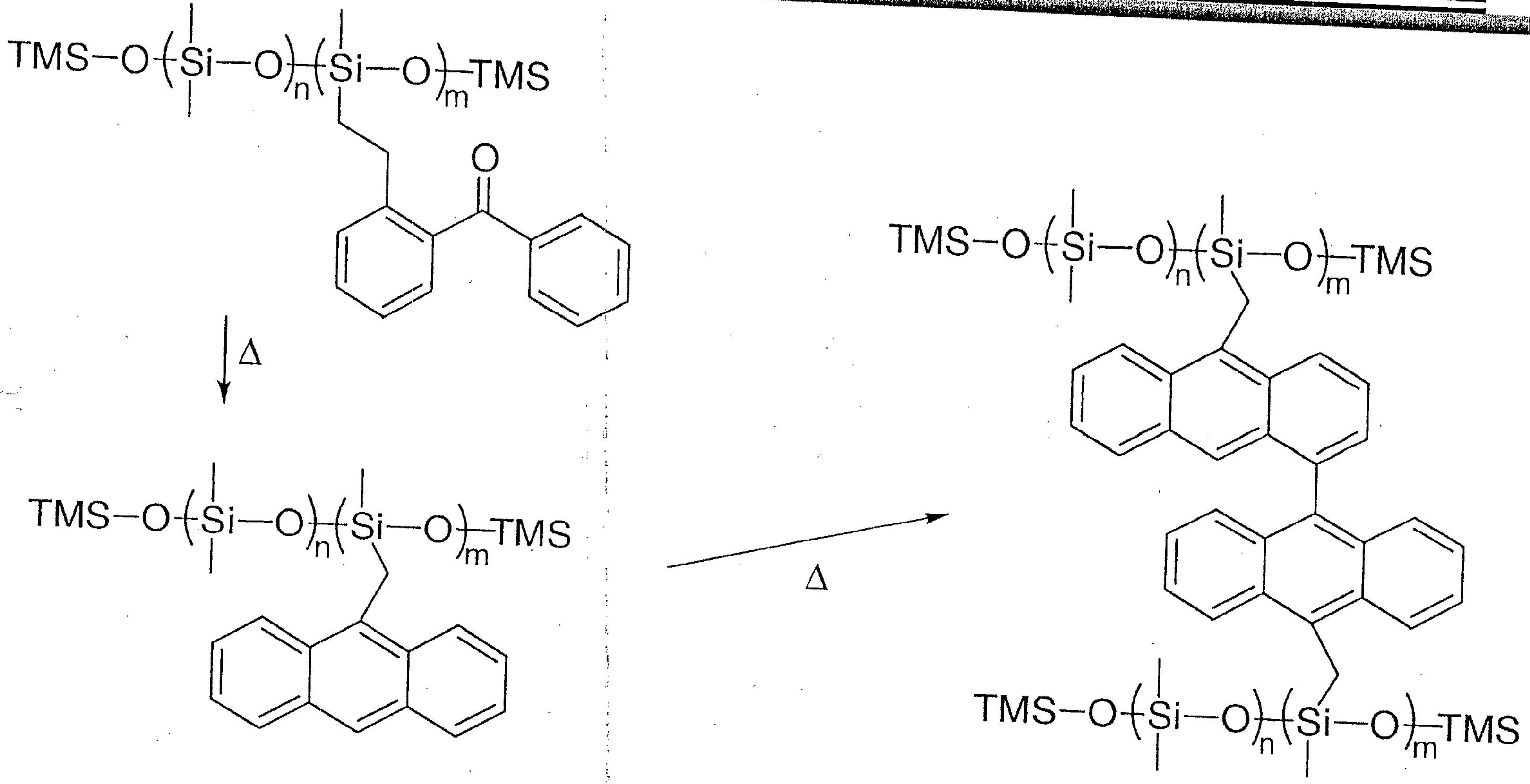
Polymer Crosslinking



- Crosslinks may interfere with reversion reaction

Summary

- Low T_gs 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

Notes

- Typical characteristics of PDMS (low T_g and thermal stability) were successfully retained.
- Characteristics of aromatic diketones (electochemical 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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