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# Ring opening metathesis polymerization of 1,1-diphenyl-1-sila-cyclopent-3-ene

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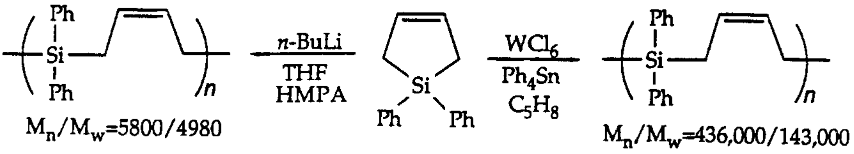
## SUMMARY

1,1-Diphenyl-1-silacyclopent-3-ene (I) has been polymerized by ring opening metathesis using tungsten hexachloride and either cyclopentene or cyclohexene as an initiator, with or without tetraphenyltin as a cocatalyst. The product polymer poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene) (II) has been characterized by $^1$H, $^{13}$C, and $^{29}$Si NMR and IR spectroscopy.

## INTRODUCTION

Recently we have reported the anionic polymerization of I using alkyllithium reagents and hexamethylphosphoramide as cocatalyst in THF.[1] For most 1,1-disubstituted silacyclopent-3-enes, other than I, this technique produces polymers of high molecular weight.[1,2] Anionic polymerization of I, despite considerable effort, yields low molecular weight polymers, $M_w/M_n$ = 13,400/7,900. In order to study the effect of increasing molecular weight on polymer physical properties, we have sought alternative methods to produce high molecular weight II.

There are two reported examples of ring opening metathesis polymerization of 1,1-dimethyl-1-silacyclopent-3-ene.[3,4] The reported molecular weights of poly(1,1-dimethyl-1-silapent-3-ene) were less than 5,500. Olefin metathesis using W/Sn catalyst systems has been extensively studied.[5,6]



## EXPERIMENTAL

$^1$H, $^{13}$C and $^{29}$Si NMR spectra were obtained using a Bruker AM-360 MHz FT NMR spectrometer. $^{13}$C NMR spectra were acquired with broad band proton decoupling. One percent solutions in chloroform-*d* were used to obtain all NMR spectra. $^1$H and $^{13}$C NMR spectra were internally referenced to chloroform. $^{29}$Si NMR spectra were acquired using a NONOE pulse sequence and externally referenced to tetramethylsilane in chloroform-*d*.[7] IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer on NaCl plates.

GPC analysis of the polymer molecular weight distribution was performed on a Waters system comprised of a U6K injector, a 510 pump, a R401 differential refractometer and an 820 Maxima Control system. A Waters 7.8 mm x 30 cm Ultrastyragel linear gel column packed with less than 10 µm particles of mixed pore size cross-linked styrene divinylbenzene copolymer was used for the analysis. HPLC grade THF at a flow rate of 0.6 mL/min was used as the elution solvent. Retention times were

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*To whom offprint requests should be sent calibrated against monodisperse polystyrene standards of molecular weight 612,000, 114,200, 47,500, 18,700 and 5,120, having $M_w/M_n$ of less than 1.09.

Thermal stability of the polymer was determined by TGA. A Perkin-Elmer TGS-2 with nitrogen flow rate of 40 cm$^3$/min was used. The temperature profile used was; 50$^o$C for 10 min followed by heating at a rate of 4$^o$C/min to 750$^o$C. The glass transition temperature ($T_g$) was determined using a Perkin-Elmer DSC-7 differential scanning spectrometer. The temperature profile began at -100$^o$C and increased at a rate of 20$^o$C/min to 150$^o$C.

Toluene and hexane were distilled from sodium benzophenone ketyl immediately prior to use. $WCl_6$ and $Ph_4Sn$ were used as received from Aldrich. The $WCl_6$ and $Ph_4Sn$ were weighted into a round bottom flask in a Vacuum Atmospheres dry box. The flask was sealed with a rubber septum before being removed from the box.

Elemental analysis of the polymer for W and Sn was performed by Galbraith Laboratories, Knoxville, TN.

### 1,1-Diphenyl-1-silacyclopent-3-ene (I)

I was prepared according the literature method.[8,9]

### Polymerization of 1,1-diphenyl-1-silacyclopent-3-ene (I)

A series of reactions was performed. Solvent, cocatalyst and initiator were varied according to Table I. The typical experimental was conducted as follows. Tungsten hexachloride (20.3 mg) and $Ph_4Sn$ (36.6 mg) were weighed into a dry 50 mL round bottom flask containing a Teflon covered magnetic stirring bar and sealed with a septum. Cyclohexene (10 l) or cyclopentene was added to the $WCl_6/Ph_4Sn$ mixture using a syringe. The catalyst system was allowed to age for 5 min. before 0.5 mL of I was added via a syringe. The mixture immediately became dark and the viscosity rapidly increased such that the stir bar was unable to turn. The mixture was allowed to stand at room temperature, under nitrogen, for 1 h before being quenched by the addition of 50 mL of MeOH. The mixture was allowed to stand 1 h as the solid material changed in color from black to white. Methanol was removed by evaporating at reduced pressure. The residue was redissolved in $CCl_4$ and filtered to remove insoluble catalyst. Most of the solvent was removed by evaporation under reduced pressure. The polymer was then precipitated with MeOH, filtered and vacuum dried. A white solid (330 mg, 66%) was recovered. Properties: $^1$H NMR $\delta$: 7.11-7.40(br m,10H), 5.25(t,2H, J = 4.76 Hz), 1.69(d,4H, J = 4.76 Hz). $^{13}$C NMR $\delta$: 135.54, 134.94, 129.22, 127.61, 123.49, 13.67. $^{29}$Si NMR $\delta$: 10.70. IR$\nu$: 3095, 3060, 3040, 1440, 1380, 1235, 1165, 1130, 1045, 770 cm$^{-1}$. GPC: $M_n/M_w$ = 436,309/142,611. $T_g$ was found to be 34.9 $^o$C.[10]

## RESULTS AND DISCUSSION

The spectral properties of II were consistent with low molecular weight polymers. A wide range of cyclic olefins have been shown to undergo ring opening metathesis polymerization using W/Sn catalyst systems.[4,5] These polymerizations occur either neat or solution at room temperature to yield unsaturated polymers which contain a mixture of *cis* and *trans* C-C double bonds. Toluene, chlorobenzene and hexane have been frequently utilized as solvents for such reactions. By comparison, we were unable to polymerize I in the presence of solvent, such as toluene or hexane. Small amounts of cyclopentene or cyclohexene were **essential** initiators for the polymerization of I. Tetraphenyltin, on the other hand, is not essential for polymerization but has a beneficial effect on molecular weight. It is possible that I is able to serve as a reducing agent for the $WCl_6$.[11] The order of addition of the cocatalysts, initiator and I was critical to the success of the polymerization.

When I was polymerized as above, the C-C double bonds of II were 100% *cis*. Under similar metathesis polymerization conditions, cyclopentene yields an unsaturated polymer of low molecular weight with predominately *trans* C-C double bonds.[6,12] The difference in stereochemistry may be due to the phenyl groups on silicon which sterically hinder rotation of the polymer during polymerization. The reasons for our inability to achieve polymerization of I when diluted with toluene or hexane are under study.

Thermal stability of the polymer was studied by gravimetric analysis (TGA). II having $M_w/M_n$ = 5,800/4,980 was produced by anionic polymerization.[1] The thermal stability of II was found to be a function of molecular weight (See Figure). In the case of high molecular weight II, a 11% residue was found. Elemental analysis of high molecular weight II shows the sample contains 0.58% W and less than 0.56% Sn. This demonstrates that the char can not result exclusively from the presence of catalyst residues.

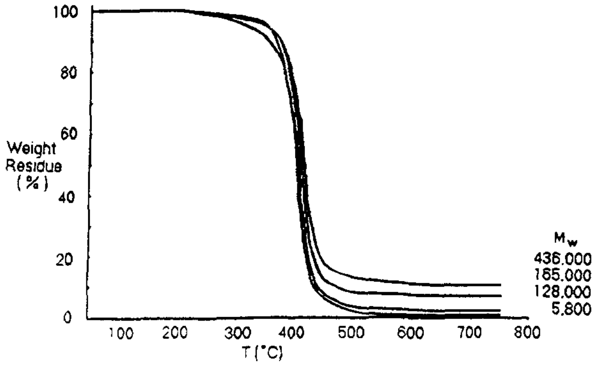

**Table 1. Effect of catalysts on Molecular weight of II**

| Polymer | $WCl_6$ (mg) | $Ph_4Sn$ (mg) | $C_5H_8$ ( L) | $C_6H_{10}$ ( L) | $M_w/M_n$ |
|---|---|---|---|---|---|
| A | 40 | 86 | 20 | | 99,700/35,000 |
| B | 20 | 34 | | 10 | 436,309/143,611 |
| C | 18 | 10 | | | 165,346/74,355 |
| D | 11 | | | | N/R |

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