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# Birch reduction of the dichlorocarbene adduct of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) ($Cl_2C$-I): synthesis and characterization of poly(1,1-dimethyl-3,4-methylene-1-sila-*cis*-pent-3-ene) $CH_2$-I)

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## SUMMARY

Birch reduction of the dichlorocarbene adduct of poly(1,1-dimethyl-1-sila-cis-pent-3-ene) ($Cl_2C$-I) yields poly(1,1-dimethyl-3,4-methylene-1-sila-cis-pent-3-ene) ($CH_2$-I) which has been characterized by $^1H$, $^{13}C$ and $^{29}Si$ NMR spectroscopy as well as by elemental analysis. The molecular weight distribution of $CH_2$-I has been determined by GPC and its thermal stability by TGA. Its glass transition temperature was obtained by DSC.

## INTRODUCTION

There is considerable interest in the chemical modification of polymers.[1-4] While it has been possible to stereospecifically quantitatively add dichloro[5-8] and difluorocarbene[9] to the C-C double bonds of 1,4-polybutadiene, it has not been possible to achieve complete cyclopropanation of the C-C double bonds of 1,4-polybutadiene by use of the Simmons-Smith reaction.[8]

## EXPERIMENTAL

$^1H$,$^{13}C$ and $^{29}Si$ NMR spectra were obtained on an IBM-Bruker WP-270-SY spectrometer operating in the Fourier transform mode. Five to ten percent weight/volume solutions of polymer $CH_2$-I in chloroform-d were used to obtain $^1H$ NMR spectra, whereas ten to fifteen percent solutions were utilized for $^{13}C$ and $^{29}Si$ NMR spectra. Chloroform was used as an internal standard for $^1H$ and $^{13}C$ NMR spectra. Heteronuclear proton/carbon chemical shift correlations (2D NMR) were run on a Brucker AM-360 spectrometer. A DEPT pulse sequence was used to obtain $^{29}Si$ NMR spectra. This was effective because the silicon atoms all have at least two methyl groups bonded to them.[10] All $^1H$, $^{13}C$ and $^{29}Si$ NMR chemical shifts reported were externally referenced to TMS.

The IR spectrum of $CH_2$-I was recorded on a Perkin-Elmer PE- 281 spectrometer as a film between NaCl plates ν: 3040, 2980, 2940, 2900, 2860, 1405, 1350, 1240 (s), 1180, and 830(s) $cm^{-1}$.

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GPC analysis of the molecular weight distributions of the polymers was performed on a Perkin-Elmer series 10 liquid chromatograph equipped with an LC-25 refractive index detector (maintained at 25°C), a 3600 data station and a 660 printer. A 32 cm x 77 mm Perkin-Elmer PL 10 μm particle size, mixed pore size crosslinked polystyrene gel column was used for the separation. The eluting solvent was HPLC grade THF at a flow rate of 0.7 ml/min. The retention times were calibrated against known monodisperse polystyrene standards: $M_p$ 3,600,000, 194,000, 28,000, 7,600, and 2550 whose $M_w/M_n$ are less than 1.09.

The DSC of $CH_2$-I was run on a Perkin Elmer DSC-4 instrument. The temperature program was begun at -80°C. After stabilization, the temperature was increased at a rate of 20°C/min to 20°C. The TGA of the polymers was carried out on a Perkin-Elmer TGA-2 instrument with a nitrogen flow rate of 40 cc/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 5°C/min to 550°C.

Elemental analysis was performed by Galbraith Laboratories Knoxville, TN.

## poly(1,1-Dimethyl-1-sila-cis-pent-3-ene) (I)

I was obtained by the anionic ring opening polymerization of 1,1-dimethyl-1-silacyclopent-3-ene, $M_w/M_n$ = 65,000/29,000.[11]

## Dichlorocarbene adduct of I ($Cl_2C$-I)

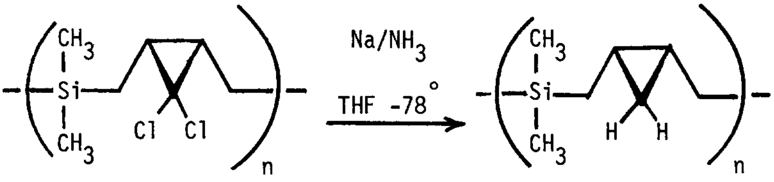
$Cl_2C$-I was prepared by the addition of dichlorocarbene to I under PTC conditions at 0°C, 92% yield, $M_w/M_n$ = 29,100/16,500.[12]

## Birch Reduction of $Cl_2C$-I

In a 500 ml three neck round bottom flask equipped with a cold finger reflux condenser, an inert gas inlet, and a rubber septum was placed 8.0 g of freshly prepared sodium dispersion and 100 ml of dry THF and a glass covered magnetic stirring bar. Dry ice/acetone slush was added to the cold finger condenser. The flask was partially immersed in a Dewar flask containing a dry ice/acetone slush. Dry ammonia gas was condensed into the flask until a deep blue color appeared. At this time the solution consisted of approximately at 1:1 ratio of THF to ammonia. The reaction was stirred and the temperature maintained at -78°C while a solution of 0.2 g of $Cl_2C$-I in 120 ml of THF was slowly added to the reducing medium. The blue color in the solution was maintained at all times. After completion of the addition, the reaction was stirred for 3.5 h and was then allowed to slowly warm to room temperature. After all the ammonia had evaporated, the THF solution was decanted from the unreacted sodium lumps in the reaction flask. The flask was washed with 250 ml of ether and the combined organic solution was washed with saturated aqueous $NH_4Cl$ solution, dilute HCl and finally with water. The organic layer was dried over activated 4 A° molecular sieves, filtered and the solvent removed by evaporation under reduced pressure. The product polymer was dissolved in THF and purified by precipitation from methanol. This process was repeated twice. Finally it was dried under vacuum overnight. In this way, 0.12 g of $CH_2$-I was obtained, 93% yield. $M_w/M_n$ = 35,600/10,000. Elemental Anal. Calc. for $C_7H_{14}Si$: C, 66.66; H, 11.11. Found: C, 65.63; H, 11.10.

## RESULTS AND DISCUSSION

We have been able to achieve complete dichlorocyclopropanation of the C-C double bonds of poly(1,1-dimethyl-1-sila-cis-pent-3-ene) (I) to yield $Cl_2C$-I by addition of dichlorocarbene under phase transfer catalysis (PTC) conditions.[12] On the other hand, we have only been able to add methylene to sixty percent of the C-C double bonds of I to prepare poly(1,1-dimethyl-3,4- methylene-1-sila-cis-pent-3-ene) ($CH_2$-I) by use of the Simmons Smith reagent.[13] We should like to report that it is possible to achieve this result by quantitative Birch reduction of $Cl_2C$-I. We believe, this is the first example of reduction of dichlorocyclopropane units to cyclopropane units in a polymer system or for that matter of the application of the Birch reaction to polymer systems. We are currently exploring the scope of Birch reductions in polymer systems. Birch reductions have been utilized to reduce dichlorocyclopropanes to cyclopropanes in monomeric systems.[14,15]



The thermal stability of $CH_2$-I as determined by TGA was found to be virtually the same as that of I (see figure 1). Rapid weight loss does not occur until $CH_2$-I is heated above 300°C. This thermal stability is significantly greater than that of $Cl_2C$-I which undergoes rapid weight loss on heating above 110°C. Clearly the thermal instability of $Cl_2C$-I does not result from the strain of the cyclopropane ring but rather from the presence of C-Cl bonds which can undergo heterolytic ionization with concerted ring opening of the cyclopropane ring to yield a silyl stabilized allylic carbocation intermediate as we have previously proposed.[12] The glass transition temperature for $CH_2$-I was found to be -30°C. This is significantly higher than the glass transition temperature of I which has been found to be -63°C.[16]

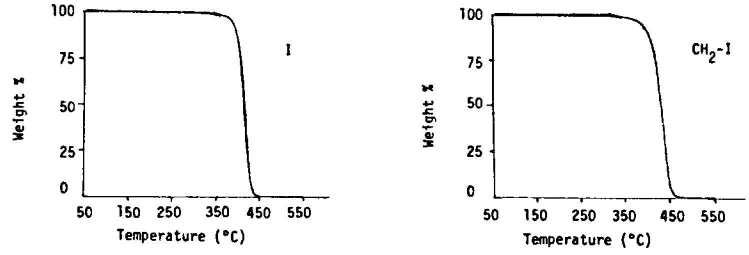
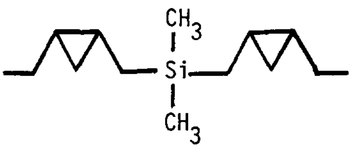
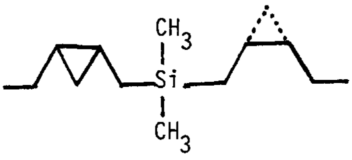


Figure 1. TGA of I and $CH_2$-I

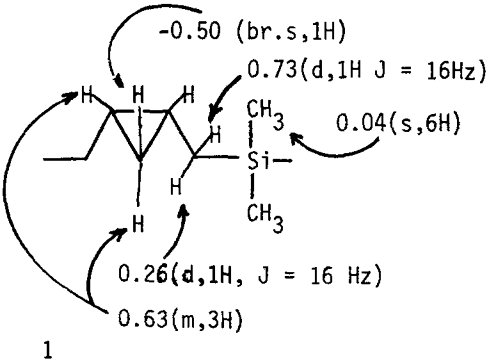
$^{29}$Si NMR spectroscopy was particularly informative concerning the microstructure of $CH_2$-I. Two signals of equal intensity were observed in the $^{29}$Si NMR at 4.58 and 4.54 ppm. One of these results from silyl centers which have both neighboring cyclopropane rings on the same side of the polymer chain, while the other resonance results from silyl center which have neighboring cyclopropane rings on opposite side of the polymer chain.





Consistent with this, the methyl groups bonded to silicon give rise to three signals in the $^{13}$C NMR at -2.68, -2.76 and -2.83 ppm (1:2:1). The first and third result from methyl groups bonded to silicon in which adjacent cyclopropane rings are on the same side of the polymer chain. On the other hand, the second resonance arises from the methyl groups bonded to silicon in which the cyclopropane rings are on opposite sides of the polymer chain.

Neither the $^1$H nor the $^{13}$C NMR provide additional information concerning microenvironments of the polymer. This is surprising since under similar conditions the $^1$H and $^{13}$C of both $Cl_2C$-I[12] and $F_2C$-I[16] provide significant information. The proton decoupled $^{13}$C NMR spectrum of $CH_2$-I is characterized by six lines. Three of these have been previously assigned to methyl groups bonded to silicon. In addition to these three, resonances are observed at 11.10 (cyclopropane methine carbons), 13.95 (methylene carbons bonded to silicon), and 14.49 (cyclopropane methylene carbons). These have been assigned by use of coupled spectra. The $^1$H NMR spectra of $CH_2$-I can be assigned by comparison with that reported for cis-1,2-dimethylcyclopropane.[17] This was confirmed by a 2D NMR experiment.



$^1$H NMR Chemical Shift Assignments

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