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Addition of dichlorocarbene to *cis*-1,4-poly(2-trimethylsilylmethyl-1,3-butadiene)

Fluoride catalyzed elimination of trimethylchlorosilane from *cis*-1,4-poly(2,3-dichloromethylene-2-trimethylsilylmethyl-1,3-butadiene)

Wan Jiang, Yi-Xiang Ding, and William P. Weber*

K.B. and D.P. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

SUMMARY

Copolymers made up of 1,4-(2,3-dichloromethylene-2-trimethylsilylmethyl-1,3-butadiene) (I) and 1,5-(3-chloro-2-methylene-pent-3-ene) (II) units have been prepared by potassium fluoride elimination of trimethylchlorosilane from cis-1,4-poly(2,3-dichloromethylene-2-trimethylsilylmethyl-1,3-butadiene) (III). III was prepared by the addition of dichlorocarbene to 1,4-poly- (2-trimethylsilylmethyl-1,3-butadiene) (cis/trans = 9/1) (IV). Polymer III was characterized by ^{1}H, ^{13}C and ^{29}Si NMR as well as by elemental analysis. The copolymer was characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The ratio of I and II units in the copolymer were determined by ^{1}H NMR and elemental analysis.

INTRODUCTION

There is considerable interest in the chemical modification of intact polymers (1-4). 1,4-Poly-(2-trimethylsilylmethyl-1,3-butadiene (cis/trans 9/1) has been prepared by Ziegler-Natta polymerization of 2-trimethylsilylmethyl-1,3-butadiene (5). Dichlorocarbene, efficiently generated under phase transfer catalysis (PTC) conditions by reaction of concentrated aqueous potassium or sodium hydroxide with chloroform in the presence of a catalytic amount of a quaternary ammonium salt, has been added stereospecifically to the carbon-carbon double bonds of cis and trans-1,4-polybutadiene (6-9). Addition of dichlorocarbene generated under PTC condition to IV gives III. Treatment of III with potassium fluoride dihydrate in DMSO/THF results in partial 1,4-Grob type elimination (10) of trimethylchlorosilane and formation of a copolymer composed of I and II units. Fluoride ion has been used to carry out similar 1,2 and 1,4-eliminations (11).

EXPERIMENTAL

^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broad band proton decoupling. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra (12).

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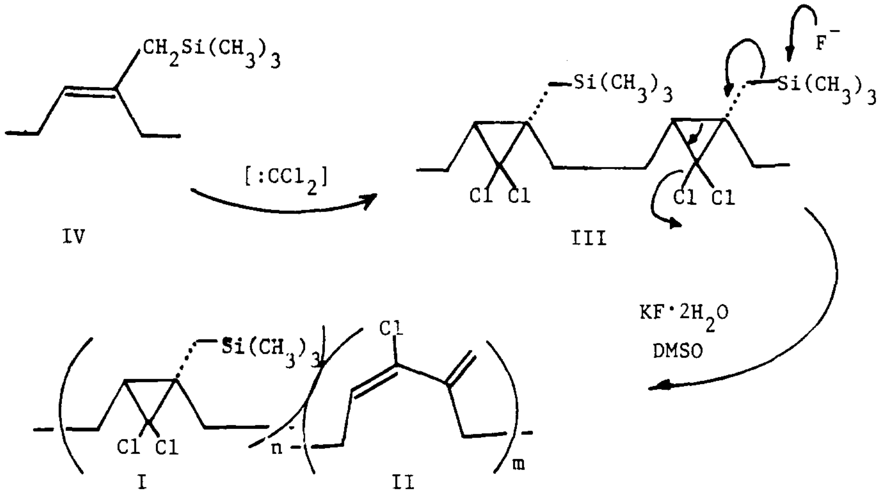
*To whom offprint requests should be sent



This was effective since all the silicon atoms have three methyl groups bonded to them. Five percent solutions in chloroform-d were used to obtain ^{1}H NMR spectra, while ten percent solutions were used for ^{13}C and ^{29}Si NMR spectra. Chloroform was utilized as an internal standard. All chemical shifts reported were externally referenced to tetramethylsilane. IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. GPC analysis of the molecular weight distribution 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. Two 32 cm x 77 mm Perkin-Elmer PL 5 and 10 µm particle size, mixed pore size, crosslinked polystyrene gel columns connected in series were used for the separation. The eluting solvent was THF at a flow rate of 0.9 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p = 3,600,000, 194,000, 28,000, 2,550 whose M_w/M_n are less than 1.09. TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at 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 800°C. Elemental analysis was performed by Galbraith Laboratories Knoxville, TN.

Poly-1,4-(2,3-dichloromethylene-2-trimethylsilylmethyl-1,3-butadiene) (III)

In a 50 mL round bottom flask equipped with a Teflon covered magnetic stirring bar was placed IV (M_w/M_n = 114,00/84,500) (0.2 g, 1.4 mmol), tetra-n-butylammonium chloride (0.05 g) and chloroform (20 mL). To this reaction mixture was added dropwise a solution of sodium hydroxide (3 g) in 3 mL of water. The mixture was vigorously stirred at rt for 2 h. It was transferred to a separatory funnel, methylene chloride (60 mL) was added and the organic layer was washed with water until neutral. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed by evaporation under reduced pressure. The light brown residue was dissolved in THF. It was purified by precipitation from methanol three times. In this way, 0.28 g (90% yield) of III M_w/M_n = 81,400/62,300 was obtained, ^{1}H NMR δ: 1.95-1.30(br.s, 5H), 1.22- 0.5(br.s,2H), 0.11(s,1H)-*trans*, 0.05(s,8H)-*cis*. ^{13}C NMR δ: 72.99, 72.78, 72.51, 72.40, 40.22, 40.10, 39.85, 35.05, 34.64, 34.31, 33.91, 30.52, 30.41, 29.99, 29.71, 22.89, 22.78, 22.66, 22.58, 22.45, 22.39, 22.12, -0.032. ^{29}Si NMR δ: 1.486 *trans*, 1.332 *cis*. IR ν: 2940, 2920, 2880, 1440, 1240, 1190, 830 cm^{-1}. Elemental analysis calcd. for $C_9H_{16}Cl_2Si$: C, 48.45; H, 7.23; Cl, 31.78. Found: C, 49.48; H, 7.66; Cl, 32.23.

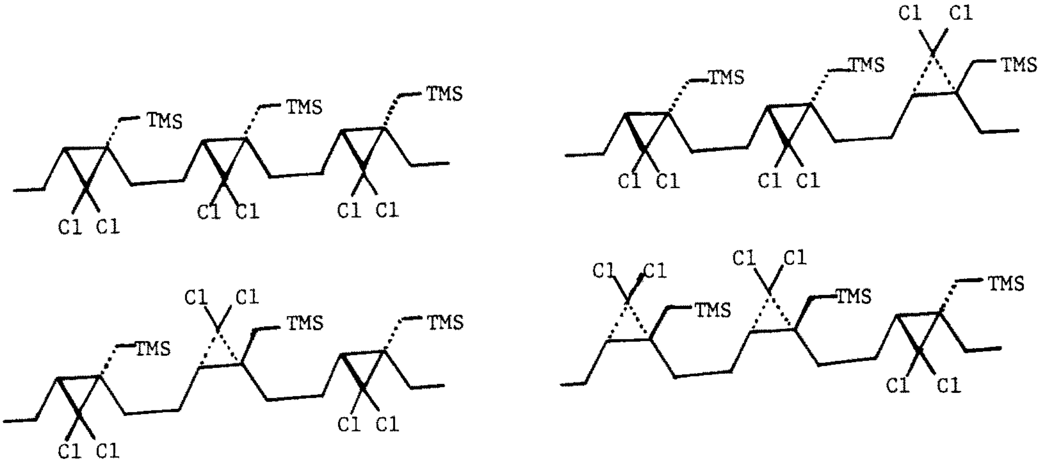
Copolymer

In a 50 mL round bottom flask equipped with a Teflon covered magnetic stirring bar and a reflux condenser was placed 0.28 g of III, 20 mL of THF, KF $2H_2O$ (0.8 g) and DMSO 5 mL. The suspension was stirred and heated to reflux for 72 h. The mixture was poured into a separatory funnel. The reaction flask was rinsed with 200 mL of ether and 30 mL of water. These were added to the separatory funnel. A small amount of white material which floated between the aqueous and organic layers was removed. The organic layer was washed several times with water, dried over anhydrous magnesium sulfate, filtered and the solvents removed by evaporation under reduced pressure. The residue, a light brown sticky oil was purified by precipitation from methanol. A 60% yield was obtained, M_w/M_n = 40,000/17,400. ^{1}H NMR δ: 5.89(br.s,0.7H), 5.49(s,0.7H), 5.06(s,0.7H), 2.43(br.s,2.8H), 1.85-0.5(br.s,1.8H), 0.08(s,1.8H)-*trans*, 0.05(s,0.9H)-*cis*. ^{13}C NMR δ: 143.97, 143.53, 142.89, 134.86, 134.43, 134.05, 126.52, 126.30, 125.55, 116.12, 115.56, 114.87, 72.87, 72.34, 39.97, 39.45, 34.59, 34.26, 34.05, 33.51, 32.69, 30.36, 30.04, 29.71, 29.60, 29.44, 26.24, 25.65, 22.54, 22.18, -0.03. ^{29}Si NMR δ: 1.388, 0.899. IR ν: 2900(w), 1675(w), 1600, 1440, 1360, 1240, 830 cm^{-1}. UV λ_{max} 242 nm, $\varepsilon = 21{,}000$. Elemental analysis calcd.: C, 58.24; H, 6.51; Cl, 31.22. Found: C, 58.24; H, 6.63; Cl, 29.83.

RESULTS AND DISCUSSION

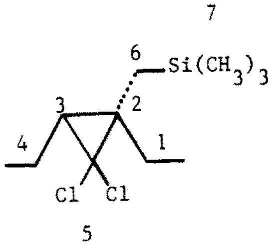
The addition of dichlorocarbene to IV proceeded quantitatively since neither vinyl hydrogens nor carbons were observed in ^{1}H or ^{13}C NMR of the product polymer III. The starting polymer IV contained both *cis*-1,4 and *trans*-1,4 units in a ratio of 9/1. The observation of two resonances in the ^{29}Si NMR of III is consistent with the presence of both *cis* and *trans*-dichlorocyclopropane units in III. Nevertheless, the ^{13}C NMR of III can be analyzed on the basis of triads made up only of the predominant *cis* units. Four distinct types of triads result from this analysis. Since there are seven unique carbons in each unit, this leads to a prediction of seven groups of four or twenty-eight ^{13}C resonances. In fact only twenty-three signals are observed. The major source of this discrepancy results from the fact that the methyl carbons bonded to silicon gives rise to a single signal rather than to the four predicted. This lack of sensitivity may result from the length of the carbon-silicon bonds (1.89 A^o). Further, C_2 and C_6 each give rise to only three signals rather than the four expected. This may result from fortuitous coincidence or overlap of these signals (see Figure 1).

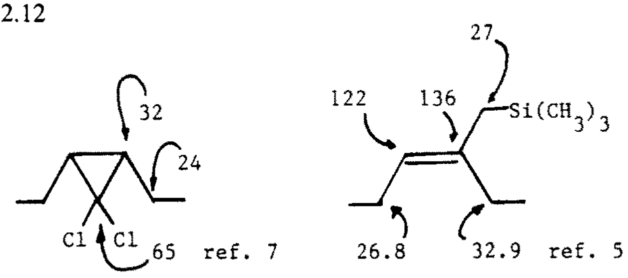
Triad Analysis of III



TMS = Si(CH$_3$)$_3$

C$_1$	30.52, 30.41, 29.99, 29.71
C$_2$	40.22, 40.10, 39.85
C$_3$	35.05, 34.64, 34.31, 33.91
C$_4$	22.89, 22.78, 22.66, 22.58
C$_5$	72.99, 72.78, 72.51, 72.40
C$_6$	22.45, 22.39, 22.12
C$_7$	-0.03





^{13}C NMR Chemical Shifts of Model Compounds

Figure 1. ^{13}C NMR Chemical Shifts of
1,4-Poly(2,3-dichloromethylene-2-trimethylsilylmethyl-1,3-butadiene)

TGA analysis indicates that polymer III is stable to 140°C. Rapid weight loss (37%) occurs between 140 and 190°C. Between 200 and 500°C an additional 47% of the initial sample weight is lost. A residue of 14% remains at 800 °C (Figure 2).

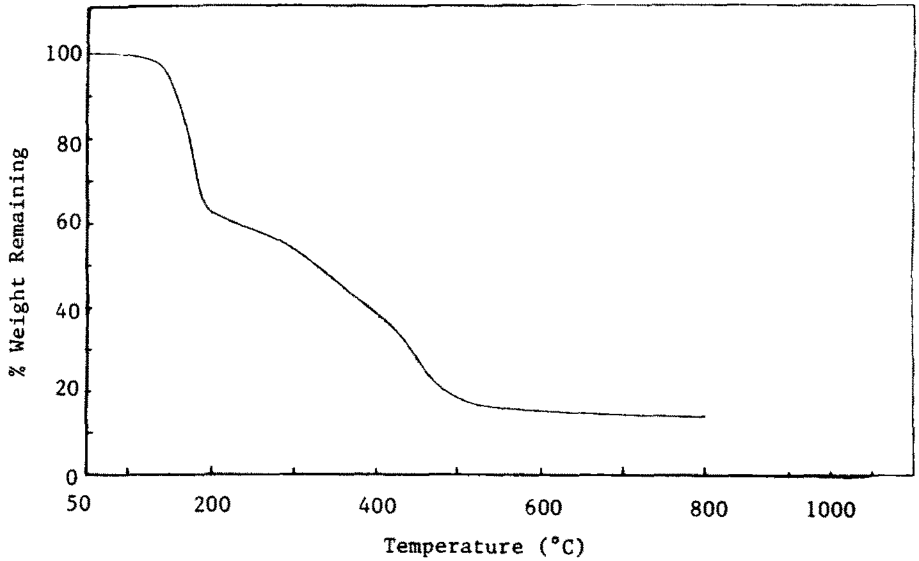
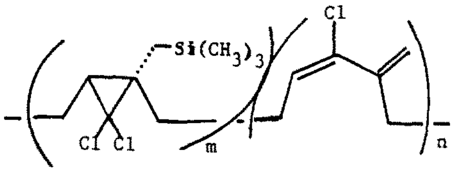


Figure 2. TGA of poly-1,4-(2,3-dichloromethylene-2-trimethylsilyl-1,3-butadiene) (III).

III was treated with KF in DMSO in order to effect elimination of trimethylchlorosilane and formation of poly-1,5-(3-chloro-2- methylene pent-3-ene). However, even after heating for 72 h, analysis revealed that only partial elimination had occurred. This results in formation of a copolymer made up of I and II units. Integration of the ^{1}H NMR spectrum indicated that the ratio of I:II units was 28:72. It is also clear from the ^{1}H NMR spectrum that elimination of trimethylchlorosilane is much more favorable from *cis* units than from those which have a *trans* geometry. This is expected from the continuous orbital overlap required for a concerted Grob type elimination (10).

The percent composition of carbon, hydrogen and chlorine was determined for the copolymer. The calculated value for hydrogen and chlorine were determined on the assumption that the carbon value was correct. The ratio of I:II units in the copolymer determined in this way 20:80 was in reasonable agreement with the value determined by ^{1}H NMR integration.



n + m = 1

Molecular weight of polymer = MW = n(6C+7H+Cl) + m(9C+16H+2Cl+Si)

%C = (6nC + 9mC)/MW, %Cl = (nCl +2mCl)/MW, %H = (7nH +16mH)/MW, where Cl, H, Si and C are the respective atomic weights of these elements.

The ^{13}C spectrum of the copolymer can be understood by application of a triad analysis. Three types of triads with a II unit at the center are predicted (II,II,II; I,II,II = II,II,I, I,II,I). Since there are four distinct vinyl carbons and two unique allylic carbons in II, this analysis leads to a prediction of twelve vinyl carbons and six allylic carbons as is observed. Seven types of triads with I units at the center are predicted. Since the concentration of I units is low we assume that the four triads made up of I units (see Figure 1) make no contribution. Two of the three probable triads are made up of two I units and one II unit. In one of these the dichlorocyclopropanes of the I units are on the same side of the polymer chain while in the other the dichlorocyclopropane units are on opposite sides of the polymer chain. The final triad is II,I,II. These three probable triads lead to a prediction of twenty-one ^{13}C resonances. If we assume that the methyl carbons bonded to silicon are insensitive as previously observed we might anticipate nineteen signals. In fact only thirteen unique signals are observed. This observation may result from the coincidence of ^{13}C NMR signals for the two I,I,II triads.

TGA analysis indicates that the copolymer is stable to 150 °C. Between 150 and 500 °C, 85% of the initial sample weight is gradually lost. A residue of 10% remains at 800°C (Figure 3).

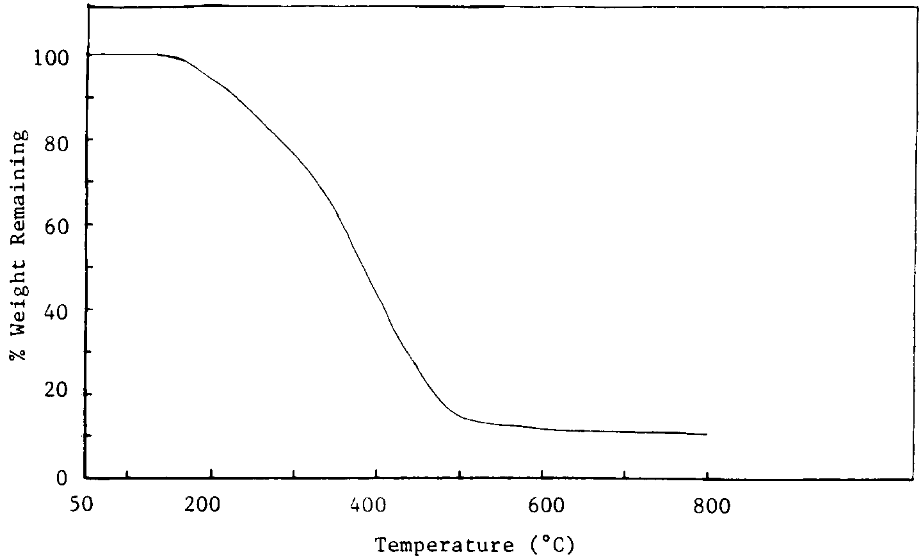


Figure 3. TGA of copolymer.

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