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Addition of Dichlorocarbene to Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) and Poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene). Characterization of Microstructures by ^{13}C and ^{29}Si NMR

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ABSTRACT: Dichlorocarbene generated under phase-transfer catalysis conditions was added to poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I). Catalytic isomerization of I by photochemically generated phenylthio radicals gave poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene) (II). Dichlorocarbene was also added to II. The microstructures of these dichlorocarbene adduct polymers were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR. Their thermal stabilities were determined by thermogravimetric analysis. They were found to be considerably less stable than the starting polymers I or II. These dichlorocarbene adduct polymers slowly undergo spontaneous depolymerization at room temperature. The mechanism of this process is considered.

There is considerable interest in the chemical modification of polymers.[1,2] Dichlorocarbene, efficiently generated by reaction of concentrated aqueous solutions of potassium or sodium hydroxide with chloroform in the presence of catalytic amounts of quaternary ammonium salts phase-transfer catalysts (PTC), has been added stereospecifically to the carbon–carbon double bonds of the backbones of *cis*- and *trans*-1,4-polybutadiene.[3–6] Difluorocarbene has also been added to the carbon–carbon double bonds of 1,4-polybutadienes.[7]

We should like to report the addition of dichlorocarbene, generated under PTC conditions, to poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I) and to poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene) (II). Anionic ring-opening polymerization of 1,1-dimethyl-1-silacyclopent-3-ene as previously reported gave I.[8] Stereospecific cis addition of dichlorocarbene to the carbon–carbon double bonds of I produces a polymer (III) whose microstructures can be analyzed by ^{13}C and ^{29}Si NMR spectroscopy. Two signals are observed in the ^{29}Si NMR at 3.88 and 3.76 ppm. The first results from the microstructure in which two consecutive dichlorocyclopropane rings are on the same side of the polymer backbone, while the second arises from the microstructure in which one cyclopropane ring is on one side while the next is on the opposite side of the polymer chain. Similarly, two signals are observed in the ^{13}C NMR for the methyl groups bonded to the silyl centers at −2.77 and −2.86 ppm (see Figure 1).

Neither the ^{13}C NMR chemical shifts of the methine carbons (29.90 ppm) nor those of the dichloro-substituted carbons (68.14 ppm) are sensitive to the neighboring units' microstructure. Triad analysis predicts three distinct microenvironments: one in which three adjacent cyclopropanes are on the same side of the polymer chain (s,s,s), one in which two adjacent cyclopropanes are on the same side while the next is on the opposite side (s,s,o), and finally one in which the one cyclopropane is on one side, the next on the opposite, and the last on the same side of the polymer chain as the first (s,o,s). Analysis of these situations leads to the prediction that the two symmetrical triads (s,s,s) and (s,o,s) will each give rise to a distinct ^{13}C NMR resonance for the methylene carbons, while the unsymmetrical triad (s,s,o) will give rise to two unique methylene carbon signals for a total of four distinct methylene resonances. In fact, only two signals are observed for the methylene carbons. This may be explained if fortuitously one of the methylene resonances for the unsymmetrical triad is coincident with the signal for the first symmetrical triad while its other ^{13}C methylene signal is coincident with that of the other symmetrical triad (see Figure 2).

An alternative way to analyze these data is to assume that the ^{13}C chemical shifts of the methylene carbons of the central unit of each triad are only affected by the stereochemical orientation of the nearest-neighbor cyclopropanes. Application of this approach to the unsym-

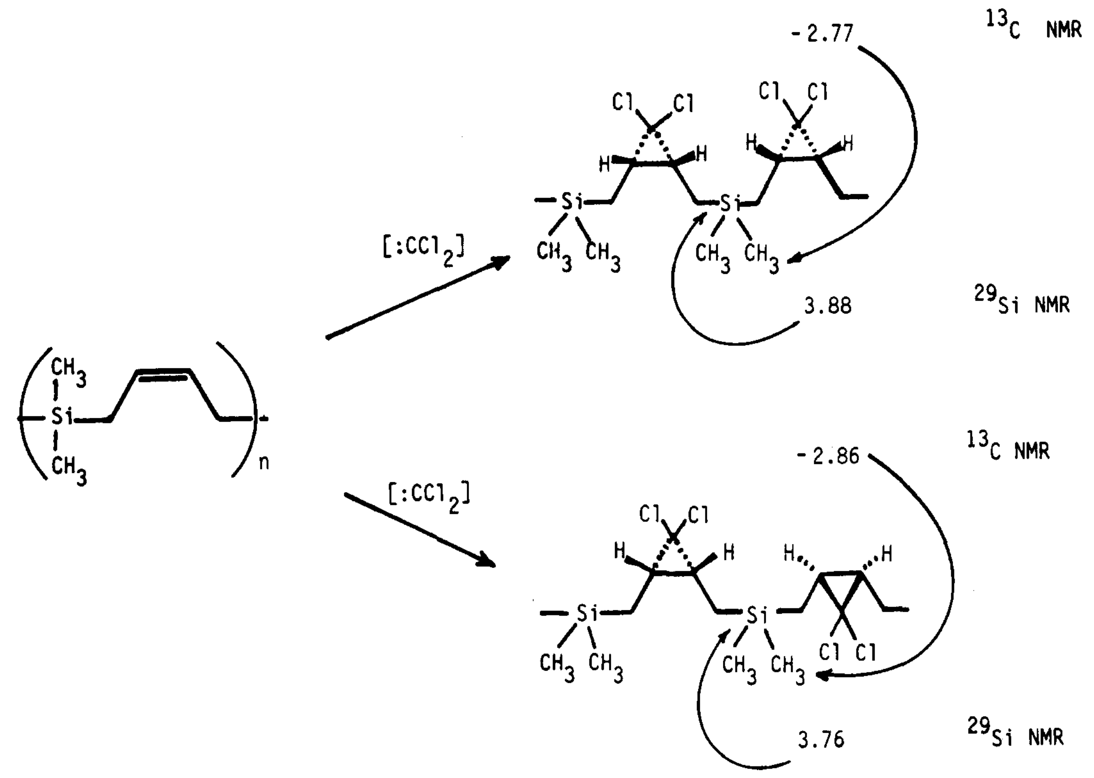


Figure 1. Microstructures of III. ^{13}C and ^{29}Si NMR chemical shifts of $(CH_3)_2Si$ groups.

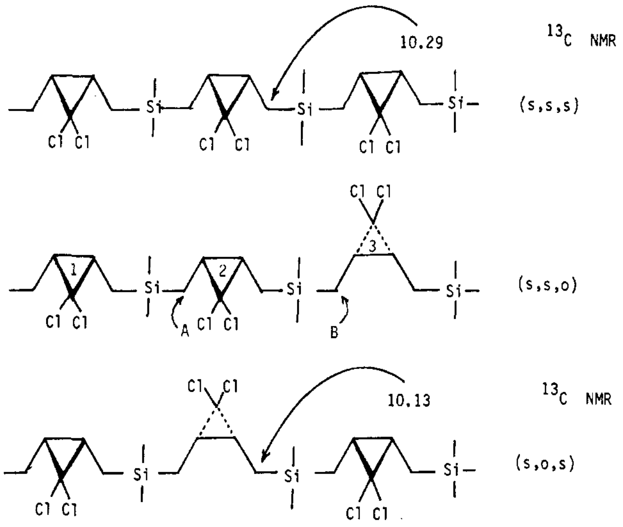


Figure 2. Triad microstructures of III; ^{13}C NMR of methylene groups.

metrical triad (s,s,o) leads to the prediction that the ^{13}C resonance of methylene A, whose chemical shift will be determined by the geometrical orientations of cyclopropanes 1 and 2, should be identical with that of the symmetrical triad (s,s,s) while that of methylene B should be coincident with that of the symmetrical triad (s,o,s). Thus this analysis predicts only two ^{13}C methylene resonances (see Figure 2).

Integration of the ^{13}C resonances of identically substituted but stereochemically different methylene carbon atoms indicates that these microstructures are formed in equal amounts. For ^{1}H NMR data see the Experimental Section.

The addition of dichlorocarbene generated under PTC conditions to the carbon–carbon double bonds of I, $\bar{M}_w/\bar{M}_n$ = 105 000/63 500, results in a polymer (III) whose molecular weight has apparently decreased, $\bar{M}_w/\bar{M}_n$ = 47 700/23 500. Scission of I at least partially results from nucleophilic attack by hydroxide ion on a silyl center with loss of an allylic anion (see Figure 3). Transfer of hydroxide anion into organic solvents has been suggested to occur under PTC conditions.[9,10]

Polymer III is significantly less thermally stable than I. This is surprising since dichlorocyclopropanation of 1,4-polybutadiene increases the thermal stability of the polymer.[7] By TGA III is stable to 110 °C. Rapid weight loss occurs between 110 and 200 °C. By 200 °C III has lost almost 55% of its original weight. A region of slow decomposition is observed between 200 and 320 °C. Rapid weight loss occurs again above 325 °C. By 500 °C only 5% of the initial weight of III remains (see Figure 4).

Upon standing at room temperature for extended periods of time, III undergoes chain scission. For example, after 2 weeks the molecular weight distribution as determined by gel permeation chromatography (GPC) has decreased from $\bar{M}_w/\bar{M}_n$ = 47 700/23 500 to $\bar{M}_w/\bar{M}_n$ = 6800/3000. This process occurs more rapidly in solvents which promote ionization, such as chloroform. We believe this process occurs by ionization of one of the carbon–chlorine bonds with concerted disrotatory opening of the cyclopropane ring to an allylic cation.[11] This symmetry-allowed process is accelerated due to the fact that the allylic cation formed is further stabilized by two β-dimethylsilyl groups. It is well-known that silicon has a profound stabilizing effect on β-carbocation centers.[12] Nucleophilic attack by the chloride anion on the dimethylsilyl center results in scission of the polymer chain. One end is now terminated by a dimethylchlorosilyl group while the other has a 2-chloro-1,3-butadiene end group (see Figure 5). It is anticipated that the reaction with adventitious water will convert the dimethylchlorosilyl group to a disiloxane unit. Absorption bands consistent with Si–O–Si units are observed in the IR at 1050 cm^{-1}. In addition, a resonance at −21.9 ppm is seen in the ^{29}Si NMR

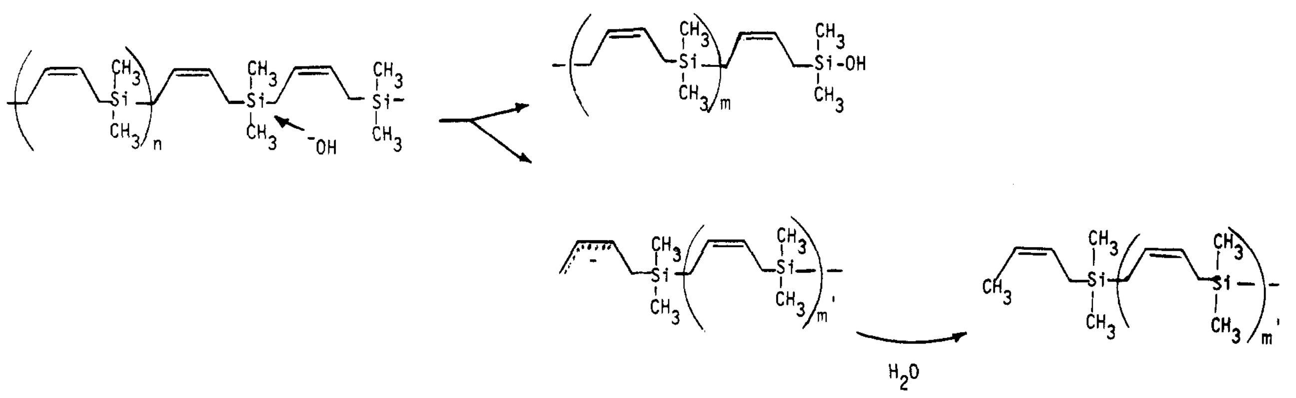


Figure 3. Scission of I by nucleophilic attack of hydroxide.

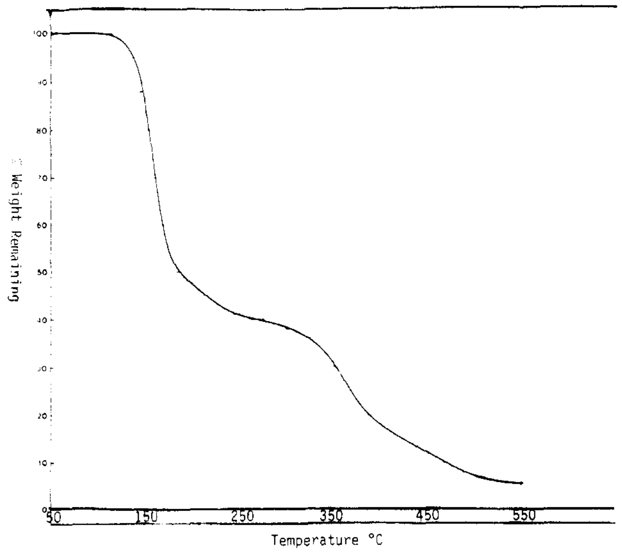


Figure 4. TGA of III.

spectrum. This is consistent with an open-chain disiloxane.[13] Evidence for 2-chloro-1,3-butadiene end groups is found in both the ^{1}H and ^{13}C NMR. In the ^{1}H NMR, four vinyl-CH resonances of equal intensity are observed at 5.1 (d of d, J = 18 and 10 Hz), 5.45 (d of d, J = 18 and 10 Hz), 5.8 (m), and 6.2 (d of d, J = 18 and 10 Hz) ppm (see Figure 6). In the ^{13}C NMR four resonances are observed in the vinyl region at 134.7, 132.0, 128.2, and 113.6 ppm. An absorption in the UV at 239 nm ($\epsilon = 10^4$) is also consistent with 2-chloro-1,3-butadiene end groups. This process may account for the low value for chlorine found on elemental analysis of this polymer. For comparison, the dichlorocarbene adduct of allyltrimethylsilane is stable to distillation at 185 °C. However, on treatment with zinc chloride at 110 °C for 4 h, it decomposes to 2-chloro-1,3-butadiene and trimethylchlorosilane.[14]

Poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene) (II) was prepared by a photoinitiated free radical catalyzed isomerization of I with thiophenol and azobis(isobutyronitrile) (AIBN).[15,16] This process leads to little change in the molecular weight distributions of the polymers: $\bar{M}_w/\bar{M}_n$ = 117 400/47 200 for I, while $\bar{M}_w/\bar{M}_n$ = 108 200/47 200 for II. The ratio of cis/trans carbon–carbon double bonds in II was determined by intergration of the distinct vinyl C–H resonances in the ^{1}H NMR. The *cis*-vinyl C–H resonance occurs at 5.29 ppm while the *trans*-vinyl C–H resonance is observed at 5.19 ppm in chloroform solvent (see Figure 7). If this isomerization is stopped after short periods of time (4 h), II is obtained with a ratio of cis/trans which is greater than unity. However, if this isomerization is carried out for longer periods of time (24 h), II is obtained with a cis/trans ratio of 1.07. Repetition of this isomerization process yields a polymer with cis/trans ratio of ~1/2.2.

The ^{13}C and ^{29}Si NMR chemical shifts of II are affected by the geometrical configuration of adjacent carbon–carbon double bonds. Specifically, the ^{13}C and ^{29}Si NMR signals of the $(CH_3)_2Si$ groups are affected by the configuration of the adjacent carbon–carbon double bonds. Three methyl ^{1}H and ^{13}C as well as three distinct ^{29}Si resonances are observed. Integration of the ^{1}H NMR signals gives a 1:2:1 intensity ratio. These may be assigned to cis-$(CH_3)_2$Si-cis, cis-$(CH_3)_2$Si-trans, and trans-$(CH_3)_2$Si-trans units respectively (Figures 7 and 8).

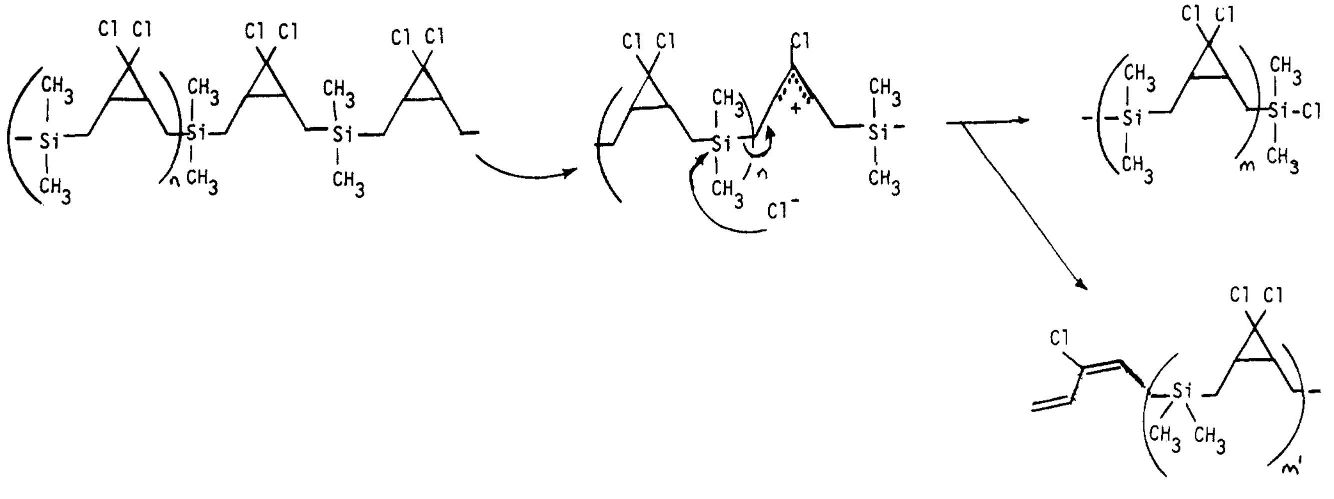


Figure 5. Heterolytic decomposition of III.

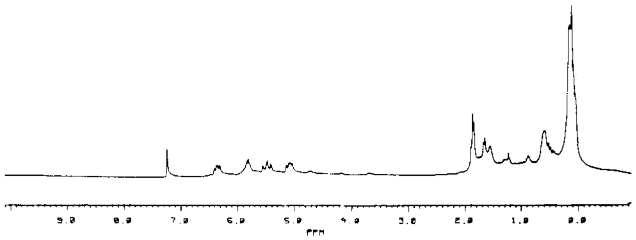


Figure 6. ^{1}H NMR of decomposed III.

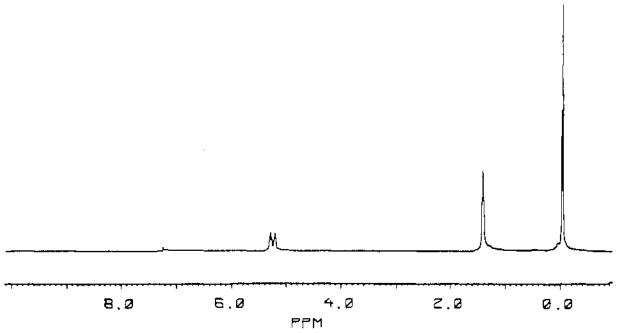


Figure 7. ^{1}H NMR of poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene) (II).

Triad analysis in which neighbors on both sides affect the ^{13}C resonances due to the vinyl and allyl carbons leads to a prediction of eight vinyl and eight allyl resonances. The symmetrical triads in which the configuration of the carbon–carbon double bonds at each end are the same, cis-cis-cis, trans-trans-trans, cis-trans-cis, and trans-cis-trans, are each predicted to give rise to one unique allyl and one unique vinyl signal. On the other hand, the unsymmetrical triads, cis-cis-trans and trans-trans-cis, are expected to yield two nonequivalent allyl and two distinct vinyl resonances, respectively. In fact, only four nonequivalent resonances of each type were observed. This may be explained if one set of allyl and vinyl resonances of the unsymmetrical triad cis-cis-trans is coincident with those of the symmetrical triad cis-cis-cis while the other set is coincident with those of the symmetrical triad trans-cis-trans. Similarly, we would propose that the two sets of allyl and vinyl resonances for the unsymmetrical triad trans-trans-cis are fortuitously coincident with the resonances for symmetrical triads trans-trans-trans and cis-trans-cis (see Figure 9). Samples of II which have a ratio of cis/trans greater than unity were particularly useful in making these ^{1}H and ^{13}C NMR chemical shift assignments. The ^{13}C NMR chemical shift assignments are consistent with those of *cis*- and *trans*-1,4-bis(trimethylsilyl)-2-butene (see Figure 10).[17] For ^{1}H NMR data

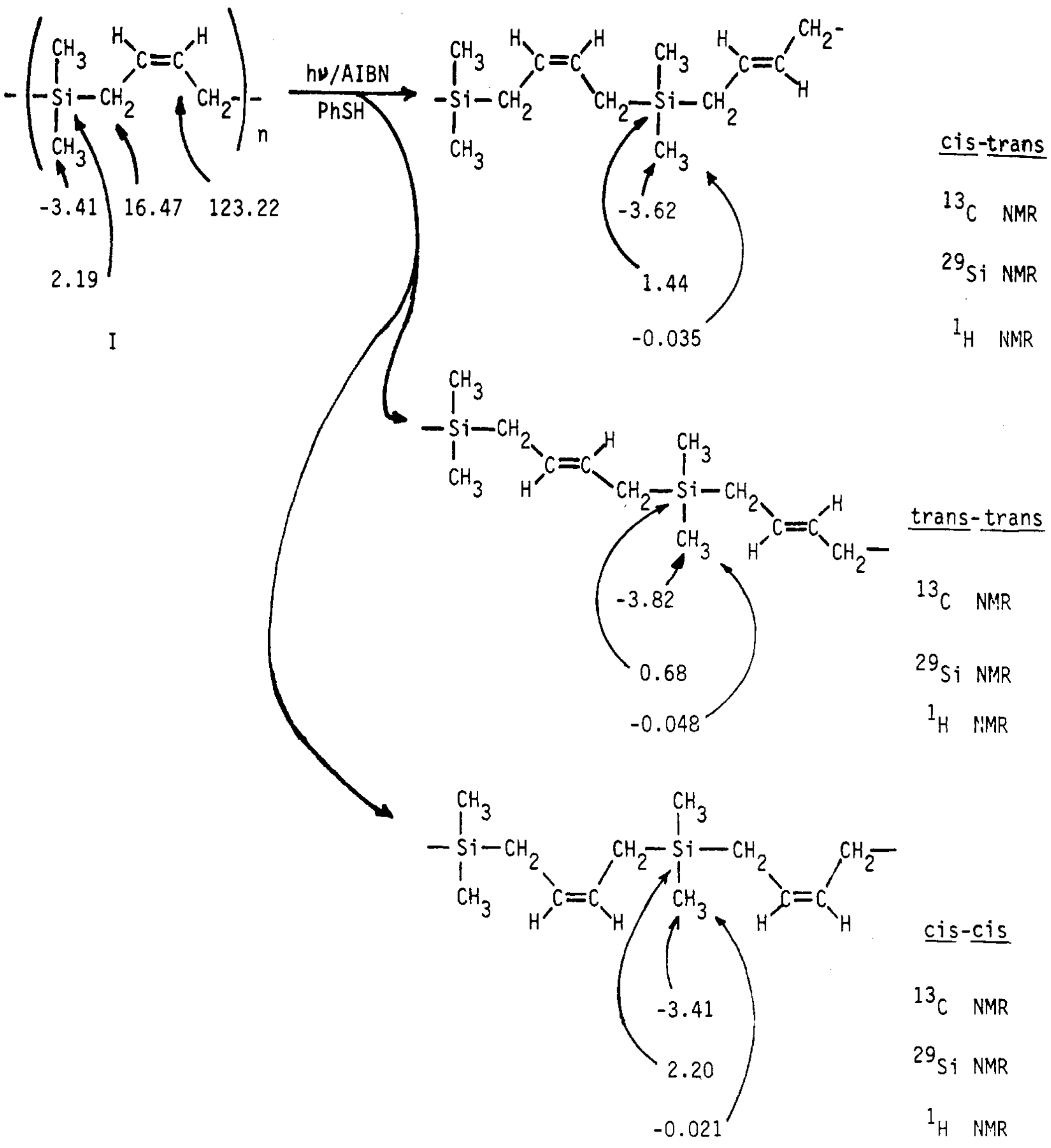


Figure 8. ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts of $(CH_3)_2Si$ groups of II.

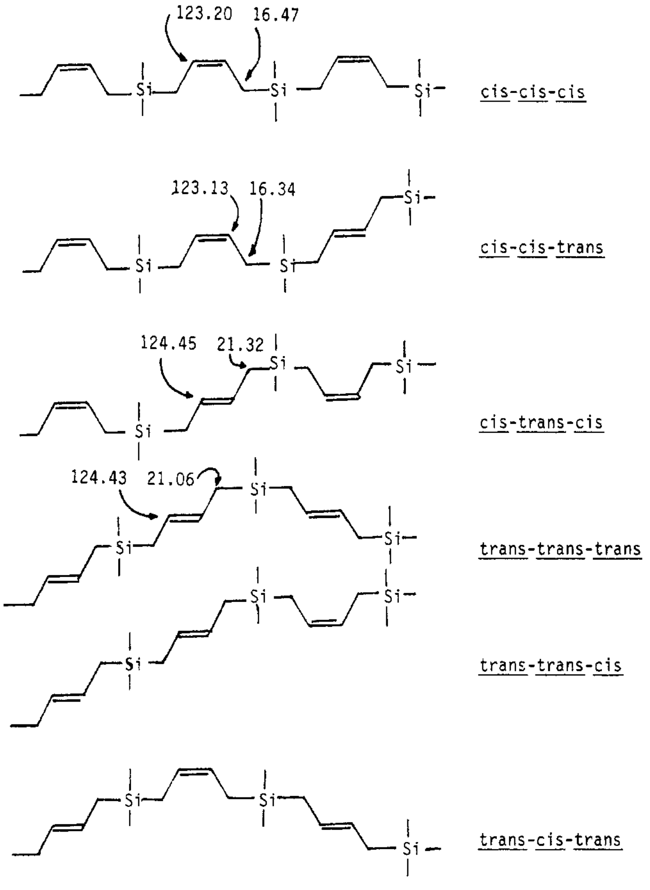


Figure 9. Triad microstructure of II; ^{13}C NMR chemical shifts of allyl and vinyl carbons.

see the Experimental Section and Figure 7.

Stereospecific cis addition of dichlorocarbene to the carbon–carbon double bonds of II (cis/trans = 1.07) produces a polymer (IV) whose microstructure can be partially analyzed by ^{13}C and ^{29}Si NMR spectroscopy. As previously discussed, there are three silicon microenvironments in II. Thus it is predicted that IV will have six silicon microenvironments since adjacent dichlorocyclopropanes can either be on the same or opposite side of the polymer chain. In fact six resonances are observed in the ^{29}Si NMR at 3.88, 3.76, 3.22, 3.14, 2.57, and 2.49 ppm (see Figure 11). Unfortunately, ^{13}C NMR yields significantly less information. For example, a similar analysis would lead one to predict six ^{13}C resonances for the methyl groups bonded to silicon, while only two signals (−2.75 and −2.87 ppm) are actually observed. The dichloro-substituted carbons (cis 68.12, 86.10, 68.07 and trans 69.39, 69.36, 69.32 ppm) and the methine carbons (cis 29.92, 29.88 and trans 34.60, 34.56 ppm) are principally affected by whether the geometry of the cyclopropane ring, of which they are part, is cis or trans. Finally, four methylene carbon resonances are observed. Two of these can be assigned to methylene adjacent to *cis*-dichlorocyclopropane rings (10.29 and 10.14 ppm) while the other two can be assigned to methylene groups adjacent to *trans*-dichlorocyclopropane rings (16.48 and 16.36 ppm). This result can be accounted for economically if we assume that the ^{13}C chemical shifts of each methylene are affected only by the stereochemical orientation of nearest-neighbor dichlorcyclopropanes as previously discussed.

The thermal stability of IV was determined by thermogravimetric analysis (TGA). It was stable to 100 °C. It undergoes rapid weight loss between 100 and 225 °C. By 255 °C, 55% of the initial weight has been lost. From 225 to 475 °C, weight is lost at a slower rate. By 475 °C only 25% of the initial weight remains. A residue of 20% is left at 600 °C (see Figure 12).

Experimental Section

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer operating in the FT mode. ^{13}C NMR spectra were run with broad-band proton decoupling. Ten to fifteen percent solutions in chloroform-*d* were used to obtain ^{13}C and ^{29}Si spectra, whereas 5% solutions were used for ^{1}H spectra. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. All chemical shifts reported were externally referenced to TMS. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least two methyl groups bonded to them.[18]

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. These were taken on films on NaCl plates. UV spectra were run on a Shimadzu UV-260 spectrometer. Spectra quality hexane has been used to prepare samples for UV spectroscopy.

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. A 32 cm × 77 mm Perkin-Elmer PL 10-μm particle size, mixed pore size, cross-linked polystryene gel column was used for the separation. The eluting solvent was HPLC THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: $\bar{M}_p$ 3 600 000, 194 000, 28,000, 7600, and 2550 whose $\bar{M}_w/\bar{M}_n$ are less than 1.09.

The TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 50 °C for 10 min followed by an increase of 5 °C/min to 600 °C.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Reaction of Dichlorocarbene with Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I). In a 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar was placed 0.2 g of I, 20 mL of methylene chloride, 5 mL of chloroform, and 50 mg of tetra-*n*-butylammonium bromide. The mixture was stirred vigorously and cooled to 0 °C. To this mixture was added a solution comprised of 4 g of potassium hydroxide dissolved in 3.5 mL of water. The reaction mixture was taken up in methylene chloride. The organic layer was washed several times with equal volumes of water, dried over anhydrous sodium sulfate, and filtered and the solvent removed by evaporation under reduced pressure. In this way, 0.32 g (92% yield) of III was obtained. It had the following properties. ^{1}H NMR δ 1.57 (br s, 2 H), 0.64 (br s, 4 H), 0.18 (br s, 6 H). For ^{13}C and ^{29}Si NMR, see Figures 1 and 2. IR ν 2950, 1380 cm^{-1}. Anal. Calcd: C, 43.10; H, 6.20, Cl, 36.35. Found: C, 43.40; H, 6.31; Cl, 34.73.

Reaction of Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I) with Hydroxide under PTC Conditions. The reaction was

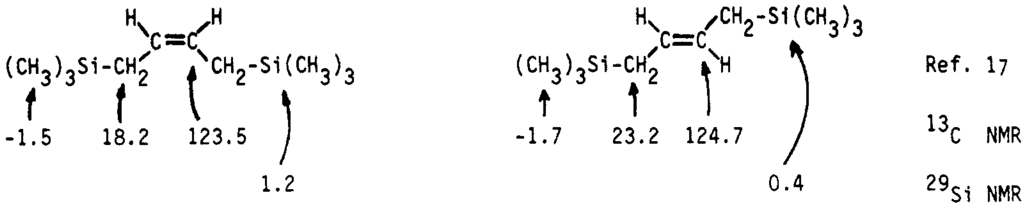
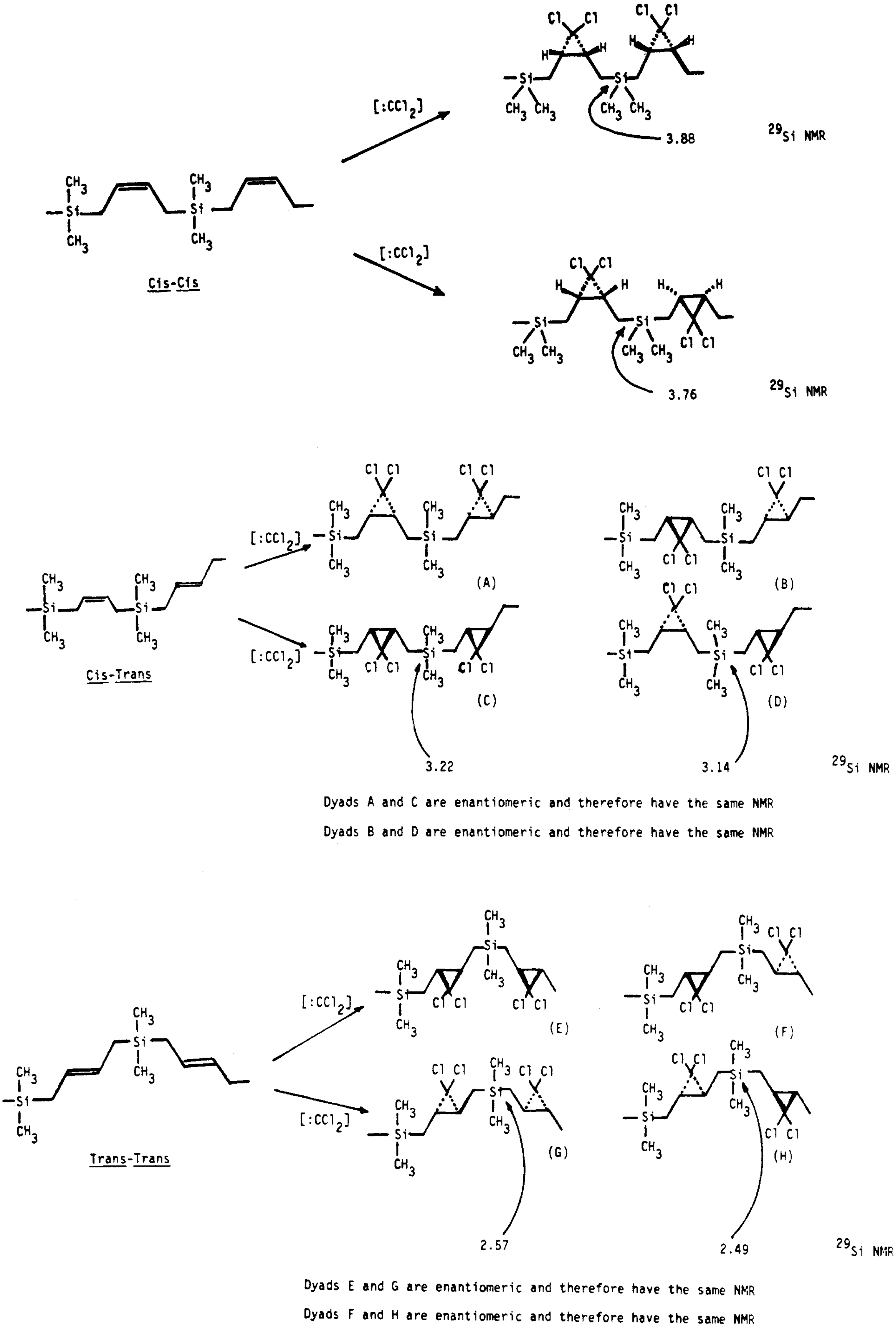


Figure 10. ^{13}C and ^{29}Si NMR chemical shifts of *cis*- and *trans*-1,4-bis(trimethylsilyl)-2-butene.



Dyads A and C are enantiomeric and therefore have the same NMR

Dyads B and D are enantiomeric and therefore have the same NMR

Dyads E and G are enantiomeric and therefore have the same NMR

Dyads F and H are enantiomeric and therefore have the same NMR

Figure 11. Microstructures of IV; ^{29}Si NMR chemical shifts of $(CH_3)_2Si$ groups.

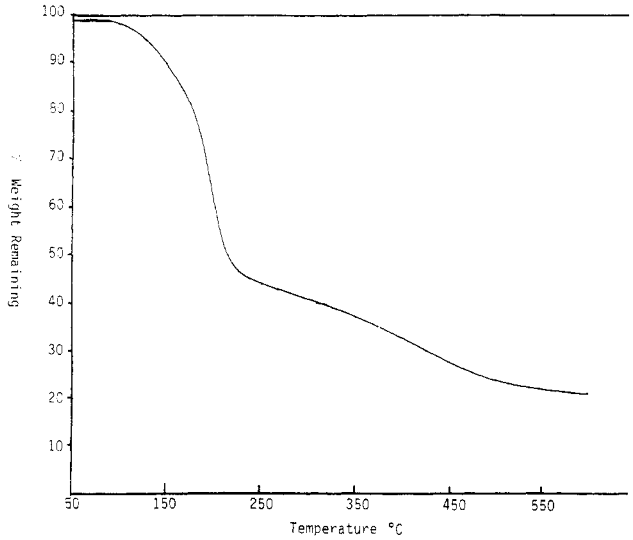


Figure 12. TGA of IV.

carried out as above except that no chloroform was added, and the reaction temperature was 20 °C. M_w/M_n of I before reaction was 125 000/68 800. After reaction recovered I had M_w/M_n = 26 300/14 700. The IR spectrum of recovered I was identical with that of starting I. Small new peaks at 0.07 ppm in the ^{1}H, at −3.1, 10.1, 30.0, and 122.7 ppm in the ^{13}C, and at 2.8 ppm in the ^{29}Si NMR were observed in addition to peaks previously assigned to I.[8]

Isomerization of Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene). One hundred milligrams of I (molecular weight distribution by GPC $\bar{M}_w/\bar{M}_n$ 117 400/47 200), 80 μL of thiphenol, and 15 mg of AIBN were dissolved in 7 mL of dry THF. This solution was placed in a quartz tube which was 1 cm in diameter and 15 cm in length. Dissolved oxygen was removed by bubbling a stream of argon gas through the solution. The tube was then sealed with a rubber septum. The sample tube was attached to a quartz photolysis well in which was suspended a 450-W Hanovia medium-pressure mercury lamp. The entire apparatus was placed in a water bath whose temperature was maintained at 25 °C. The sample was irradiated for 24 h. II was precipitated from the THF solution by addition of this solution to a large excess of methanol. If photoisomerization is to be continued, it is necessary to thoroughly clean the quartz photolysis vessel. The molecular weight distribution of the polymer by GPC was found to be $\bar{M}_w/\bar{M}_n$ = 108 200/47 200. II had the following properties. ^{1}H NMR δ 5.29 and 5.19 (cis and trans vinyl hydrogens, 2 H), 1.42, 1.40, and 1.38 (4 H), −0.02, −0.03, and −0.05 (6 H). The ratio of cis vinyl hydrogens to trans vinyl hydrogens was 1.07–1.00. ^{13}C NMR and ^{29}Si NMR data are presented in Figures 8 and 9. IR ν 2980, 1630, 1570, 1390, 1370, 1240, and 1150 cm^{-1}. Thermal analysis (TGA) indicates that the polymer is stable to 150 °C. Between 150 and 350 °C the polymer loses 5% of its initial weight. Rapid weight loss occurs between 350 and 425 °C. By 500 °C complete weight loss has occurred.

Reaction of dichlorocarbene with poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene) (II) was carried out as above. A 90% yield of IV was obtained after methanol precipitation. It had the following spectral properties. ^{1}H NMR δ 1.57 (m, cis-CH, 2 H), 1.31 (m, trans-CH, 2 H), 0.90 (m, trans-CH_2 4 H), 0.64 (m, cis-CH_2, 4 H), 0.18 (s, 6 H), 0.16 (s, 6 H). For ^{29}Si data see Figure 11. Anal. Calcd: C, 43.10; H, 6.20. Found: C, 43.40; H, 6.31.

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