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Stereoregularity in Ziegler–Natta and Anionic Polymerization of 2-[(Trimethylsilyl)methyl]-1,3-butadiene. Protodesilation of *cis*-1,4-Poly[2-[(trimethylsilyl)methyl]-1,3-butadiene]

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ABSTRACT: Ziegler–Natta polymerization of 2-[(trimethylsilyl)methyl]-1,3-butadiene (I) catalyzed by triethylaluminum and titanium tetrachloride yields a polymer whose microstructure, as established by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, is predominantly comprised of cis-1,4 units. On the other hand, anionic polymerization of I yields a polymer whose microstructure is made up of cis-1,4-, trans-1,4-, and 3,4-units. Protodesilation of *cis*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene] with iodine in D_2O yields poly(3-deuterio-2-methylenebutane). The mechanism of this reaction is discussed.

Introduction

There is considerable interest both in stereoregular polymerization of 1,3-diene monomers and in chemical modification of intact polymers.[1,2] Anionic polymerization of isoprene initiated by alkyllithium reagents in hydrocarbon solvents such as cyclohexane yields polyisoprene of narrow molecular weight distribution whose microstructure has been shown by IR,[3,4] ^{1}H NMR,[5] and ^{13}C NMR[6] to be predominantly *cis*-1,4-polyisoprene (80%). However, appreciable amounts of trans-1,4- (15%) and 3,4-units (5%) are also present. Thus the anionic polymerization of isoprene is neither completely regio- nor stereoselective. By comparison, Ziegler–Natta-type polymerization of isoprene catalyzed by trialkylaluminum and titanium tetrachloride in hydrocarbon solvent yields polyisoprene whose microstructure is 95% cis-1,4. This reaction is highly regio- and stereoselective.[7,8]

We were interested in achieving stereo- and regioselective 1,4-polymerization of 2-[(trimethylsilyl)methyl]-1,3-butadiene. Such a polymer would have reactive allylic silane functional groups regularly arranged along the polymer backbone. While there has been considerable work done on regiospecific electrophilic substitution reactions of monomeric allylic silanes,[9] similar reactions in polymeric systems have not been explored.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating in the FT mode. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{1}H and ^{29}Si NMR spectra were obtained on a Brucker WP-270-SY spectrometer operating in the FT mode. Ten to fifteen percent solutions in chloroform-d_1 were used to obtain ^{29}Si spectra, whereas five percent solutions were used for ^{1}H and ^{13}C spectra. Chloroform was utilized as an internal standard for ^{1}H, ^{13}C, and ^{29}Si 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 one methyl group bonded to them.[10]

IR spectra were recorded on a Perkin-Elmer PE 281 spectrometer. These were taken on films on NaCl plates.

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 polystyrene gel column was used for the separation. The eluting solvent was reagent THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: $\bar{M}_p$ 3600000, 194000, 28000, and 2550 whose $\bar{M}_w/\bar{M}_n$ 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 cm^3/min. The temperature program for the analysis was 100 °C for 10 min followed by an increase of 5 °C/min to 500 °C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN. Satisfactory analyses (±0.6%) were obtained for polymers prepared both by Ziegler–Natta catalysis as well as that made by anionic polymerization.

2-[(Trimethylsilyl)methyl]-1,3-butadiene was prepared by the reaction of [(trimethylsilyl)methyl]magnesium chloride with 2-chloro-1,3-butadiene catalyzed by the nickel chloride complex of 1,3-bis(diphenylphosphino)propane. It had properties in complete agreement with literature values.[11]

Polymerization Reactions. Polymerizations were carried out in flame-dried apparatus under an atmosphere of prepurified nitrogen. In a 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar and a rubber septum was placed 50 mL of hexane (freshly distilled from sodium metal). The flask and its contents were cooled to 0 °C. To this were added via a syringe 0.11 mL (0.2 mmol) of titanium tetrachloride and triethylaluminum (Aldrich) (0.22 mmol, 0.6 mL of a 25% solution in CH_2Cl_2). The contents of the flask were stirred for 1 h while it warmed to room temperature. 2-[(Trimethylsilyl)methyl]-1,3-butadiene (3.5 g, 25 mmol) was added via syringe. The reaction mixture was stirred for 4 h at room temperature. The reaction was quenched by addition of a mixture of tetrahydrofuran and methanol. The polymer was precipitated from the tetrahydrofuran solution by addition of methanol. This process was repeated several times. In this way, 1.4 g (40% yield) of a white rubbery polymer was obtained. Removal of the solvents from the su-

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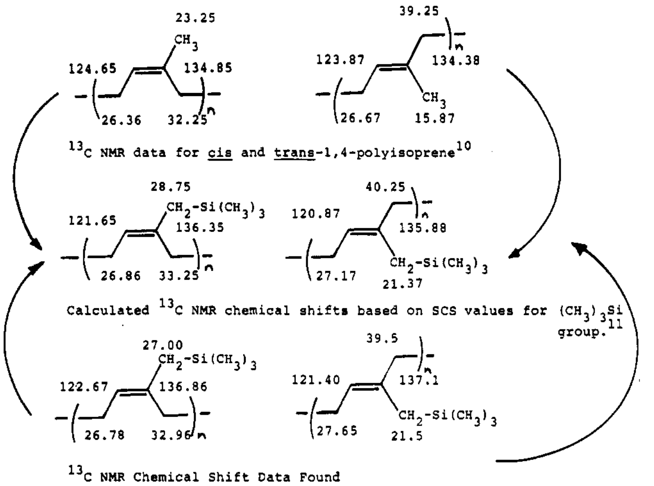


Figure 1. Comparison of calculated and observed ^{13}C NMR chemical shifts for *cis*- and *trans*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene].

pernatant largely gave recovered monomer.

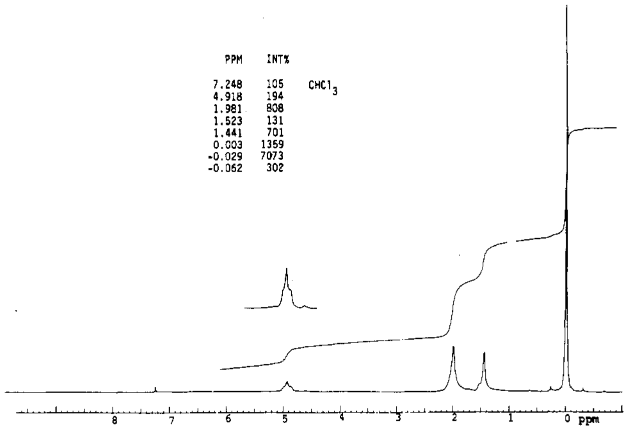
Anionic polymerization were carried out in a similar manner, except that the alkyllithium reagents was added to a solution of the monomer in hexane.

Results and Discussion

Polymerization of 2-[(Trimethylsilyl)methyl]-1,3-butadiene (I) and Characterization of the Polymer Microstructure. We should like to report on the stereoregularity observed in the anionic and Ziegler–Natta polymerizations of 2-[(trimethylsilyl)methyl]-1,3-butadiene (I).

Ziegler–Natta-type polymerization of I using triethylaluminum and titanium tetrachloride in hexane at room temperature gave a 40% yield of polymer. GPC analysis of this material revealed a trimodal molecular weight distribution with $\bar{M}_w/\bar{M}_n$ = 310 600/69 400. The microstructure of the polymer was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The reaction is both regio- and stereoselective. The stereochemical assignments are based on ^{13}C NMR spectroscopy. The anticipated ^{13}C NMR chemical shifts for *cis*- and *trans*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene] can be calculated from the ^{13}C NMR spectrum of *cis*- and *trans*-1,4-polyisoprene[12] by use of the substituent chemical shifts (SCS)[13] value for a trimethylsilyl group.[14] (See Figure 1.) All the major peaks in the ^{13}C NMR spectra can be assigned to the predominant cis-1,4-units. Two resonances which result from unique vinyl carbons are found at 136.86 and 122.67 ppm, while the absorptions at 32.96, 27.00, and 26.78 ppm are assigned to the three nonequivalent allylic carbons. The resonance due to the methyl carbons bonded to silicon comes at −1.12 ppm.

The ^{1}H NMR spectrum can be seen in Figure 2. The peak at −0.03 ppm is assigned to the methyl groups bonded to silicon of the cis-1,4-units. The signal at 0.00 ppm results from the methyl groups bonded to silicon of the trans-1,4-units while that at −0.06 ppm arises from methyl groups bonded to silicon which are part of the 3,4-units. Integration of these peaks yields the following analysis for the microstructure of the polymer: 84% cis-1,4; 11% trans-1,4; 4.5% 3,4. The small chemical shift differences between these peaks makes accurate integration difficult. It is likely that this analysis only constitutes a lower limit for the percentage of cis-1,4-units. In the vinyl region of the ^{1}H spectrum, the broad peak at 4.9 ppm results from the overlap of vinyl hydrogens of both cis- and trans-1,4-units, while the small peak at 4.6 ppm is assigned to the terminal methylene group of the 3,4-units. A broad allylic resonance is observed at 1.98 ppm (4 H) while a sharp resonance at 1.44 ppm (2 H) is assigned to the allylic methylene group bonded to silicon.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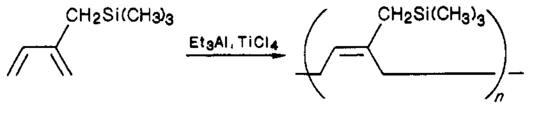
   PPM    INT%

  7.248   105    CHCl3
  4.918   194
  1.981   808
  1.523   131
  1.441   701
  0.003  1359
 -0.029  7073
 -0.062   302
```

Figure 2. ^{1}H NMR Spectrum of poly[2-[(trimethylsilyl)methyl]-1,3-butadiene] prepared by Ziegler–Natta catalysis.

A single peak at 0.34 ppm dominates the ^{29}Si NMR. A carbon–carbon double bond stretch is observed at 1640 cm^{-1} in the IR spectrum. These spectral data are consistent with a polymer principally composed of cis-1,4-units.



Anionic polymerization of I initiated by *sec*-butyllithium (3%) in hexane at −78 °C gave a 10% yield of polymer. GPC analysis revealed a monomodal molecular weight distribution $\bar{M}_w/\bar{M}_n$ = 32 900/17 400. The low yield and broad molecular weight distribution may result from competition between initiation and metalation of the allylsilane functionality. In this regard, it should be noted that *sec*-butyllithium is a more effective metalating agent than *n*-butyllithium.[15,16]

The microstructure of this polymer was determined by NMR spectroscopy. The ^{1}H NMR spectrum is quite similar to that of the polymer obtained by Ziegler–Natta catalysis. Integration of the peaks at 0.00 and −0.03 ppm assigned to the methyl groups bonded to silicon indicates that the polymer is made up of 67% trans-1,4- and 33% cis-1,4-units. Two signals are observed at 1.49 and 1.44 ppm which can be assigned to the allylic methylene groups bonded to silicon bonded to the trans-1,4- and cis-1,4-units respectively. The integrated ratio of these is approximately 2:1.

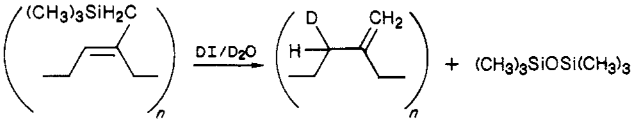
In the ^{13}C NMR there are six resonances which can be assigned to the carbons of the trans-1,4-units in addition to the six previously assigned to cis-1,4-units; see above. The ^{13}C NMR chemical shifts appear to be insensitive to the stereochemistry of neighboring units. Specifically, the trans-1,4-units contribute two vinyl resonances at 137.1 and 121.4 ppm as well as three allylic resonances at 39.5, 27.65, and 21.5 ppm in addition to a signal at −0.47 ppm, which is assigned to the methyl carbons bonded to silicon. The intensity ratio of the carbon signals at −0.47 to −1.12 ppm is two to one as expected. These ^{13}C NMR chemical shifts are consistent with those predicted for *trans*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene] from the ^{13}C NMR spectrum of *trans*-1,4-polyisoprene[12] by use of the SCS value[13] for a trimethylsilyl group.[14] (See Figure 1.)

In the ^{29}Si NMR there are two nonequivalent silicons at 1.14 and 0.34 ppm. The former is assigned to the silicon of the trans-1,4-units while the latter has been previously assigned to the silicon atoms of the cis-1,4-units. The integration ratio of these is two to one. A carbon–carbon double bond stretch is observed at 1640 cm^{-1} in the IR spectrum. All of this data are consistent with *cis*- and *trans*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene] in which the ratio of cis to trans is one to two. Similar results were obtained with *n*-butyllithium initiation at −78 °C.

On the other hand, anionic polymerization of I initiated by *n*-butyllithium (2%) in hexane at room temperature gave a high yield (93%) of polymer. GPC analysis revealed that this material has a monomodal molecular weight distribution $\bar{M}_w/\bar{M}_n$ = 10 300/7050. Analysis of the microstructure by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy reveals that in addition to cis- and trans-1,4 units, 3,4-polymerization is important. The characteristic vinyl carbon–hydrogen resonance of the 3,4-units is seen in the ^{1}H NMR at 4.62 ppm. The pendant vinyl group also yields distinct resonances in the ^{13}C NMR at 149.92 and 107.34 ppm. The methyl groups bonded to silicon in the 3,4-units produce a resonance at −0.85 ppm. Integration of the peaks assigned to the methyl groups bonded to silicon of the various types of units permits analysis of the microstructure composition of the polymer: trans-1,4 (22.6%); cis-1,4 (47%); 3,4 (30.4%). The vinyl and allyl regions are quite complicated. If we assume that triads which contain 3,4-units are distinct, we can account for the vinyl and allyl carbon resonances observed. Five distinct resonances are seen in the ^{29}Si NMR: 1.35, 1.03, 0.45, 0.31, and 0.27 ppm. A carbon–carbon double bond stretch is observed at 1640 cm^{-1} in the IR spectrum.

The thermal stability of *cis*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene] prepared by Ziegler–Natta catalysis was determined by TGA. The polymer was stable to 150 °C. Between 150 and 300 °C it loses weight at a rate of 2.5% for each 50 °C increase in temperature. Above 300 °C rapid weight loss occurs. By 375 °C the polymer has lost 93% of its starting weight. The polymer leaves virtually no residue.

Electrophilic Substitution Reactions. We would like to report initial results of electrophilic substitution reactions carried out on *cis*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene]. The polymer was reacted with a catalytic amount of iodine in a mixture of deuterium oxide and chloroform-d_1. This electrophilic desilation reaction yields poly(3-deuterio-2-methylenebutane) and hexamethyldisiloxane. Electrophilic substitution with allylic rearrangement and loss of the silyl group is a characteristic reaction of monomeric allylic silanes.[9] This reaction is probably initiated by regiospecific electrophilic attack on the carbon–carbon double bond of the polymer by an iodonium ion to yield a carbocation which is stabilized by a β-trimethylsilyl group. Nucleophilic attack by iodide on the silyl center yields an allyl iodide and generates trimethylsilyl iodide which reacts with deuterium oxide to give hexamethyldisiloxane and deuterium iodide. Electrophilic addition of a deuteron to a carbon–carbon double bond of the polymer yields a carbocation stabilized by a β-trimethylsilyl group. This is followed by nucleophilic attack on the silyl center to yield a 3-deuterio-2-methylene butane unit and trimethylsilyl iodide which reacts with more deuterium oxide to yield hexamethyldisiloxane and regenerate the deuterium iodide. The reaction is thus catalytic in deuterium iodide.



Poly(3-deuterio-2-methylenebutane) was characterized by ^{1}H, ^{13}C, NMR as well as IR spectroscopy. It properties were consistent with those previously reported for poly(2-methylenebutane).[17,18]

Specifically, it has a strong C–D vibration in the IR centered at 2100 cm^{-1}, as well as a carbon–carbon double stretch at 1620 cm^{-1}. In the ^{1}H NMR, the resonance at 4.70 ppm is assigned to the terminal methylene group. Allylic as well as homoallylic resonances are observed at 1.99 and 1.52 ppm, respectively. The ^{13}C NMR spectrum is also consistent with the proposed structure. Resonances due to vinyl carbons at 149.6 and 109.0 ppm, in addition to resonances due to allylic carbons at 35.7 ($CH_2C{=}C$) and 35.40 ppm ($CDHC{=}C$)[19] as well as a resonance due to homoallylic carbons at 25.7 ppm, are seen.

Despite this success, one should not underestimate the difficulty in transferring reactions with monomer to polymer systems. While our preliminary results with other electrophilic reactions are encouraging, significant further work is needed.

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Registry No. I, 70901-64-3; I (homopolymer), 115339-43-0; Et_3Al, 97-93-8; $TiCl_4$, 7550-45-0; *sec*-butyllithium, 598-30-1; *n*-butyllithium, 109-72-8.

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