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Stereospecific 1,4-polymerization of 2,3-bis(trimethylsilyl)-1,3-butadiene

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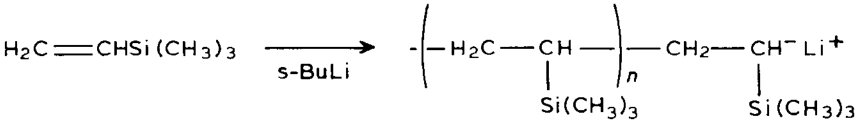
Abstract

Polymerization of 2,3-bis(trimethylsilyl)-1,3-butadiene in hexane/HMPA catalyzed by n-butyllithium yields *trans*-1,4-poly[2,3-bis(trimethylsilyl)-1,3-butadiene]. This polymer has been characterized by ^1H, ^{13}C and ^{29}Si NMR as well as IR spectroscopy and elemental analysis. The stereochemistry of the carbon–carbon double bonds has been established by protodesilation of the polymer with HI. The molecular weight distribution of the polymer has been determined by gel permeation chromatography and its thermal stability by thermogravimetric analysis.

Introduction

We should like to report the stereo-regular anionic polymerization of 2,3-bis(trimethylsilyl)-1,3-butadiene. We were interested in this problem for the following reasons: while both 1,3-butadiene and isoprene are well known to undergo anionic stereospecific polymerization initiated by alkyllithium reagents in hydrocarbon solvents to yield *cis*-1,4-poly-butadiene and *cis*-polyisoprene respectively, no polymerization reactions of silyl substituted dienes have been reported. On the other hand, vinyltrimethylsilane undergoes anionic polymerization catalyzed by s-butyllithium (eq. 1) [1,2].



$$H_2C{=}CHSi(CH_3)_3 \xrightarrow[s\text{-}BuLi]{} -\left(-H_2C-\underset{Si(CH_3)_3}{\underset{|}{CH}}-\right)_n-CH_2-\underset{Si(CH_3)_3}{\underset{|}{CH^-}}\,Li^+ \qquad (1)$$

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* Dedicated to Professor Colin Eaborn in recognition of his many significant contributions to organosilicon chemistry.

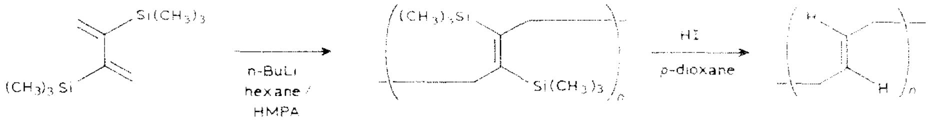
The fact that anionic polymerization of methyl α-trimethylsilyl acrylate initiated with phenyl- or n-butyl-lithium in tetrahydrofuran (THF) or hydrocarbon solvent results only in partial polymerization [3], as well as the observations that neither α-trimethylsilylstyrene, 1-bromovinyltrimethylsilane, 1-chlorovinyltrimethylsilane nor α-trimethylsilylacrylic acid undergoes homopolymerization under normal radical, cationic, or anionic initiation [4] increased the synthetic challenge of the project.

1,4-Polymerization of 2,3-bis(trimethylsilyl)-1,3-butadiene would yield a polymer which would possess vinylsilane functional groups regularly arranged along the polymer backbone. Such a polymer would be expected to undergo electrophilic substitution with loss of the trimethylsilyl groups, since it is well known that monomeric vinylsilanes undergo regio- and stereo-specific substitution reactions by a wide variety of electrophiles [5]. In this way it should be possible to convert such a polymer into a variety of novel polymers by reactions with appropriate electrophiles.

Results and discussion

No reaction occurred when 2,3-bis(trimethylsilyl)-1,3-butadiene was treated with either n-butyl- or methyl-lithium in hydrocarbon solvents. This may result from the fact that 2,3-bis(trimethylsilyl)-1,3-butadiene can not assume a cisoid conformation. On the other hand, treatment of 2,3-bis(trimethylsilyl)-1,3-butadiene with a catalytic amount of n-butyllithium in either THF, or THF/hexamethylphosphoric triamide (HMPA) 10/1 or hexane/HMPA 10/1 at −25 °C resulted in the formation of *trans*-1,4-poly[2,3-bis(trimethylsilyl)-1,3-butadiene] in 55% yield and oligomers in 25% yield. Both the polymer and oligomer fractions had identical spectral properties which did not depend on the solvent system which was utilized. However, the molecular weight distribution of the polymer as determined by gel permeation chromatography (GPC) depends on the solvent system. It was found to be highest when hexane/HMPA was used: $\overline{M}_w/\overline{M}_n = 24300/13600$.

The observation of only a single allylic C–H resonance in the ^{1}H NMR as well as single allyl and vinyl carbon resonances in the ^{13}C NMR establishes that stereoregular 1,4-polymerization has occurred. However, from these data it is not possible to establish whether the carbon–carbon double bonds of the polymer are *cis* or *trans*. This question was resolved by protodesilation of the polymer by treatment with HI in a mixture of water and *p*-dioxane to yield *trans*-1,4-polybutadiene whose structure was determined by infrared spectroscopy [6]. Protodesilation of vinylsilanes has previously been shown to occur stereospecifically with retention of configuration [7,8]. On this basis we believe the carbon–carbon double bonds of the polymer have a *trans* geometrical arrangement.



The thermal stability of the polymer was studied by thermogravimetric analysis (TGA). The polymer was stable to 150 °C. Between 150 and 230 °C slow decomposition occurs. Beyond 230 °C rapid weight loss occurs. Almost 95% of the weight of the polymer is lost by 300 °C. See Fig. 1.

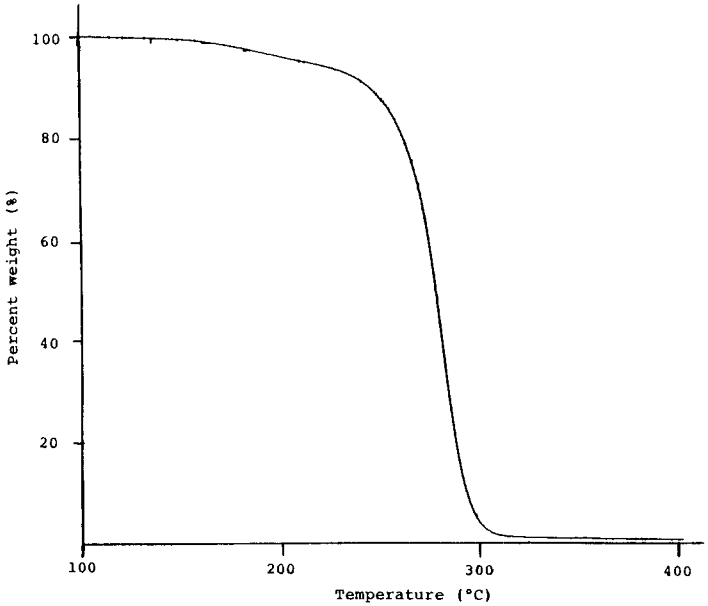


Fig. 1. TGA of *trans*-1,4-poly[2,3-bis(trimethylsilyl)-1,3-butadiene].

Experimental

^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating in the Fourier Transform mode. ^{13}C NMR spectra were run with broad band proton decoupling. ^{29}Si NMR spectra were obtained on a Brucker WP-270-SY spectrometer operating in the Fourier Transform mode. Ten to fifteen percent solutions in chloroform-*d* were used to obtain ^{29}Si NMR spectra whereas five percent solutions were used for ^1H, ^{13}C NMR spectra. Chloroform was utilized as an internal standard for ^1H, ^{13}C, and ^{29}Si NMR spectra. All chemical shifts reported are externally referenced to tetramethylsilane. 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 [9]. IR spectra were recorded on a Perkin-Elmer PE 281 spectrometer. These were taken on chloroform solutions in NaCl cells.

GPC analysis of the molecular weight distribution of the polymers was performed on a Perkin-Elmer series 10 liquid chromatography 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 crosslinked polystyrene gel column was used for the separation. The eluting solvent was HPLC grade reagent THF at a flow rate of 0.7 ml/min. The retention times were calibrated against known monodispersed polystyrene standards: $\overline{M}_p$ 194000, 28000, and 2550 whose $\overline{M}_w/\overline{M}_n$ 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 per min to 500 °C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

2,3-Bis(trimethylsilyl)-1,3-butadiene was prepared by treatment of 1-bromovinyltrimethylsilane with magnesium in THF at reflux [10]. The required starting material 1-bromovinyltrimethylsilane was prepared by addition of bromine to vinyltrimethylsilane at −78 °C followed by dehydrohalogenation with diethylamine [11].

Polymerizations were carried out in flame dried apparatus under an atmosphere of pre-purified nitrogen. In a 25 ml round-bottom flask, equipped with a Teflon covered magnetic stirring bar and a rubber septum, was placed 2,3-bis(trimethylsilyl)-1,3-butadiene (1 g, 5 mmol) and 10 cm^3 THF which had been freshly distilled from sodium benzophenone ketyl. The reaction flask was cooled to −25 °C while n-butyllithium (0.15 ml, 1.4 N) was added. The mixture was allowed to stir overnight. The reaction was diluted with ether and the organic layer was washed with aqueous ammonium chloride, water. It was then dried over anhydrous magnesium sulfate, filtered and methanol added to precipitate the polymer. In this way 0.55 g or 55% yield of a solid white polymeric material was obtained. It had a melting range of 200–220 °C. $\overline{M}_w/\overline{M}_n$ 4 200/3 380. Concentration of the methanol/ether solution gave a 23% yield of an oligomeric oil.

trans-1,4-Poly[2,3-bis(trimethylsilyl)-1,3-butadiene] has the following properties. ^1H NMR: δ (ppm) 0.17 (br.s,18H), 2.34 (br.s,4H). ^{13}C NMR: δ (ppm) 2.95 (6C), 40.3 (2C), 155.4 (2C). ^{29}Si NMR: δ (ppm) −9.99. IR: ν 1240, 830 cm^{-1}. Elemental Anal. Found C, 60.64; H, 11.17. $C_{10}H_{22}Si_2$ calcd.: C, 60.52; H, 11.17%. The polymer was soluble in a variety of non-polar solvents: ether, THF, *p*-dioxane, benzene, carbon tetrachloride and chloroform. It was only slightly soluble in polar solvents such as acetone, acetonitrile, DMSO, isopropanol, or methanol.

Alternatively, the polymerization can be carried out in hexane and HMPA in a 10/1 ratio. In this manner a 55% yield of solid polymer having a similar melting range and identical spectral properties was obtained. $\overline{M}_w/\overline{M}_n = 24\,300/13\,600$.

Polymerization as above with THF/HMPA in a 10/1 ratio gave a polymer with $\overline{M}_w/\overline{M}_n = 14\,300/9\,380$.

Protodesilation of trans-1,4-poly[2,3-bis(trimethylsilyl)-1,3-butadiene]. In a 50 ml round bottom flask equipped with a Teflon covered magnetic stirring bar was placed 0.4 g of the polymer, 30 ml of *p*-dioxane, and 1 ml of 47.5% aqueous HI solution. The mixture was stirred for 70 h under a nitrogen atmosphere at room temperature. Ten percent sodium hydroxide solution was added to neutralize the acid. Ether was added. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent and hexamethyldisiloxane removed by evaporation under reduced pressure. The polymer residue 85 mg (91% yield) was analyzed by ^1H NMR and IR spectroscopy [6]. ^1H NMR: δ (ppm) 2.03 (br.s,4H) and 5.35 (br.s,2H). IR (film): ν 1650 (C=C), and 965 (*trans*) cm^{-1}.

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