

Epoxidation of *E*-1,4-poly(2-triethylsilyl-1,3-butadiene) and *E*-1,4-poly-[2,3-bis(trimethylsilyl)-1,3-butadiene]
Stereochemical analysis of *E*-1,4-poly(2,3-epoxy-2-triethylsilyl-1,3-butadiene) and *E*-1,4-poly-[2,3-bis(trimethylsilyl)-1,3-butadiene]
by ^{13}C and ^{29}Si NMR

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SUMMARY

Reaction of *E*-1,4-poly(2-triethylsilyl-1,3-butadiene) (I) with *m*-chloroperbenzoic acid (MCPBA) yields *E*-1,4-poly(2,3-epoxy-2-triethylsilyl-1,3-butadiene) (II). Similar reaction of *E*-1,4-poly[2,3-bis(trimethylsilyl)-1,3-butadiene] (III) with MCPBA gives *E*-1,4-poly[2,3-epoxy-2,3-bis(trimethylsilyl)-1,3-butadiene] (IV). The product polymers have been characterized by ^1H , ^{13}C , and ^{29}Si NMR, IR, GPC, TGA and elemental analysis. ^{13}C and ^{29}Si NMR permit stereochemical analysis on the microstructures of II and IV.

INTRODUCTION

There is considerable interest in chemical modification of intact polymers (1-4). In this regard, stereoselective *cis*-epoxidation of polybutadiene and polyisoprene with peracids have been reported (5-7). While the reaction of monomeric vinylsilanes with peracids to yield α,β -epoxysilanes has been studied (8,9) similar reactions on polymeric vinyl silane systems are unexplored. Monomeric α,β -epoxysilanes are of synthetic interest since, for example, they can be converted into carbonyl groups by acidic hydrolysis. This transformation is regio-specific in that the silyl substituted carbon is converted to the carbonyl carbon (10).

EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating in the Fourier Transform (FT) mode. ^{29}Si NMR spectra were run on an IBM Bruker WP-270-SY spectrometer operating in the FT mode. ^{13}C NMR spectra were run with broad band proton decoupling. Ten percent solutions in chloroform- d_1 were used to obtain ^{29}Si spectra, whereas five percent solutions were used for ^1H and ^{13}C . All chemical shifts reported were externally references to TMS. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have methylene or methyl groups bonded to them (11).

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 a 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 reagent 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 and 2,550 whose M_w/M_n are less than 1.09.

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TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 5°C/min to 700°C.

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

Epoxidation of I

To a suspension of MCPBA (0.27 g, 1.3 mmol, 85%) and Na₂HPO₄·7H₂O (0.28 g) in CH₂Cl₂ (15 mL) in a 50 mL round bottom flask equipped with a Teflon covered magnetic stirring bar was added dropwise a solution of I (0.2 g, 1.2 mmol) (12) $\overline{M}_w/\overline{M}_n = 27,800/19,980$ in CH₂Cl₂ (3 mL). The reaction mixture was stirred at room temperature for 20 h, extracted with alkali and then washed several times with water. The product (II) was precipitated from the CH₂Cl₂ solution by addition of methanol. II was redissolved in CH₂Cl₂ and reprecipitated by addition of methanol several times. In this way, a 95% yield of a sticky, water white, oil was obtained.

Polymer II had the following properties. ¹H NMR δ: 2.43(br.s,1H), 1.67(br.s,4H), 0.94(t,9H, J = 6.8 Hz), 0.61(q,6H, J = 6.8 Hz). ¹³C NMR δ: 59.94, 59.73, 56.31, 55.99, 28.20, 27.71, 25.49, 25.11, 7.45, and 2.14. ²⁹Si NMR δ: 7.06, 6.97. IR ν: 2945, 2860, 1455, 1410, 1235, 1145, 1000, and 850 cm⁻¹. Elemental Anal. Calc. for C₁₀H₂₀OSi: C, 65.17; H, 10.95. Found: C, 64.81; H, 10.70. The molecular weight distribution of polymer II was found to be $\overline{M}_w/\overline{M}_n = 25,600/17,580$. While the molecular weight of the product polymer II is lower than that of the starting polymer I, the ratio of $\overline{M}_w/\overline{M}_n$ for both I (1.39) and II (1.46) are quite similar.

Epoxidation of III

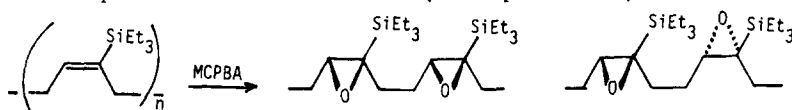
To a suspension of MCPBA (0.14 g, 0.7 mmol, 85%) and Na₂HPO₄·7H₂O in CH₂Cl₂ (10 mL) was added to a solution of III (13) $\overline{M}_w/\overline{M}_n = 19,590/9,630$ in CH₂Cl₂ (5 mL) as above. The product polymer IV was purified by precipitation from THF by addition of methanol. White transparent crystals of IV, mp = 174.5-177°C, were obtained in 94% yield.

Polymer IV had the following properties: $\overline{M}_w/\overline{M}_n = 15,680/8,040$. ¹H NMR δ: 1.74(br.s,4H), 0.21(br.s,18H). ¹³C NMR δ: 66.50, 65.31, 65.03, 64.00, 34.59, 34.37, 34.16, 33.88, 1.76, 1.22, 1.06, 0.63. ²⁹Si NMR δ: 3.24, 2.01, 1.76, 0.67. IR ν: 2960, 1455, 1420, 1250, 850, 730, 680, 640 cm⁻¹. Elemental Anal. Calc. for C₁₀H₂₂OSi₂: C, 56.00; H, 10.34. Found: 55.19; H, 10.24.

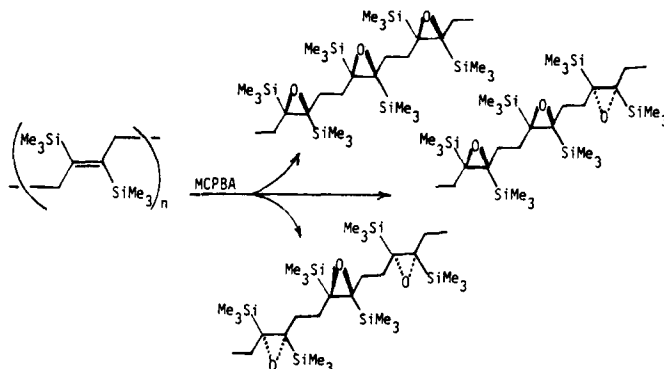
RESULTS AND DISCUSSION

Peracid oxidation of E and Z-1,4-polybutadiene and E and Z-1,4-polyisoprene has been shown to proceed in a stereospecific cis manner (5-7). Similarly, MCPBA oxidation of E-1,4-poly(2-triethylsilyl-1,3-butadiene) (I) proceeds in essentially quantitative yield to give E-1,4-poly(2,3-epoxy-2-triethylsilyl-1,3-butadiene) (II). A suspension of Na₂HPO₄·7H₂O was utilized in the oxidation to remove m-chlorobenzoic acid as it was formed. This prevents acid catalyzed ring opening of epoxide functional groups which would result in formation of 1,4-(2-m-chlorobenzoate-3-hydroxybutane) units in the polymer chain.

The ^{13}C NMR of II is characterized by ten resonances. These result from the presence of diastereoisomeric dyad pairs. Consistent with this interpretation, two signals are observed in the ^{29}Si NMR as expected for two diastereoisomeric silyl centers. Mirror image dyad pairs such as A,B and C,D can not be distinguished by NMR in the absence of a chiral NMR shift reagent (14). On the other hand, each pair is spectroscopically distinct from the other since they are diastereoisomers. Both the methine and methylene carbons of the polymer chain are affected. The carbons of the ethyl groups bonded to silicon are magnetically equivalent. The length of the Si-C bond (1.89 Å) may place these carbons at too great a distance from the chiral centers to observe their diastereoisomeric character. The small chemical shift differences observed for each diastereoisomeric carbon (0.2 to 0.5 ppm) are similar to those observed for the diastereoisomeric carbons of the bis-epoxide of E,E-3,7-decadiene (6). Thus, both the ^{13}C and ^{29}Si NMR data for II is consistent with a stereospecific oxidation of I. (See Equation 1.)



Twelve signals are observed in the ^{13}C NMR spectrum of IV. On the basis of their chemical shifts four of these can be assigned to methyl groups bonded to silicon, four to methylene groups and finally four to quaternary carbons of the epoxide groups. The ^{13}C NMR spectra of IV can be interpreted by triad analysis. There are three types of triads. In one the oxygen atoms of three adjacent epoxide units are all on the same side of the polymer chain. The letter d and u will be used to signify down or up respectively. Thus, the first type of triad may be represented by (d,d,d) or (u,u,u). The central unit of such a symmetrical triad will give rise to three resonances in the ^{13}C NMR. In the next type of triad, the oxygen atoms of two adjacent epoxide units are alternate side of the polymer chain (u,d,u) or (d,u,d). The central unit of such a symmetrical triad will give rise to three resonances in the ^{13}C NMR. In the last, the oxygen atoms of adjacent epoxide units are on the same side while the following one is on the opposite side (d,d,u) or (u,u,d). The central unit of such an unsymmetrical triad will give rise to six resonances (three pairs of equal intensity): 65.03, 64.00; 34.37, 34.16; and 1.22, 1.06) in the ^{13}C NMR. (See Equation 2). Similarly, four resonances are observed in the ^{29}Si NMR.



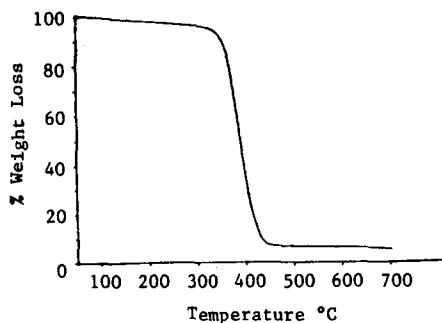


Figure 1. TGA of Polymer II.

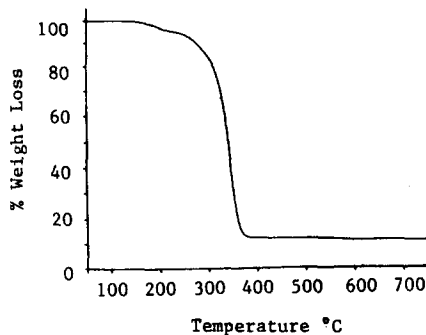


Figure 2. TGA of Polymer IV.

The thermal stability of II was determined by TGA. The polymer loses about four percent of its initial weight between 50 and 300°C. Between 300 and 425°C II undergoes rapid weight loss. Above 450°C about five percent residue is left. (See Figure 1.) Polymer IV is less thermally stable than II. IV loses about five percent of its initial weight between 50 and 250°C. Between 250 and 350°C IV undergoes rapid weight loss. Above 375°C about seven percent residue remains. (See Figure 2.) Of particular interest is the observations that the epoxide silane polymers II and IV are thermally more stable than their vinyl silane polymer precursors I and III (12,13).

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