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Reaction of *E*-1,4-poly(2-triethylsilyl-1,3-butadiene) with bromine
Stereoselective sythesis of *Z*-1,4-poly(2-bromo-1,3-butadiene)

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SUMMARY

Addition of bromine to E-1,4-poly(2-triethylsilyl-1,3-butadiene) (I) followed by treatment with potassium fluoride dihydrate yields Z-1,4-poly-(2-bromo-1,3-butadiene) (II). The mechanism of this reaction is discussed. The product polymer has been characterized by ^{1}H, ^{13}C NMR, IR, GPC, TGA and elemental analysis.

INTRODUCTION

There is considerable interest in chemical modification of intact polymers (1-3). Regio- and stereoselective electrophilic substitution reaction with loss of the silyl group is a characteristic reaction of monomeric vinyl silanes (4). While protodesilation of poly(trimethylsilylacetylene) to yield poly(acetylene) has been reported (5-7), reactions of polymeric vinyl silane systems with halogens are unexplored.

EXPERIMENTAL

^{1}H 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. Five percent solutions in chloroform-d_1 were used to obtain ^{1}H and ^{13}C 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. 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 chromatograph equipped with an 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: Mp 3,260,000, 194,000, 28,000 and 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 cm^3/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.

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Bromination of *E*-1,4-Poly(2-triethylsilyl-1,3-butadiene) (I)

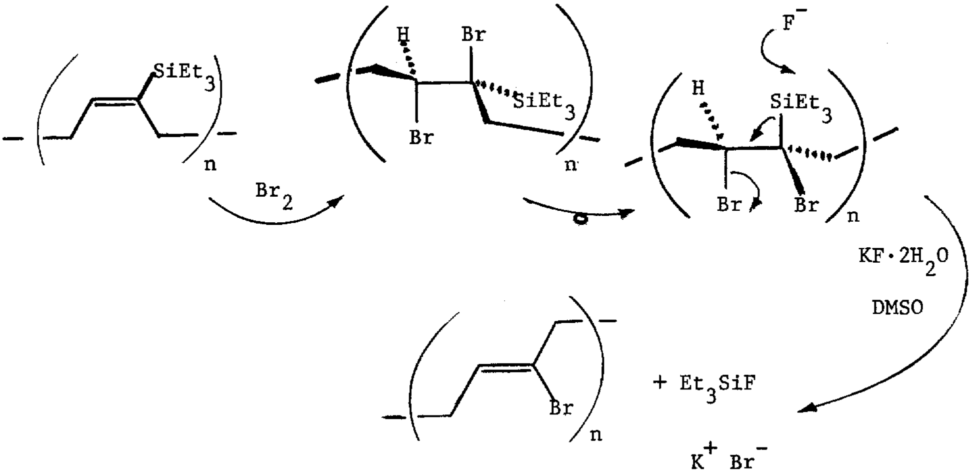
One hundred milligrams of I (8) was dissolved in 0.6 mL of chloroform-d_1. The solution was placed in a dried 5 mm NMR tube which was sealed with a rubber septum. The solution was cooled to 0°C and a solution of bromine (0.6 mmol, 35 μL) dissolved in 0.5 mL of chloroform-d_1 was added dropwise through the rubber septum via a syringe. The addition was followed by ^{1}H NMR. The disappearance of the signal due to the vinyl-CH proton at 5.70 ppm as well as the appearance of the CHBr proton resonance of 1,4-poly-(2,3-dibromo-2-triethylsilylbutane) (III) at 4.25 ppm were monitored. After 45 min, all of the polymer in solution had reacted. The reaction was allowed to warm to room temperature overnight. The yellow solution was decanted from a white precipitate which was identified as partially reacted I (25 mg, 25%). The NMR of the solution indicated some loss of triethylsilyl bromide from III.

Elimination of Triethylsilyl Bromide from III

Completion of the elimination of triethylsilyl bromide from III, was achieved in the following manner. In a 25 mL round bottom flask equipped with a Teflon covered magnetic stirring bar was placed the yellow solution of III, 10 mL of methylene chloride, 3 mL of DMSO and potassium fluoride dihydrate (0.5 g, 4.4 mmol). The mixture was stirred at room temperature for 8 h. The solution was then diluted with 20 mL of methylene chloride and the reaction was quenched by addition of water. The organic layer was separated, washed with several equal portions of water, dried over calcium chloride, filtered and the solvents removed by evaporation under reduced pressure. A yellow oil (70 mg, 75%) was obtained. Its properties were consistent with those expected for II. ^{1}H NMR δ: 5.63(br.t,1H, $J = 5.3$ Hz), 2.46 (br.s,4H). ^{13}C NMR δ: 128.31, 127.17, 40.22, 30.36. IR ν: 2900, 1640, 1420, 1090 cm^{-1}. GPC: I characterized by M_w/M_n = 9,145/7,080 gave II M_w/M_n = 7,300/5,420 while I characterized by M_w/M_n = 27,800/19,980 gave II M_w/M_n = 19,670/14,140. While the molecular weights of the product polymers II are lower than those of the starting polymers I, in both cases the ratio of M_w/M_n for I and II are quite similar. Elemental Anal. Calc. for C_4H_5Br: C, 36.38; H, 3.82; Br, 59.81. Found: C, 36.41; H, 4.03; Br, 59.44.

RESULTS AND DISCUSSION

Electrophilic substitution reactions on monomeric vinyl silanes by halogens have been shown to proceed regio- and stereoselectively (4). For example, *E*-2-trimethylsilyl-2-heptene reacts with bromine to yield a dibromide which undergoes loss of trimethylsilyl bromide to give *Z*-2-bromo-2-heptene. Likewise, *Z*-2-trimethylsilyl-2-heptene reacts with bromine to give *E*-2-bromo-2-heptene (9,10). This stereoselectivity has been attributed to a *trans* addition of bromine to the carbon-carbon double bond of the vinyl silane followed by *trans* elimination of the elements of trimethylsilyl bromide. No similar halogenation reactions have been reported on polymeric vinyl silanes. In this regard, we should like to report our results on the reaction of I with bromine followed by treatment with potassium fluoride dihydrate. Fluoride ion has been utilized to facilitate *trans*-1,2-elimination reactions of alkyltrimethylsilanes in which the alkyl group is substituted with a leaving group in the β-position (11). The product of this reaction sequence is found to be *Z*-1,4-poly(2-bromo-1,3-butadiene) (II). The molecular weight distribution (M_w/M_n) of the product polymer II as determined by gel permeation chromatography (GPC) is only slightly different from that of the starting polymer I.



While 2-bromo-1,3-butadiene has been previously polymerized under a variety of conditions (12-14), none of this work has resulted in regio or stereospecific polymerization of this monomer. Hence, the two step bromodesilation procedure reported here constitutes the first specific preparation of Z-1,4-poly(2-bromo-1,3-butadiene).

We have followed the course of this two step reaction by ^1H NMR spectroscopy. The first step probably involves a trans-addition of bromine to the carbon-carbon double bonds of I. This process can be followed easily by ^1H NMR by the disappearance of the vinyl hydrogen of I which comes at 5.70 ppm as well as by the appearance of the hydrogen signal due to the CHBr group of 1,4-poly(2,3-dibromo-2-triethylsilylbutane) (III) at 4.25 ppm. For comparison, the signal due to the hydrogen of the n-BuCHBr group of 1,2-dibromo-1-trimethylsilylhexane comes at 4.02 ppm (15). If III is allowed to stand overnight, 1,2-elimination of triethylsilyl bromide partially occurs. Treatment of this material with potassium fluoride facilitated the complete elimination of triethylsilyl bromide. This led to 1,4-Z-poly(2-bromo-1,3-butadiene). The stereochemistry was established by ^1H and ^{13}C NMR spectroscopy. The vinyl proton resonance comes at 5.63 ppm. For comparison, the vinyl proton resonance for Z-5-bromo-5-decene comes at 5.57 ppm while that for E-3-bromo-3-octene comes at 5.76 ppm (10). Further, only two unique vinyl carbon and two unique allyl carbon resonances are observed in the ^{13}C NMR. Thus, the addition of bromine to I occurs in a stereoselective trans manner while the elimination of triethylsilyl bromide from III to give II also occurs in a stereoselective trans manner.

The thermal stability of the polymer II was determined by TGA. The polymer II is thermally stable to 150°C. Between 170 and 350°C the polymer loses weight at a rate of about 3.5% for each ten degree increase in temperature. By 350°C 65% of the initial weight of the polymer has been lost. Between 350 and 475°C the polymer loses weight more slowly. Above 475°C rapid weight loss occurs. Above 500°C no further weight loss occurs. Approximately 18% residue is left. (See Figure)

Despite this success, one should not underestimate the difficulty in cleanly transferring reactions from monomer to polymer systems.

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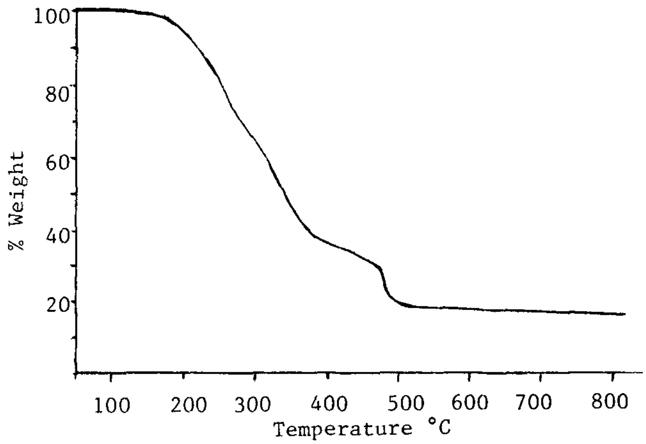

Figure. TGA of polymer 2.

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