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Reaction of *E*-1,4-poly(2-triethylsilyl-1,3-butadiene) with iodine monochloride

Wan Jiang and William P. Weber*

K.B. and D.P. Loker Hydrocarbon Research Institute, Department of Chemistry,
University of Southern California, Los Angeles, CA 90089-1661, USA

SUMMARY

Addition of iodine monochloride to E-1,4-poly(2-triethylsilyl-1,3-butadiene) (I) followed by treatment with potassium fluoride dihydrate yields a copolymer comprised of E and Z-1,4-(2-iodo-1,3-butadiene) (E and Z-II) units and Z-1,4-(2-chloro-1,3-butadiene) (Z-III) units. The mechanism of this reaction is discussed. The product copolymer has been characterized by ^{1}H and ^{13}C NMR, IR, UV, GPC, TGA and elemental analysis.

INTRODUCTION

There is considerable interest in chemical modification of intact polymers (1-4). Regio- and stereoselective electrophilic substitution reactions with loss of the silyl group is a characteristic reaction of monomeric vinyl silanes (5,6). Only a few examples of such reactions on polymeric silane systems have been reported. The protodesilation of poly(trimethylsilylacetylene) to yield poly(acetylene) has been most extensively studied (7-9). While the reaction of iodine monochloride with monomeric E and Z-1-trimethylsilylalkenes has been reported (10,11), the analogous reaction with polymeric vinyl silane systems has not been studied. The reaction of I with bromine which yields Z-1,4-poly(2-bromo-1,3-butadiene) is a closely related example (12).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer operating in the Fourier transform mode. The ^{13}C NMR spectra were run with broad band proton decoupling. Five percent solutions in chloroform-d were used to obtain ^{1}H NMR spectra, while ten percent solutions were used for ^{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 neat oils between NaCl

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*To whom offprint requests should be sent plates. GPC analysis of the molecular weight distribution of the polymer 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: M_p 3,600,000, 194,000, 28,000 and 2,550 whose M_w/M_n are less than 1.09. TGA of the polymer was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 mL/min. The temperature program for the analysis was initially at 50°C for 10 min, followed by an increase of 5°C/min up to 700°C. Elemental analysis was performed by Galbraith Laboratories Knoxville, TN.

Addition of ICl to I

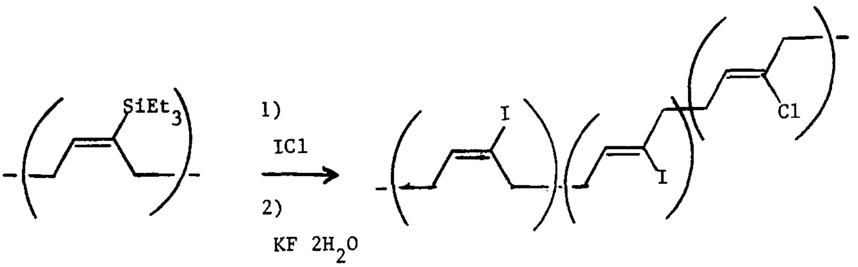
In a flame dry two neck 50 mL round bottom flask equipped with a Teflon covered magnetic stirring bar was placed I, M_w/M_n = 9150/7080, (13) (1.8 mmol, 0.3 g) and CH_2Cl_2 (5 mL). One neck of the flask was connected to nitrogen while the other was sealed with a rubber septum. The flask was cooled in an ice/water bath. Iodine monochloride (Aldrich) (1.9 mmol, 310 mg) dissolved in 5 mL of CH_2Cl_2 was added via a syringe. The initial colorless solution turned dark brown almost immediately. The reaction was stirred at 0°C for 2 h. It was then stirred at RT for 10 h.

Elimination of Triethyliodosilane and Triethylchlorosilane from Adduct Polymer

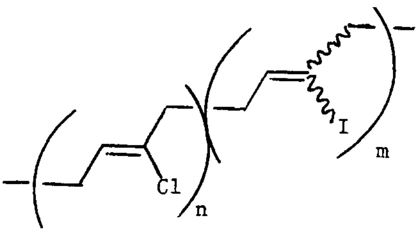
To the above reaction mixture was added, CH_2Cl_2 (20 mL), $KF \cdot 2H_2O$ (0.8 g) and DMSO (3mL). The mixture was heated to reflux for 4 h and then was allowed to stir at RT for 12 h. The reaction mixture was poured into a separatory funnel. The reaction flask was rinsed with ether (30 mL). The combined purple brown colored organic layer was extracted with an aqueous solution of sodium thiosulfate (15 mL). After this process, the organic layer was almost colorless. The organic layer was then washed several times with equal volumes of water. A small amount of brownish colored oil (60 mg) which did not dissolve well in ether was separated. The ether solution was dried over anhydrous calcium chloride, filtered and volatile solvents removed by evaporation under reduced pressure. The dark oil, obtained in this way, was purified by dissolving it in THF and then precipitating it by addition of methanol. This process was repeated several times. In this way a 70% yield of copolymer was obtained. It had the following properties: M_w/M_n = 7725/6035. IR ν: 2960, 2890, 1660, 1450, 1100, 840 cm^{-1}. ^1H NMR δ: 2.28(br.s, 2.4H), 2.46(br.s, 1.8H), 5.46(br.s, 0.76H), 6.08(br.s, 0.24H). ^{13}C NMR δ:140.39, 140.06, 139.96, 139.63, 135.08, 134.81, 134.21, 133.89, 133.73, 133.35, 133.18, 123.92, 123.76, 109.40, 109.08, 108.81, 102.96, 102.58, 102.31, 45.15, 44.77, 44.39, 44.07, 43.80, 39.03, 38.76, 38.06, 37.73, 37.51, 36.49, 36.11, 34.59, 32.64, 30.85, 30.42, 28.74, 28.47, 26.79. UV λ_{max} 236 mn, ε = 548; λ_{max} 250 nm, ε = 350. Elemental analysis calcd: C, 30.35; H, 3.19; Cl, 5.39; I, 61.19. Found: C, 30.53; H, 3.28; Cl, 3.75; I, 61.19.

RESULTS AND DISCUSSION

A copolymer comprised of E-II, Z-II, and Z-III units has been prepared by addition of iodine monochloride to I followed by elimination of triethyliodosilane or triethylchlorosilane from the adduct polymer by treatment with potassium fluoride in DMSO. The formation of Z-II and Z-III groups can be explained by a non-regiospecific trans addition of iodine monochloride across the carbon-carbon double bond of the vinyl silane groups, followed by a trans 1,2-elimination of triethyliodosilane or triethylchlorosilane. The formation of E-II groups may result from cis elimination of triethylchlorosilane from the adduct polymer. Alternatively, E-II units may result from iodine catalyzed cis/trans isomerization. Iodine is well known to catalyzed such isomerization reactions (14,15). Reaction of iodine monochloride with monomeric 1-trimethylsilyl alkenes has produced similar results (10,11).



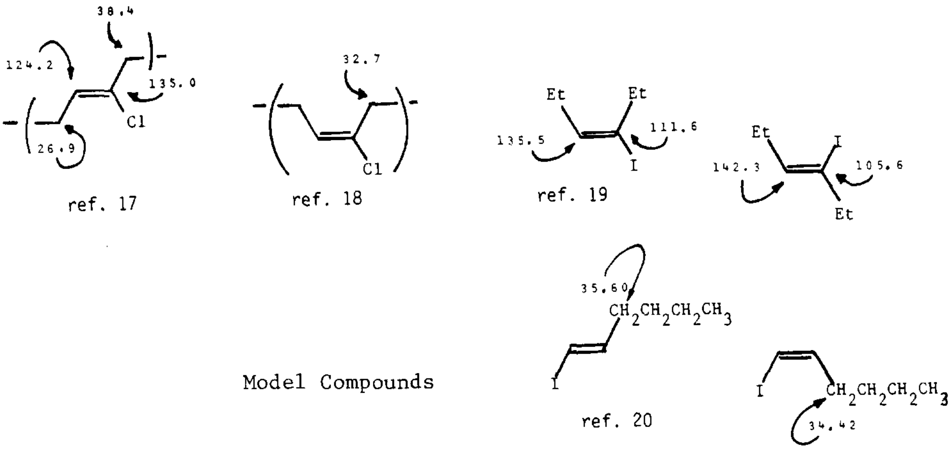
The percentage of E-II, Z-II and Z-III units was determined by integration of the vinyl ^{1}H NMR signals and elemental analysis. The signal at 6.08 ppm (24%) was assigned to the vinyl proton of E-II units, by comparison with model compounds, (16). On the other hand, the resonance at 5.46 ppm (76%) results from the overlap of signals from Z-II (16) and Z-III (17) units. The percent composition of carbon, hydrogen, iodine and chlorine was determined for the copolymer. The calculated values for carbon, hydrogen and chlorine were determined on the assumption that the iodine value was correct.



n + m = 1, n = percent Z-III units (24%), m = percentage of E-II and Z-II units (76%).
Molecular weight of copolymer = MW = n(Cl+4C+5H) + m(I+4C+5H)
%I = mI/MW, %C = 4C(n+m)/MW, %H = 5H(n+m)/MW, %Cl = nCl/MW
where C, Cl, H and I are the respective atomic weights of these elements.

The ratio of E-II (24%): Z-II (52%): Z-III(24%) units in the copolymer determined in this way was in reasonable agreement with the values determined by integration of the vinyl ^{1}H NMR signals.

The ^{13}C NMR signals can be assigned to E and Z-II and Z-III units by comparison with chemical shifts of carbons in model compounds (see Figure 1). However, the ^{13}C signals due to specific triads have not been assigned.



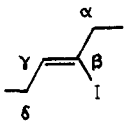
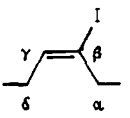
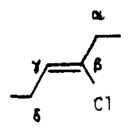
Cα	Cβ	Cγ	Cδ		
45.15	102.96	140.39	37.73		Z-II
44.77	102.58	140.06	37.51		
44.39	102.31	139.96	36.49		
		139.63	36.11		
			34.59		
44.07	109.40	134.21	32.64		E-II
43.80	109.08	133.89	30.85		
	108.81	133.73	30.42		
		133.35			
		133.18			
39.03	135.08	123.92	28.74		Z-III
38.76	134.81	123.76	28.47		
38.06			26.79		

Figure 1. ^{13}C NMR Chemical Shifts of Model Compounds and Chemical Shifts Assigned to E-II, Z-II and Z-III Units.

UV spectrum, λ_{max} 250 nm, $\varepsilon = 350$ and λ_{max} 236 nm, $\varepsilon = 548$, of the copolymer is consistent with that expected on the basis of the uv spectrum of monomeric model compounds: Z-4-iodo-3-heptene λ_{max} 249 nm, $\varepsilon = 400$; E-4-iodo-3-heptene λ_{max} 243 nm, $\varepsilon = 400$ (16); and chloroprene λ_{max} 223, $\varepsilon = 14{,}000$ (21). The low energy band transition in the copolymer probably arises from absorption due to Z-II units. On the other hand, the higher energy transition may result from overlap of absorptions due to both E-II and Z-III units.

While the molecular weight distribution of the product copolymer is slightly lower than I, the dispersity of the product copolymer and I are quite similar. The thermal stability of the product copolymer was determined by TGA. The copolymer was stable to about 80°C. A slow linear weight loss occurs to 200°C. At this temperature, eight percent of the initial sample weight has been lost. Rapid weight loss occurs between 200°C and 250°C and again between 450 and 525°C. By 250°C 55% of the initial weight has been lost. After the second region of rapid weight loss only 8% of the initial sample weight remains (see Figure 2).

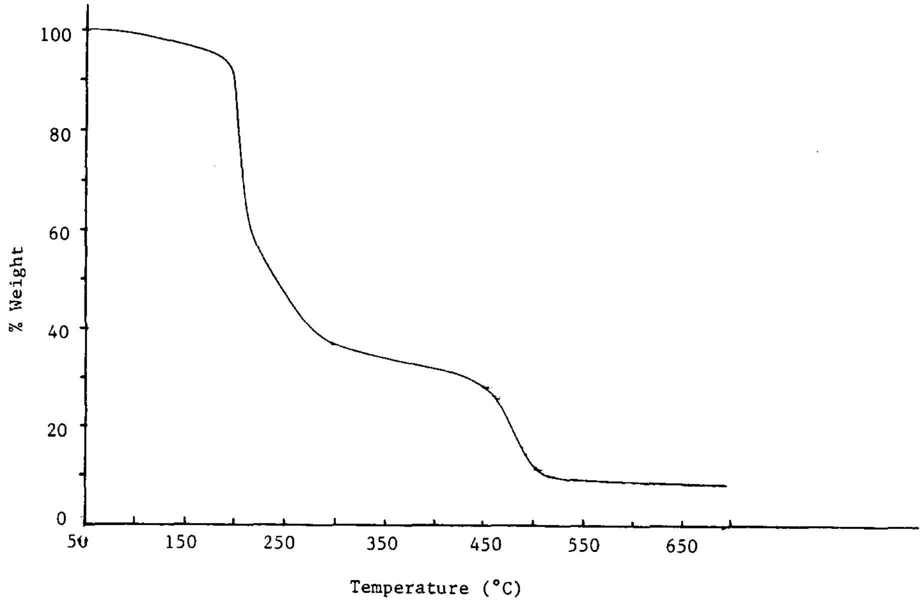


Figure 2. TGA of Copolymer.

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