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Reductive silylation of chloroprene

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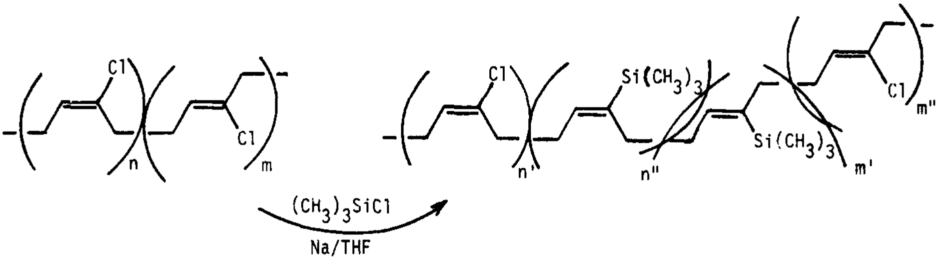
SUMMARY

Copolymers made up of 1,4-(2-trimethylsilyl-1,3-butadiene) (I) and 1,4-(2-chloro-1,3-butadiene) (II) units have been prepared by reaction of chloroprene with trimethylchlorosilane and sodium dispersion in THF. The ratio of I:II units in the copolymers have been determined by IR, ^{1}H NMR and elemental analysis. The E:Z ratio of these units has been determined by ^{1}H NMR. ^{13}C and ^{29}Si NMR of these copolymers is discussed.

INTRODUCTION

There is considerable interest in the chemical modification of intact polymers (1-4). We have prepared copolymers made up of 1,4-(2-trimethylsilyl-1,3-butadiene) (I) and 1,4-(2-chloro-1,3-butadiene) (II) units by reaction of chloroprene with trimethylchlorosilane and sodium dispersion in THF solvent. The composition of these copolymers has been varied from I:II 44:56 to 95:5 by changing the molar ratio of sodium to chloroprene as well as by changing the reaction time. This reaction is modeled after the known reductive silylation of monomeric vinyl chlorides. For example, 1-chlorocyclohexene reacts with trimethylchlorosilane and sodium metal in ether solvent at room temperature to yield 1-trimethylsilylcyclohexene (5).



1,4-poly(2-Trimethylsilyl-1,3-butadiene) has been previously prepared by the ring opening metathesis reaction of 1-trimethylsilylcyclobutene (6), while E-1,4-poly(2-triethylsilyl-1,3-butadiene) has been prepared by anionic polymerization of 2-triethylsilyl-1,3-butadiene (7).

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EXPERIMENTAL

^1H, ^{13}C and ^{29}Si NMR spectra were obtained on an IBM Brucker WP-270-SY spectrometer operating the Fourier transform mode. ^{13}C NMR spectra were run with broad band proton decoupling. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra (8). This was effective since all the silicon atoms have three methyl groups bonded to them. Five percent solutions in chloroform-d_1 were used to obtain ^1H NMR spectra, while ten percent solutions were used for ^{13}C and ^{29}Si 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. 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. Two 32 cm x 77 mm Perkin-Elmer PL 5 and 10 μm particle size, mixed pore size, crosslinked polystyrene gel columns connected in series were used for the separation. The eluting solvent was THF at a flow rate of 0.9 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_p 3,600,000, 194,000, 28,000, 2,550 and 480 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 cc/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.

Chloroprene M_w/M_n = 353,900/124,800, 1,4-Z:E 85:15 was obtained from Aldrich. The Z to E ratio was determined by ^1H NMR (9). Neither 1,2 nor 3,4 units were determined. IR ν: 1650 cm^{-1}. It was used as received.

Silylation Procedure

In a flame dried 200 mL three neck flask was equipped with a reflux condenser, a 0.5" ultrasonic probe which was connected to a 500 W Tekmar Sonic Disruptor and a nitrogen gas inlet was placed sodium metal (0.1 g, 4.6 mmol) and 30 mL of toluene. The flask was heated until the toluene began to reflux. At this point, the ultrasound power was turned on at a 30% output level for 10 min. The suspension was allowed to cool and 150 mL of pentane was added. It was then allowed to stand overnight. The hydrocarbon solvent mixture was removed via a syringe and 80 mL of THF was added. Finally a solution of trimethylchlorosilane (1.0 mL, 7 mmol) and chloroprene (0.2 g, 2.3 mmol) in THF (40 mL) was added. The mixture was stirred at 45 to 55°C for 6 to 12 days. Isopropanol (20 mL) was added to destroy the excess sodium. Ether was added to the reaction mixture. The mixture was first washed with saturated sodium bicarbonate and then with water. The ether solution was dried over anhydrous magnesium sulfate, filtered and the solvents removed by evaporation under reduced pressure. The yellow-brown rubber like polymeric residue was purified by dissolving in THF and precipitation by addition of methanol several times.

Copolymer III

Copolymer III was prepared by reaction of a 10:4:1 ratio of sodium to trimethylchlorosilane to II units of chloroprene for 12 days at 55 °C. After purification as above a 70% yield was obtained. It had the following properties. M_w/M_n = 72,700/30,300. IR ν: 2920, 2840, 1600, 1440, 1400, 1240, 830 (s) cm^{-1}. ^{1}H NMR δ: 0.05(s, 1.2H), 0.12(s, 7.0H), 2.05(br.s, 3.6H), 2.35(s, 0.4H), 5.12(s, 0.01H), 5.43(br.s, 0.07H), 5.48(s, 0.02 H), 5.71(s, 0.15H), 5.92(br.s, 0.75H). ^{13}C NMR δ: -0.95, -0.68, 0.46, 0.95, 1.60, 29.77, 32.48, 32.64, 32.75, 33.51, 33.61, 38.49, 39.95, 138.66, 139.14, 139.25, 139.36, 139.47, 140.28, 142.34, 142.50, 142.72, 143.21. ^{29}Si NMR δ: -7.46, -7.65, -7.75, -7.79, -8.75. Elemental Analysis calcd.: C, 66.14; H, 10.98; Cl, 1.35. Found : C, 67.15; H, 10.82; Cl, 1.35. ^{1}H NMR integration gave I:II 90:10, while elemental analysis yields I:II 95:5.

Copolymer IV

Copolymer IV was prepared by the reaction of a 2:3:1 ratio of sodium to trimethylchlorosilane to II units of chloroprene for ten days at 55°C. After purification as above a 70% yield was obtained. It had the following properties. M_w/M_n = 68,450/33,100. IR ν: 2920, 2900, 2840, 1650 (w), 1600, 1440, 1400, 1345, 830 (s) cm^{-1}. ^{1}H and ^{29}Si NMR were similar to copolymer III. On the other hand, the ^{13}C NMR was more complicated due to the presence of triads comprised of E-I, Z-I, E-II and Z-II units. Elemental analysis calcd.: C, 64.45; H, 10.23; Cl, 6.78. Found: C, 63.39; H, 9.74; Cl, 6.78. ^{1}H NMR integration gave I:II 70:30, while elemental analysis yields I:II 77:23.

Copolymer V

Copolymer V was prepared by the reaction of a 2:3:1 ratio of sodium to trimethylchlorosilane to II units of chloroprene for six days at 45°C. After purification as above a 78% yield was obtained. It had the following properties. M_w/M_n = 282,800/106,600. IR ν: 2930, 2910, 1650, 1600, 1430, 1240, 830 (s) cm^{-1}. ^{1}H and ^{29} Si NMR were similar to those reported for copolymer III. On the other hand, the ^{13}C NMR was more complicated due to triads composed of E-I, Z-I, E-II and Z-II units. Elemental analysis calcd. C, 60.80; H, 8.60; Cl 18.79. Found C, 61.09; H, 8.64; Cl 18.79. ^{1}H NMR integration gives I:II 42:58, while elemental analysis yields I:II, 44:56.

RESULTS AND DISCUSSION

Copolymers composed of I and II have been prepared by the reaction of chloroprene with trimethylchlorosilane and a sodium dispersion. Increasing the reaction time or the ratio of sodium to chloroprene resulted in a higher ratio of I:II units in the product copolymer. The ratio of these units in the copolymers could be determined qualitatively by IR and quantitatively by both ^{1}H NMR and elemental analysis.

Chloroprene has a distinctive carbon-carbon double bond stretch at 1650 cm^{-1} in the IR, whereas E-1,4-poly(2-triethylsilyl-1,3-butadiene) has a carbon-carbon double bond stretch at 1597 cm^{-1}. Thus in copolymer V in which the ratio of I:II is 44:56 (by analysis) two bands of approximately equal intensity are observed at 1650 and 1600 cm^{-1}, while in copolymer IV, I:II 77:23, the band at 1650 is weaker than that at 1600 cm^{-1}. Finally in copolymer III, I:II 95:5, only a band at 1600 cm^{-1} is observed.

^{1}H NMR resonances due to vinyl hydrogens of I and II units are well resolved. Thus the vinyl ^{1}H signal for Z-I units is centered at 5.92 ppm while that for E-I units is found at 5.71 ppm. The vinyl ^{1}H NMR signals for Z-II units is observed at 5.43 ppm while that for E-II units is seen at 5.12 ppm. A small unidentified resonance is seen at 5.48 ppm. Integration of these signals permits analysis of the ratio of I:II units in the copolymers. The ratio of E:Z-I units in the copolymers is similar to the ratio of E:Z units in the starting chloroprene 85:15 and to the ratio of E:Z-II units in the copolymers.

The allyl ^{1}H signals for I and II units are also distinct. The ^{1}H signal for II units is a singlet at 2.35 ppm, while that for I units is a broad singlet centered at 2.05 ppm. The integration of these allylic ^{1}H NMR signals is consistent with the integration of ^{1}H NMR vinyl resonances. Finally, the ^{1}H NMR signal which results from the methyl hydrogens bonded to silicon of the E-I units is found at 0.12 ppm, while that for the Z-I units is observed at 0.05 ppm. The ratio of these signals is consistent with those of the vinyl hydrogens assigned to E-I and Z-I units.

We can interpret the ^{13}C NMR spectrum of copolymer III based on a triad analysis. The five most probable triads made up of Z-I and E-I units are drawn below (see Figure 1). This predicts a total of twenty five ^{13}C NMR signals. In fact five signals for distinct methyl carbons bonded to silicon as well as ten unique vinyl carbons are observed. However, only eight allylic ^{13}C NMR signals are detected. This may result from accidental coincidence of two of these resonances. In additions several signals of significantly lower intensity are found. These probably result from triads in which Z-II units are incorporated.

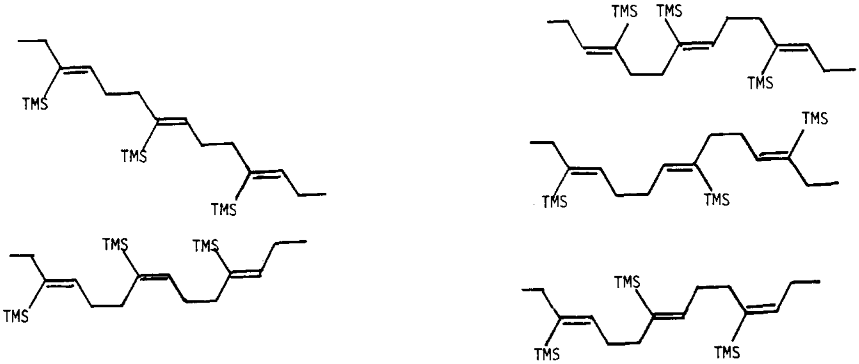
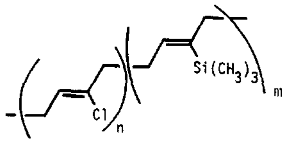


Figure 1. Most probable triads of copolymer III.

Likewise five distinct resonances are observed in the ^{29}Si NMR of copolymer III. The one of highest intensity at -7.79 ppm maybe assigned to the most probable triad made up of Z-I units all of which are linked in a head to tail arrangement.

The percent composition of carbon, hydrogen and chlorine was determined for the copolymers. The calculated values for carbon and hydrogen were determined on the assumption that the chlorine value was correct. The ratio of I:II units in the copolymers determined in this way was in reasonable agreement with the values determined by integration of the vinyl ^{1}H NMR signals.



n + m = 1

molecular weight of polymer = MW = n(Cl + 4C + 5H) + m(Si + 7C +14H)
%Cl = n x Cl/MW , %C = (4nC + 7mC)/MW; %H = (5nH + 14mH)/MW
where Cl, H, and C are the respective atomic weights of these elements.

TGA analysis indicates that copolymers III, IV and V are significantly less stable than chloroprene. In fact, the order of stability is chloroprene > V > IV > III. Apparently, the higher the percent of I units in the copolymer, the lower the thermal stability. This is surprising since both 1,4-E-poly(2-triethylsilyl-1,3-butadiene) and 1,4-E and Z-poly(2-triethylsilyl-1,3-butadiene) have been found to be significantly more stable than chloroprene by TGA (7). Proximity of I and II units must significantly decrease copolymer thermal stability (see Figure 2).

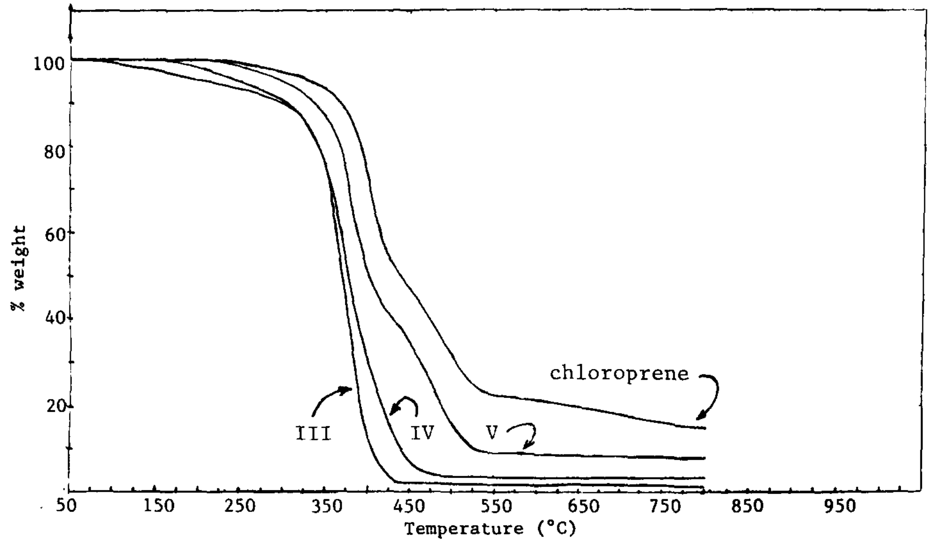


Figure 2. TGA of chloroprene and copolymers III, IV and V.

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