Polymer Bulletin 20, 7–10 (1988)

Polymer Bulletin

Reaction of 1,4-poly(2-trimethylsilylmethyl-1,3-butadiene) with phenylsulfenyl chloride

Synthesis of poly(3-methylene-2-phenylthiobutane

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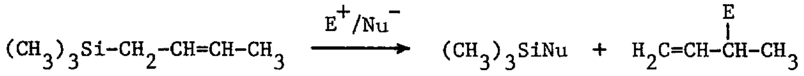
SUMMARY

Reaction of 1,4-poly(2-trimethylsilylmethyl-1,3-butadiene) with phenylsulfenyl chloride yields predominantly poly(3-methylene-2-phenylthiobutane). The mechanism of this reaction is discussed. The product polymer has been characterized by ^1H, ^{13}C NMR, IR, GPC, TGA, and elemental analysis.

INTRODUCTION

There is considerable interest in chemical modification of intact polymers (1-3). Electrophilic substitution with allylic rearrangement and loss of the silyl group is a characteristic reaction of monomeric allylic silanes (4). Similar reactions have not been explored with polymeric systems.



$$(CH_3)_3Si\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3 \xrightarrow{E^+/Nu^-} (CH_3)_3SiNu + H_2C{=}CH\text{-}\overset{E}{\overset{|}{C}}H\text{-}CH_3$$

EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating the FT mode. ^{13}C NMR spectra were run with broad band proton decoupling. Five percent solution were used for ^1H and ^{13}C spectra. Chloroform was utilized as an internal standard. All chemical shifts reported were externally referenced to TMS. IR spectra were recorded on a Perkin Elmer PE 281 spectrometer.

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 tetrahydrofuran at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards Mp 3,600,000, 194,000, 28,000 and 2,550 whose $\overline{M}_w/\overline{M}_n$ 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 cc/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 5°C/min to 550°C. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

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Cis- and *trans*-1,4-poly(2-trimethylsilylmethyl-1,3-butadiene)

Ziegler-Natta polymerization of 2-trimethylsilylmethyl-1,3-butadiene (5) catalyzed by triethylaluminum and titanium tetrachloride gave the desired polymer with a *cis/trans* ratio of 9 to 1 as previously reported (6). $\overline{M}_w/\overline{M}_n$ = 107,000/9,100.

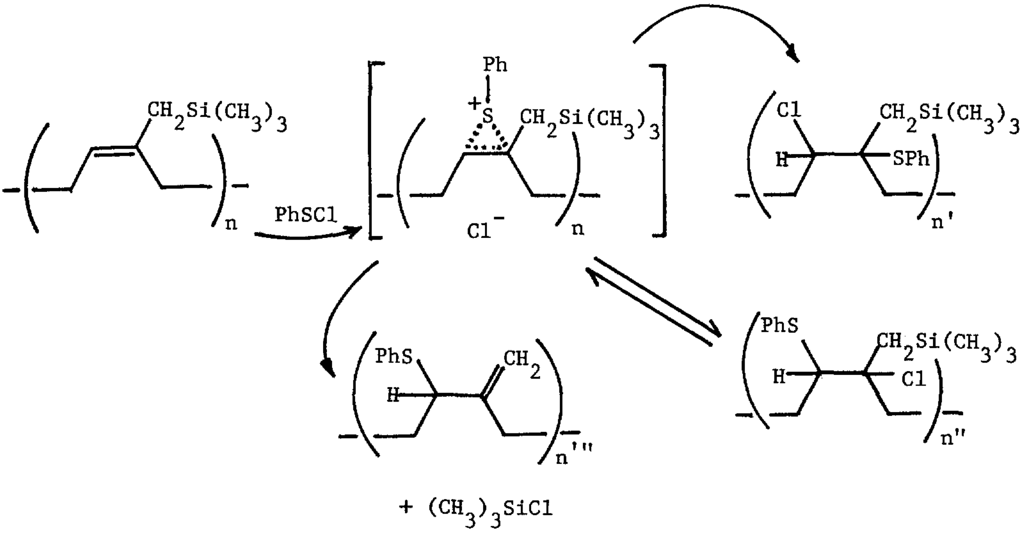
Reaction of Polymer with Phenylsulfenyl Chloride

The reaction was carried out under an atmosphere of pre-purified nitrogen. In a dry 50 mL round bottom flask equipped with a Teflon covered magnetic stirring bar was placed 0.14 g (1 mmol) of the polymer and 15 mL of methylene chloride. The solution was cooled to 0°C and 0.16 g (1.1 mmol) of phenylsulfenyl chloride was added. The yellow color of the solution faded over 10 min. Methanol was then added to precipitate the polymer. The polymer was dissolved in tetrahydrofuran and reprecipitated by addition of methanol. This process was repeated at least three times. The product polymer was then dried under vacuum at 57°C. It had the following spectral properties: ^{1}H NMR δ: 7.24 (br.s, 5H), 4.70 (br.s, 2H), 3.50 (br.s, 1H), 2.30-1.60 (br.m, 4H). ^{13}C NMR δ: 146.94, 134.97, 132.75, 128.63, 127.11, 112.43, 55.39, 31.44, 29.92. In addition to these resonances which can be assigned to 1,4-poly(3-methylene-2-phenylthiobutane), small signals in the ^{13}C NMR at 0.24 and -0.19 ppm characteristic of trimethylsilyl groups are observed. Likewise, additional resonances were observed in the ^{1}H NMR at 5.00 (br.s) and 0.00 (br.s, 2.5 H). The signal at 5.00 is assigned to the vinyl-CH of the starting polymer while that at 0.00 is due to trimethylsilyl groups. IR ν: 3060, 2940, 1630, 1580, 1475, 1440, 1245, 1090, 1025, 890, 850, 740, and 685 cm^{-1}. GPC $\overline{M}_w/\overline{M}_n$ = 117,600/9,900. Elemental Anal. Calc. for $C_{11}H_{12}S$: C, 74.95; H, 6.86; S, 18.19. Found: C, 72.33; H, 7.71; S, 15.86; Cl, 1.37.

RESULTS AND DISCUSSION

Cis- and *trans*-1,4-poly(2-trimethylsilylmethyl-1,3-butadiene) has reactive allylic silane functional groups regularly arranged along the polymer backbone. While there has been considerable work done on regiospecific electrophilic substitution reaction of monomeric allylic silanes (4), similar reactions with polymeric systems have not been explored. Reaction of this polymer with phenylsulfenyl chloride yields predominantly 1,4-poly(3-methylene-2-phenylthiobutane). For comparison, the reaction of 1,4-polybutadiene with phenylsulfenyl chloride yields an addition product: 1,4-poly(2-chloro-3-phenylthiobutane) (7-9).

This reaction is probably initiated by regiospecific electrophilic attack on the carbon-carbon double bond of the polymer by a phenylsulfenium cation. This yields an unsymmetrical thiiranium cation intermediate in which more of the positive charge is centered at the tertiary carbon than at the secondary center. This is not only due to the greater stability of tertiary carbocations compared to secondary ones, but also due to the well known stabilizing effect of a *beta*-trimethylsilyl group on carbocation centers (10). These two effects are mutually reinforcing. Nucleophilic attack by chloride anion on the secondary carbocation center leads to formation of 1,4-(2-chloro-3-phenylthio-3-trimethylsilylmethylbutane) units (11%). For comparison, 4-chlorobenzenesulfenyl chloride adds to 2-methyl-2-butene to give 2-chloro-2-methyl-3-phenylthiobutane and 3-chloro-2-methyl-2-phenylthiobutane in a ratio of 92:8 under thermodynamic control (11). This latter product corresponds to the minor product in our reaction. The major reaction pathways involve nucleophilic attack by chloride anion either on the tertiary carbocation center or at the silyl center. Attack at the tertiary carbocation center leads to 2-chloro-3-phenylthio-2-trimethylsilylmethylbutane units. These are unstable and undergo heterolytic ionization of the tertiary carbon-chlorine bond to regenerate the intermediate thiiranium cation. On the other hand, nucleophilic attack by chloride anion on the silyl center results in loss of trimethylsilyl chloride and formation of the major product 3-methylene-2-phenylthiobutane units as outlined below. Unreacted units of starting polymer (8%) are also found. These are assumed to have a trans-geometry, based on the observation that when the reaction is carried out with a deficiency of phenylsulfenyl chloride cis carbon-carbon double bonds of the polymer react significantly faster than those with trans geometry. Similar reactive differences have been previously observed with monomeric olefins (11).



The product polymer was characterized by ^1H, ^{13}C NMR, as well as by IR spectroscopy. The molecular weight distribution as determined by GPC was not changed by this chemical transformation. Elemental analysis -- C, H, S and Cl as well as spectroscopic data was consistent with a product polymer of the following composition: 1,4-poly(2-phenylthio-3-methylenebutane) (81%), 1,4-poly(2-chloro-3-phenylthio-3-trimethylsilylmethylbutane) (11%) and unreacted trans-1,4-poly(2-trimethylsilylmethyl-1,3-butadiene) (8%). The thermal stability of the polymer was determined by TGA. The polymer was stable to 150°C. Rapid decomposition occurs above 160°C. (See Figure)

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

ACKNOWLEDGEMENT: This work was supported by the Air Force Office of Scientific Research Grant No. 86-0042.

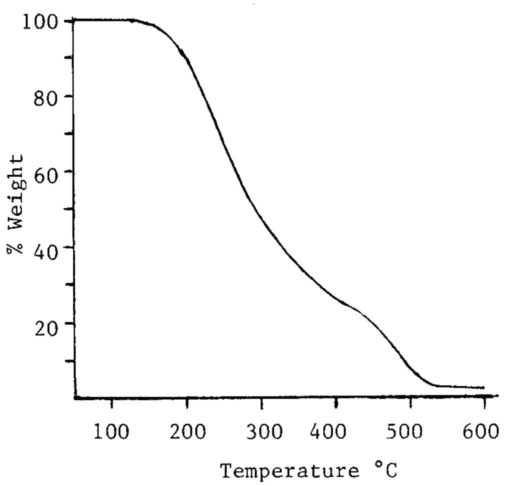


Figure. TGA of polymer.

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Accepted April 13, 1988 K