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Selective cationic ring-opening polymerization of 6-thiatricyclo[3.2.2.$0^{2,4}$]non-8-ene

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Summary

The monomer 6-thiabicyclo[3.2.2.$0^{2,4}$]non-8-ene (**4**) was prepared by $LiAlH_4$ reductive dechlorination of the 1:1 adduct **3** formed on heating cycloheptatriene with thiophosgene. Cationic initiated polymerization of **4** with boron trifluoride etherate as catalyst gave a white solid polymer (**8**, $\overline{M}_n$ = 6,300), in 83% yield. The polymer structure was established by comparison of the ^1H NMR spectrum with that of the model compound 5-mercaptobicyclo[4.1.0]hept-3-ene-2-methanol (**6**).

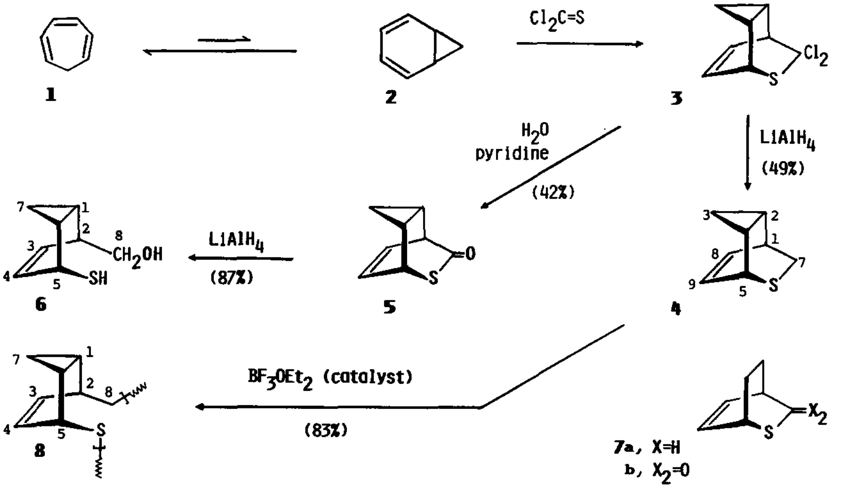
Introduction

Ring-opening polymerizations of cyclic alkenes, cyclopropanes, and cyclic sulfides are well known (1). Herein we report on the polymerization of 6-thiatricyclo[3.2.2.$0^{2,4}$]-non-8-ene (**4**), a monomer constituted of all three of these functionalities.

Results and discussion

The synthesis of **4** was achieved by an approach similar to that used by Reich and Trend (2) to prepare 2-thiabicyclo[2.2.2]octene (**7a**) from cyclohexadiene. Thus reaction between thiophosgene and the norcaradiene valence-isomer (**2**) of cycloheptatriene (**1**) led to the Diels-Alder adduct **3** (Scheme 1). Compound **3** is mal-odoriferous and moisture sensitive, and its isolation was not attempted. Treatment of crude **3** with $LiAlH_4$ resulted in the reductive removal of the chlorine substituents to give **4** in 49% yield. When stored at ambient temperatures **4** was found to slowly polymerize within days.

SCHEME 1



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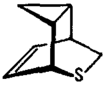
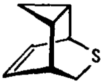
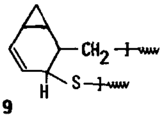
The monomer **4** was characterized by spectral data (see Experimental). Importantly, the ^1H NMR spectrum shows two sets of one proton multiplets at $\delta 0.04$ and $\delta 0.08$, diagnostic of cyclopropane methylene hydrogens; the remaining resonances are in close agreement to those reported for the corresponding protons in the related heterocycle **7a** (2). By analogy with other Diels-Alder reactions of cycloheptatriene with dienophiles (3), the adduct **3**, and hence its transformed products **4-6**, and **8** are assigned the *anti* stereochemistry as shown in Scheme 1. Also we note here that the structure designated as **4** is a racemic mixture of the enantiomers **4a** and **4b**. For the purposes of simplicity, only enantiomer **4a**, and its derivatives, are depicted throughout this article.



4a



4b



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Attempts to initiate polymerization of **4** under catalytic radical (AIBN, benzene at reflux, N_2) or anionic (n-BuLi at 0°C, N_2) conditions failed. However, cationic initiation with boron trifluoride etherate as catalyst led cleanly to a white polymer, mp 155-157°C, in 83% yield; the average molecular weight was 6,300, as determined by gel permeation chromatography.

The structure **8** assigned to the polymer was derived from ^{13}C NMR (Fig. 1) and ^1H NMR spectral data, and elemental combustion analysis for sulfur. In the ^1H NMR spectrum, the chemical shifts of ring-attached protons of the polymer are closely similar to those of the model compound **6** (note Table 1). This observation, together with the demonstration (spin decoupling, homonuclear 2D-COSY) of large coupling (4.0 Hz) between the low-field allylic H-C-S proton and one of the cyclopropyl methine hydrogens, permits us to rule out **9** as a possible contending structure for the polymer motif.

Model compound **6** was obtained in 81% yield from $LiAlH_4$ reduction of thiolactone **5** (ν C=O 1680 cm^{-1}; cf. 1680 cm^{-1} for **7b** (2)), which in turn was isolated in 42% yield from the basic hydrolysis of the initial adduct **3**.

If it is assumed that the growing chain end is a sulfonium-containing (more or less dissociated) ion pair, then the polymerization can be envisaged as proceeding via an S_N2 process involving attack at C_7 of the initial complex **10**, as depicted in Scheme 2. An alternative rationale involving S_N1 opening of the C_5-S bond of complex **10**, appears to be less reasonable since this would lead to the delocalized carbocation **12**, and subsequent substitution at C_2, C_5, or C_8 in important relative proportions, and would thus engender a mixture of polymer structural units. Given the *grosso-modo* simplicity of the ^{13}C NMR spectrum, operation of this mechanism is unlikely to be significant.

TABLE 1. *The ^1H 400 MHz NMR data of ring-attached protons in* **6** *and polymer* **8**.

	Signal positions δ and description	
	6	**8**
H-1	1.20 m	1.32 m
H-2	2.71 m	2.68 m
H-3	5.45 dd	5.53 dd
H-4	5.77 dd	5.60 dd
H-5	3.77 m	3.82 m
H-6	1.34 m	1.43 m
H-7	0.67 dt	0.68 dt
H-7	0.45 q	0.47 q

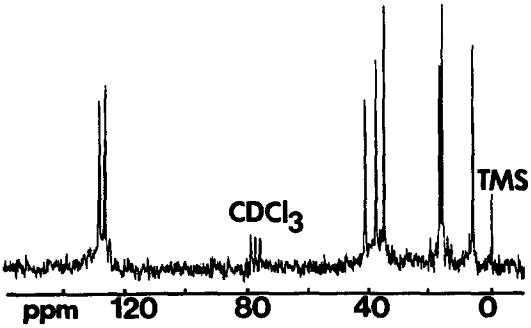
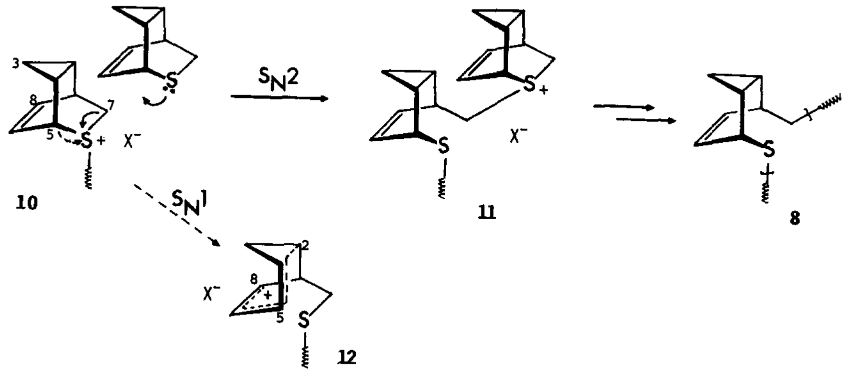


FIG. 1. *Proton decoupled ^{13}C NMR spectrum of polymer* **8** *at 20.15 MHz.*

SCHEME 2



Experimental

6-Thiatricyclo[3.2.2.$0^{2,4}$]non-8-ene (4)

A solution of 3.5659 g (38.8 mmol) of cycloheptatriene and 7.54 g (65.6 mmol) of thiophosgene in 15 mL of CCl_4 was refluxed under nitrogen for 18 h (reaction progress followed by NMR), then cooled, diluted with hexane (200 mL) and filtered. The filtrate was concentrated in *vacuo* to give 4.74 g (59%) of crude **3** as a light brown oil; ^1H NMR (δ, 60 MHz, CCl_4): 0.23-0.72 (m, 2H), 1.56-1.92 (m, 2H), 3.90 (m, 1H), 4.23 (m, 1H), and 5.94-6.42 (m, 2H). The oil was dissolved in ether (100 mL) and added dropwise with stirring to 3 g (79.1 mmol) of $LiAlH_4$ in 300 mL of ether during 1 h, then refluxed an additional 2 h, cooled, and quenched with water. The ether layer was decanted, washed with 5% KOH solution, followed by water, dried with $MgSO_4$, and concentrated in *vacuo*. The residue was chromatographed on basic alumina with hexane solvent. Fractions containing **4** were combined and distilled (0.1 Torr, 40°C) onto a cold finger, cooled by liquid nitrogen; 2.6125 g (49%) of **4** were obtained as a colourless oil; IR (film): 3050, 3000, 2920, 2845, 1440, 1370, 1305, and 1270 cm.$^{-1}$; ^1H NMR (δ, 200 MHz, $CDCl_3$): -0.08 (m, H-3), 0.04 (m, H-3′), 0.93 (m, H-2), 1.41 (m, H-4), 2.55 (dd, H-7, $J_{1,7}$ = 2.5, $J_{7,7'}$ = 10 Hz), 3.04 (dd, H-7′, $J_{7',1}$ = 2.5, $J_{7',7}$ = 10 Hz), 3.22 (m, H-1), 3.67 (ddd, H-5, $J_{5,4}$ = 3.5, $J_{5,9}$ = 7.5, $J_{5,8}$ = 1 Hz), 5.76 (br t, H-8, $J_{8,9}$ = $J_{8,1}$ = 7.5, $J_{8,5}$ = 1 Hz), and 6.11 (br t, H-9, $J_{9,8}$ = $J_{9,5}$ = 7.5, $J_{9,1}$ = 1 Hz); the above assignments and couplings were confirmed by spin decoupling experiments. Mass spectrum *m/e* (rel. intensity): 138 (26), 92 (32), 91 (100).

6-Thiatricyclo[3.2.2.$0^{2,4}$]non-8-en-7-one (5)

A 4.50 g sample of **3**, prepared as above from 3.5142 g (38.2 mmol) of cycloheptatriene and 7.54 g (65.6 mmol) of thiophosgene, was dissolved in 20 mL of benzene, and diluted with 200 mL of hexane. To this solution 5 mL of pyridine and 2 mL of water were added. The mixture was stirred at rt for 24 h, then filtered through $MgSO_4$. The filtrate was concentrated and the residue, dissolved in 5 mL of benzene, was chromatographed on silica gel with 4% ethylacetate-hexane as solvent. Fractions containing **5** were combined, concentrated, and the residue sublimed (0.1 Torr, 60°C). The sublimate crystallized from hexane to give 2.4386 g (42%) of colourless **5**, mp 64-66°C; IR (KBr): 1680 cm^{-1}, C=O; ^1H NMR (δ, 60 MHz, $CDCl_3$): 0.45-0.85 (m, 2H), 1.17-2.05 (m, 2H), 3.65 (sym. m, 1H), 4.29 (sym. m, 1H), 5.93 (br t, 1H, J = 7.5 Hz), and 6.34 (br t, 1H, J = 7.5 Hz). Mass spectrum *m/e*: 152 (1), 92 (86), 91 (100). *Anal.* Calcd. for C_8H_8OS: C, 63.13; H, 5.30; S, 21.06. Found: C, 63.43; H, 5.38; S, 20.99.

5-Mercaptobicyclo[4.1.0]hept-3-ene-2-methanol (**6**)

Under a nitrogen atmosphere, a solution of 149.4 mg (0.98 mmol) of thiolactone **5** in 15 mL of ether was added dropwise to a stirred slurry of 144.1 mg (3.8 mmol) of $LiAlH_4$ in 15 mL of ether during 10 min. The mixture was refluxed a further 3.5 h, then cooled and quenched with saturated NH_4Cl solution. The ether layer was washed with water, dried with $MgSO_4$, concentrated, and the residue chromatographed on silica gel with 5% methanol-benzene solvent to give 124 mg (81%) of **6** as a viscous, colourless oil; IR (film): 3350 cm^{-1}, OH; 2540 cm^{-1}, SH; ^1H NMR (δ, 400 MHz, $CDCl_3$), note Table 1, and in addition: 3.72 (dd, H-8), 3.81 (dd, H-8′), 2.10 (hump, OH, concentration dependent), and 2.15 (d, SH): the assignments in Table 1 and the following coupling constants were confirmed by spin-decoupling experiments: $J_{1,7} = J_{6,7} = 8.5$ Hz; $J_{1,7'} = J_{6,7'} = J_{7,7'} = J_{2,3} = J_{4,5} = 5$ Hz; $J_{2,8'} = J_{2,8} = 6$ Hz; $J_{3,4} = 10$ Hz; $J_{5,SH} = 7.5$ Hz; and $J_{8,8'} = 11$ Hz.

Poly(6-thiatricyclo[3.2.2.0^{2,4}]non-8-ene) (**8**)

To a stirred, cooled (0°C) solution of 1.7952 g (13.0 mmol) of **4** in 10 mL of dry CH_2Cl_2, 10 μL of boron trifluoride etherate was added. The mixture was stirred at 0°C for 6 h and the reaction was quenched by the addition of 40 mL of methanol. The resulting polymer was filtered off, washed with methanol and purified by two reprecipitation-filtration procedures to give 1.4854 g (83%) of **8**, a white solid, mp 155-157°C, after vacuum drying; ^1H NMR (δ, 400 MHz, $CDCl_3$), note Table 1, and in addition 2.68 (m, H-8), and 2.83 (m, H-8′); the assignments in Table 1 and the following couple constants were confirmed by spin-decoupling (including homonuclear 2D-COSY) experiments: $J_{1,7} = J_{6,7} = 8.5$ Hz; $J_{1,7'} = J_{6,7'} = J_{7,7'} = 5$ Hz; $J_{3,4} = 10$ Hz; $J_{1,2} \simeq J_{2,5} \simeq 0$ Hz; and $J_{2,3} = J_{4,5} = J_{5,6} = 4.0$ Hz. ^{13}C NMR (ppm, 20.15 MHz, $CDCl_3$), note Fig. 1 and : 6.22, 16.04, 16.81, 34.98, 37.71, 41.27, 126.39, and 128.40. *Anal.* Cald. for $[C_8H_{10}S]_n$: S, 23.19. Found: S, 23.47. A value of $\overline{M}_n = 6{,}300$ for **8** was obtained via gel permeation chromatography using a Waters 6000 A HPLC equipped with R.I. and UV detectors: μ Styragel 10^3Å x 10^5Å x 10^6Å columns, run in THF solvent (flow rate 1 mL/min); calibration was against polystyrene standards (Merck).

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