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Cationic Degradation of Poly (cyclohexene sulfide)

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SUMMARY

The polymerization of cyclohexene sulfide initiated by triethyloxonium tetrafluoroborate is quantitative in a few minutes (at 0°C) but is followed by a complete degradation of the polymer to cyclic tetramer and an equimolar mixture of a 1,2,5-trithiepane derivative and cyclohexene. Also poly(cyclohexene sulfide), obtained by coordinative polymerization, degrades to the same compounds when it is treated with a trace of triethyloxonium tetrafluoroborate. The active species for the polymerization as well as for the degradation is believed to be the thiiranium ion. A revised mechanism for the trithiepane formation is proposed.

INTRODUCTION

The cationic polymerization of thiiranes is known to be accompanied by a degradation of the polymers leading to a mixture of low molecular weight compounds (VAN OOTEGHEM, GOETHALS, 1974; VAN CRAEYNEST, GOETHALS, 1976; SIMONDS et al. 1978). The same degradation occurs when a poly-thiirane, obtained by other mechanisms than cationic polymerization, is treated with a strong alkylating agent (SIMONDS, GOETHALS, 1978; GOETHALS et al. 1980). In the present paper these phenomena are described for the case of cyclohexene sulfide.

RESULTS AND DISCUSSION

The polymerization of cyclohexene sulfide initiated by triethyloxonium tetrafluoroborate in methylene chloride at 0°C is quantitative in a few minutes. It is followed by a degradation of the polymer (at room temperature), which ultimately leads to a mixture of low molecular weight compounds. This is shown in Fig. 1 where the GPC analysis of the reaction mixtures obtained after different reaction times, are compared.

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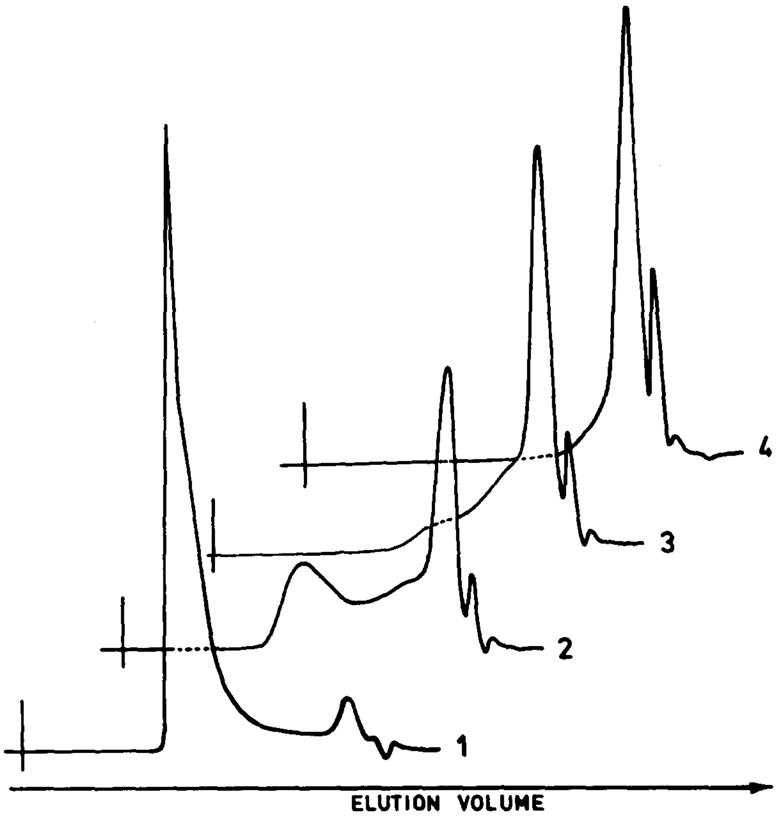


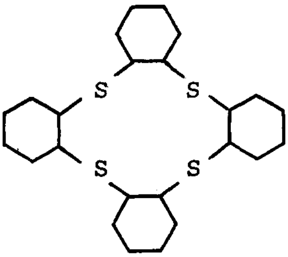
FIG. 1. Gel permeation chromatography analysis of a polymerization-degradation mixture. Monomer conc.: 1.0 mol.l^{-1}, triethyloxonium tetrafluoroborate concn.: 0.01 mol.l^{-1}, solvent: methylene chloride.

1 : after 5 mins at 0°C;
2 : after 20 mins at 25°C;
3 : after 50 mins at 25°C;
4 : after 3 hrs at 25°C.

Analysis performed on a 60 cm column, 10^3 Å (Polymer Laboratories), Eluent THF, UV-detection at 254 nm

Poly(cyclohexene sulfide) obtained by coordinative polymerization (initiator diethylzinc/alcohol) is a stable compound which does not show any tendency to degradation at ambient temperature. When a solution of this polymer is treated with a trace amount of triethyloxonium tetrafluoroborate, a degradation takes place which leads to a reaction mixture which as judged by GPC analysis, is similar to the mixture obtained via cationic polymerization-degradation.

Based on the elution volumes and in analogy with the degradation of poly(cis-2,3-dimethylthiirane) (VAN CRAEYNEST, GOETHALS, 1976) the degradation products were expected to be the cyclic tetramer (1) (accompanied with small amounts of cyclic pentamer) and an equimolar mixture of the trithiepane derivative (2) (2,3,10-trithiatricyclo[7,4,0,$0^{4,9}$]pentadecane) and cyclohexene (3).



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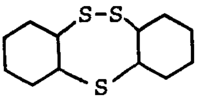

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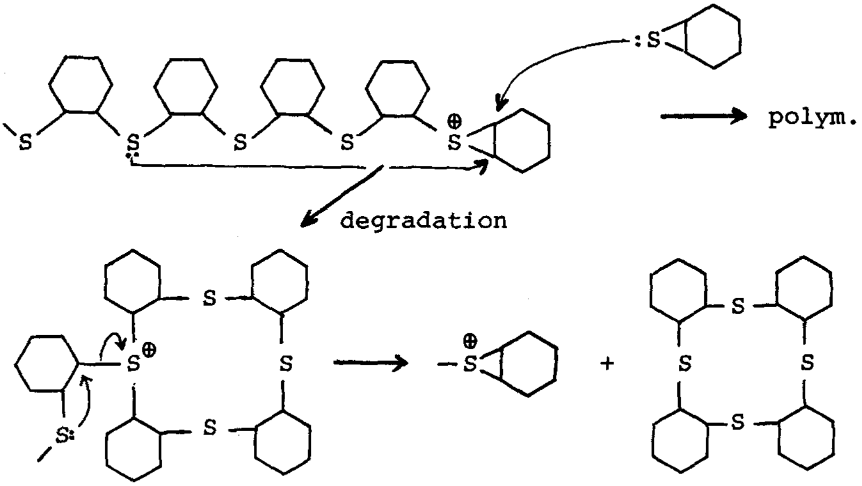
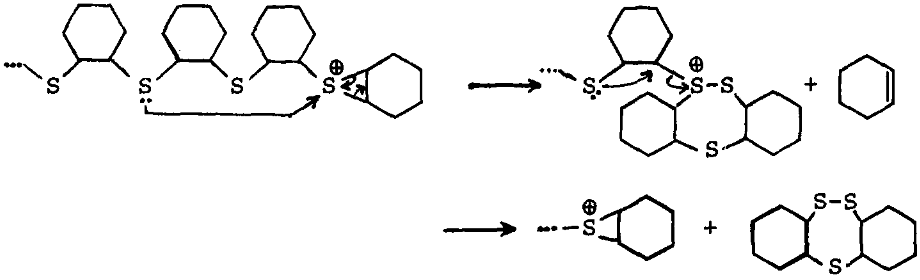
Analysis of the degraded reaction mixture by means of gas chromatography coupled with a mass spectrometer allowed to detect the cyclohexene and the trithiepane. The cyclic tetramer could not be detected by gas chromatography, because its volatility is too low. It was isolated by preparative GPC. Its structure was confirmed by sulfur analysis, ^{1}H-NMR spectroscopy and chemical ionisation mass-spectroscopy using helium as reactant gas.

The mechanism of formation for these products can be described as follows : The active species for the cationic polymerization as well as for the degradation is believed to be the thiiranium ion. It is known that thiiranium ions are intermediates in reactions of sulfides which have a good leaving group in β-position (RICHTER et al. 1972; FUSON, KOEHNEKE, 1949). Such thiiranium ions are strong electrophilic reagents which are known to react with nucleophiles in at least two ways (SCHMID, 1977): (1) the nucleophile can attack on the α-carbon atom of the thiiranium ring leading to the ring-opened product or, (2) the nucleophile can attack directly on the positive sulfur atom leading to a sulfur-nucleophile bond and an alkene (OWSLEY et al. 1969). The first reaction path is responsable for the propagation reaction and for the formation of the cyclic oligomers (tetramer and pentamer). The latter occurs via a back-biting reaction followed by regeneration of the thiiranium ion :



By the second reaction path the thiiranium ion is attacked at its sulfur atom forming a surfur-sulfur bond and cyclohexene. Subsequent intramolecular attack of the neighboring sulfur atom on the α-carbon of the sulfonium function gives the trithiepane and regenerates the active species :



In our earlier publications (VAN OOTEGHEM, GOETHALS, 1974; VAN CRAEYNEST, GOETHALS, 1976; SIMONDS et al. 1978; SIMONDS, GOETHALS, 1978; GOETHALS et al., 1980) the formation of a trithiepane and an alkene from a poly-thiirane was depicted as one concerted mechanism starting from a sulfonium ion. The mechanism proposed in the present paper differs from the previous one by the fact that the thiiranium ion is now regarded as a key intermediate which is more in accordance with the known episulfonium chemistry (SCHMID, 1977). This mechanism, which was already described earlier by one of us (NUYTTEN, 1980), is believed to be valid for all cationic degradations of poly-thiiranes to trithiepanes. In this way all processes occurring during the cationic polymerization-degradation of thiiranes proceed with the same active species: the thiiranium ion.

EXPERIMENTAL

Cyclohexene sulfide was synthesized from cyclohexene oxide and thioureum as described (SEARLES et al. 1962). It was distilled from calcium hydride before use. b.p.: 71-72 at 20 Tor. Polymerization-degradations were carried out in methylene chloride under an atmosphere of dry nitrogen. Typical reaction conditions are: monomer concentration 1 mol/l (1.14 g/10 ml), triethyloxonium concentration: 0.01 mol/l, temp. 0°C. After 5 min the mixture was allowed to warm up to 25°C. Poly(cyclohexene sulfide obtained by coordinative polymerization of cyclohexene sulfide with the system diethylzinc/tert.butyl glycol was kindly supplied by Dr. Spassky of the University of Paris. The degradation of this polymer was carried out at 25°C using the same concentrations as for the polymerization.

The degradation products were analyzed by chemical ionization mass spectrometry using helium as the reactant gas. The mass spectrum of the trithiepane contained the following m/z peaks (%): 260 (M^+) (0.2), 227 (0.1), 195 (0.3), 178 (1.3), 144 (1.0), 81 (100), 79 (28), 67 (28), 55 (13), 54 (21), 53 (28), 45 (35), 41 (60).

The mass spectrum of the cyclic tetramer contained the following peaks m/z, (%): 456 (M^+)(1.5), 342 (0.5), 261 (3), 229 (8), 147 (7), 145 (6), 115 (24), 113 (17), 81 (100), 79 (18).

Sulfur analysis of the cyclic tetramer: 28,3% (calcd.: 28.07%).

Cyclohexene was identified by MS and by NMR.

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