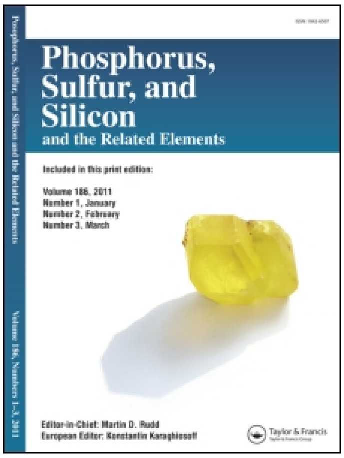

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POLYMERIZATION, DEPOLYMERIZATION AND DESULPHURIZATION OF A 1,2,3-TRITHIOLAN

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POLYMERIZATION, DEPOLYMERIZATION AND DESULPHURIZATION OF A 1,2,3-TRITHIOLAN

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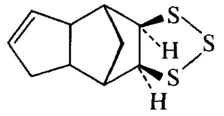
The 1,2,3-trithiolan of *endo*-dicyclopentadiene, $C_{10}H_{12}S_3$ (1) can be polymerized to give low molecular weight polymers $(C_{10}H_{12}S_3)_n$, n = 3–6, by heating or by exposure to UV irradiation. The polymers differ according to the method of polymerization as revealed by their n.m.r. spectra. Depolymerization of both types of polymer can be achieved by heating with amines, and especially with R_3N. Desulphurization of (1) by Na_2SO_3 or triphenylphosphine produces a polymer of composition $(C_{10}H_{12}S_2)_n$, n = *ca* 18–19. The depolymerization of this material by Et_3N regenerated some (1).

1,2,3-trithiolans were first reported in a patent[1] but since their discovery only a few have been made, namely the trithiolans of norbornene,[2,3] $C_7H_{10}S_3$, *endo*- and *exo*-dicyclopentadiene,[4] $C_{10}H_{12}S_3$, and tricyclopentadiene,[4] $C_{15}H_{18}S_3$. The easiest trithiolan to prepare is that of *endo*-dicyclopentadiene.[4] This can be obtained by heating together sulphur and the olefin at 100°C in the presence of triethylamine and 2,5-*bis*(octyldithio)1,3,4-thiadiazole which acts as a sulphur "activator." The compound has structure (1) with the trithiolan ring *exo* orientated, this configuration being proved in the case of $C_{15}H_{18}S_3$ by X-ray crystallography.[5]


(1)

In previous publications we have reported on the synthesis, i.r. and ^1H and ^{13}C n.m.r. spectra of the trithiolans,[4] and on their complexing ability towards palladium and platinum.[6]

The trithiolans are stable compounds, unaffected by boiling water, dilute acids and alkalis. On heating they behave rather like elemental sulphur, first melting to a pale yellow mobile liquid which darkens and becomes very viscous as the temperature rises above 170°C. The resulting polymer is not like plastic sulphur, however, but is a brittle solid which is stable at room temperature whereas plastic sulphur slowly reverts to S_8.[7]

In this communication we report on the polymerization and depolymerization of (1) and on its desulphurization which also leads to a polymer.

RESULTS AND DISCUSSION

The thermal and photo-induced polymerization of S_8 is well documented.[8] The reaction proceeds via sulphenyl diradicals and eventually leads to molecular weights of the order of 10^6. Other cyclic polysulphide compounds also polymerize readily; tetrafluoro-1,2,3-trithiolan, $CF_2CF_2S_3$ polymerizes at room temperature.[9,10] Cyclic disulphides are more stable, but catalysts will cause polymerization at room temperature, via S—S bond opening, to form linear polymers.[11] For instance, 1-oxa-4,5-dithiacycloheptane polymerizes in the presence of sodium polysulphide solutions[12] and 1,2-dithiolane will polymerize at its m.t. (30°C) or on exposure to light.[13,14] The corresponding six- and seven-membered rings, 1,2-dithiane and 1,2-dithiepane, were much less susceptible to polymerization by these means.[14] However ring size is not the principal factor since $C_{10}H_{12}S_3$ requires higher temperatures than S_8 to effect polymerization.

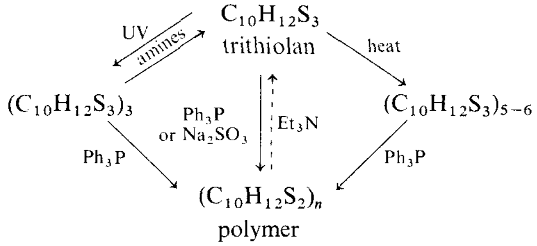
Our results indicate that the mechanism for polymerization of $C_{10}H_{12}S_3$ by heating differs from that using UV irradiation. The geminal protons of the 1,2,3-trithiolan ring are *endo* orientated with respect to the norbornyl moiety and have a very characteristic signal—a doublet at 3.69 p.p.m. – in the ^1H n.m.r. spectrum. In the thermally produced polymer this signal remains unchanged and it seems reasonable to infer from this that in the polymer these hydrogens are still *endo* orientated. This was to be expected, since it has been shown that only the central sulphur atom of trisulphides is thermally labile and that the C—S bonds remain fixed.[15] The polymer itself is of low molecular weight and may even be macrocyclic.

In the polymer produced photochemically, the geminal proton signals at 3.69 p.p.m. are absent. The inference is that UV irradiation causes C—S scission in addition to S—S scission, and again this is to be expected from other experimental evidence such as the production of Bu^tCl from an irradiated solution of $Bu^t_2S_2$ in CCl_4.[16] If C—S bonds are cleaved, then in the low molecular weight polymer which is formed there may be a mixture of *endo*- and *exo*-oriented geminal hydrogens on the same norbornyl fragment, and the characteristic spectral doublet will be lost.

Depolymerization of the photo-polymer, however, results in reconversion to the original *exo*-orientated trithiolan as shown by the reappearance of the doublet at 3.69 p.p.m. in the spectrum. The depolymerization is promoted by amines, being rapid in triethylamine, fast in the corresponding secondary amine, di-isopropylamine, but slow in the primary amine, $C_6H_{13}NH_2$. To achieve 50% depolymerization required 10, 60 and 1200 minutes respectively at room temperature.

In the polymerized trithiolan the polysulphide links may be S_2, S_3 or S_4 if only S—S cleavage is possible, as in the thermal polymerization, but may be longer or shorter if C—S cleavage is possible. In the thermal polymerization some polysulphide rearrangement back to S_3 chains is likely since trisulphide links are thermodynamically more stable than tetra-sulphide ones.[17] Even longer sulphur chains may form as demonstrated by the heating of $(C_6H_{11})_2S_4$ at 140–150°C which produced some $(C_6H_{11})_2S_6$,[18] and the heating of $(ClCH_2)_2S_3$ at 145–160°C which gave some S_8.[19]

The reactions reported in this paper are summarized in Scheme 1. The desulphurization of polysulphides by Ph_3P or Na_2SO_3 removes only the sulphur atoms which are themselves attached solely to other sulphur atoms. Thus desulphurization of $C_{10}H_{12}S_3$ removes only the central sulphur atom. The fragment remaining does not re-cyclize to form a dithietan but polymerizes to give a polymer with 18–19 units per average chain.



Scheme 1

This material is capable of regenerating some trithiolan when exposed to amine, something that should not be possible if the polymer chain has only disulphide links unless C—S fission is permitted. This is further evidence that amine induced depolymerization does indeed proceed via C—S bond breaking.

Desulphurization of the thermal- and photo-polymers by Ph_3P produced material whose i.r. and ^1H n.m.r. spectra are identical to those of the disulphide polymer.

It has recently been shown that depolymerization of plastic sulphur can be prevented by incorporating carbon atoms along the chain, e.g. by copolymerising, 1,2-propylene disulphide and S_8 a high polymer of nearly 90% sulphur content could be stabilized (mol. wt. 50,000).[20] We tried the thermal copolymerization of $C_{10}H_{12}S_3$ and S_8 and obtained a homogeneous polymeric material by heating mixtures of the two at 180°C in ratios up to 1:20 trithiolan:S_8. At higher proportions of S_8 two phases formed on cooling.

EXPERIMENTAL

Instruments N.m.r. spectra were run on samples in $CDCl_3$ with Perkin-Elmer R12B (60 MHz) spectrometer. I.r. spectra were measured with a Perkin-Elmer 457 spectrometer (CsBr optics) for nujol and hexachlorobutadiene mulls. Molecular weights were determined on samples dissolved in $CHCl_3$ using an Hitachi-Perkin-Elmer (Model 115) molecular weight apparatus calibrated with benzil.

Materials $C_{10}H_{12}S_3$ (1) was prepared from *endo*-dicyclopentadiene as previously described.[4]

Thermal Polymerization of (*1*) A typical reaction is as follows: $C_{10}H_{12}S_3$ (1) (0.094 g, 0.4 mmol) is heated at 180°C for 1 h, then cooled to room temperature. The dark-brown glassy polymer mixture was treated with $CHCl_3$ in which it all dissolved and the polymerized trithiolan (0.031 g, 0.14 mmol, 33% yield) deposited by the addition of CH_3OH. The unpolymerized starting material remains soluble in CH_3Cl_3-CH_3OH. The polymer is soluble also in CS_2 and C_6H_6. M.t. 210°C (decomp.). Found: C, 52.54; H, 5.30; S, 42.00%. Calculated for $C_{10}H_{12}S_3$: C, 52.63; H, 5.26; S, 42.11%. Mol. wt., 1120 ± 40 corresponding to $(C_{10}H_{12}S_3)_{5-7}$. The ^1H n.m.r. spectrum has δ 5.68 (2 H; multiplet; olefinic CH), 3.69 (2 H; doublet; CHS) and 1.1–2.8 (8 H; complex region; CH_2, bridge CH_2 and bridgehead CH). The spectrum is almost identical to that of (1).[4] The percentage conversion of (1) to polymer depends on the temperature as shown in Table 1.

TABLE I

Thermal polymerization of $C_{10}H_{12}S_3$

Temperature	Time	Polymer formation
°C	min.	%
175	10	12
	30	18
	60	33
185	5	26
	30	48
	60	81
195	5	92
	30	96
	60	97
	90	99

UV Polymerization of (1) A typical reaction is as follows: $C_{10}H_{12}S_3$ (1) (0.20 g, 0.90 mmol) in petroleum spirit (b.t. 40–60°C, 10 ccm) was irradiated for 10 h with a Philips 300 w broad spectrum UV lamp. A white precipitate formed which was filtered and dried. The polymer is soluble in $CHCl_3$, C_6H_6 and CS_2. M.t., 125°C (decomp.). Found: C, 51.71; H, 5.25; S, 41.16%. Mol. wt., 650 ± 20 corresponding to $(C_{10}H_{12}S_3)_3$. The ^1H n.m.r. spectrum of the polymer differs from that of the monomer and the thermal polymer by the absence of the sharp doublet at 3.69 p.p.m.

Desulphurization–Polymerization of (1) (i) Na_2SO_3: a solution of $C_{10}H_{12}S_3$ (0.8 g, 3.5 mol) in acetone (25 ccm) was added to a solution of Na_2SO_3 (0.45 g, 3.5 mol) in water (25 ccm). A dense white precipitate immediately formed and was filtered and dried (0.72 g). M.t., 130°C (decomp.). Found: C, 62.5; H, 6.26; S, 33.0%. Calculated for $C_{10}H_{12}S_2$: C, 61.2; H, 6.12; S, 32.7%. Mol. wt., 3609 ± 100 corresponding to $(C_{10}H_{12}S_2)_{18-19}$. (ii) Ph_3P: a solution of $C_{10}H_{12}S_3$ (2.28 g, 0.01 mol) in benzene (30 ccm) was mixed with a solution of Ph_3P (2.62 g, 10 mmol) in benzene (30 ccm) and heated under reflux for 15 min. The solvent was removed to yield a yellow oil that was extracted with hot ethanol to remove Ph_3PS (2.2 g, 7.4 mmol, 74% recovery). Extraction of the residue with $CHCl_3$ gave, on removal of the solvent, an amorphous white solid identical to that above as shown by its i.r. and ^1H n.m.r. spectra and its mol. wt. Found: C, 62.0; H, 6.21; S, 32.7%.

Desulphurization of the Thermal Polymer The thermal polymer, $(C_{10}H_{12}S_3)_{5-6}$ (0.5 g) and Ph_3P (0.5 g) were mixed in $CHCl_3$ (5 ccm) and heated under reflux for 1.5 h. Removal of the solvent, extraction of the Ph_3PS with ethanol, and extraction of the residue with $CHCl_3$ gave an amorphous solid with the same i.r. and ^1H n.m.r. spectra as $(C_{10}H_{12}S_2)_n$ obtained from (1). Desulphurization of the photo-polymer gave the same product.

Depolymerization of $(C_{10}H_{12}S_3)_n$ It was possible to follow the depolymerization of the photopolymer by ^1H n.m.r. spectroscopy by observing the reappearance of the doublet at 3.69 p.p.m. which characterizes (1), and the amount of this was estimated by comparing its integral with that of the olefinic protons at δ 5.6 p.p.m. Samples (20 mg) of the photopolymer in $CDCl_3$ (0.5 ccm) were treated with 0.1 ccm samples of n-hexylamine, di-isopropylamine or triethylamine. The results are given in Table 2.

TABLE II

Depolymerization of photopolymer $(C_{10}H_{12}S_3)_n$ at room temperature

Catalyst	Time min.	Degree of depolymerization %
n-hexylamine	120	19
	375	32
	3000	68
	7000	80
di-isopropylamine	2	7
	35	41
	60	50
	130	75
	450	97
triethylamine	5	47
	35	61
	65	70
	300	96

Depolymerization of $(C_{10}H_{12}S_2)_n$ To a solution of the disulphide polymer (20 mg) in $CDCl_3$ (0.5 ccm) was added 0.1 ccm triethylamine and the reaction followed by re-emergence of the doublet of (1) at 3.69 p.p.m. This increased in intensity to a maximum after 48 h, remaining constant thereafter, and corresponding to 50% depolymerization to (1). The remaining material of composition $C_{10}H_{12}S$ was not investigated.

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