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Backbone-Assisted Reactions of Polymers

4. Preparation and Structural Rearrangement of Poly(3-Chlorothietane)

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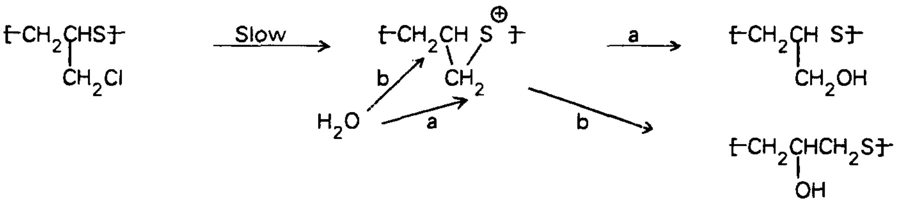
SUMMARY

The homopolymerization of 3-chlorothietane was accomplished using a variety of cationic initiators. Most successful was bulk polymerization at 0°C with ethyl trifluoromethanesulfonate as initiator and with rapid stirring of the polymerizing mixture. Poly(3-chlorothietane) undergoes a facile structural rearrangement at 35°C in CD_2Cl_2, giving at equilibrium a copolymer containing 3-chlorothietane and (chloromethyl)thiirane repeating units in a ratio of approximately 6 to 4.

INTRODUCTION

Recent studies of the synthesis and chemistry of poly[(chloromethyl)thiirane] have provided the first examples of polymer modification reactions which are subject to intramolecular catalysis by a functional group located in the polymer chain backbone (ZUSSMAN AND TIRRELL, 1981). For example, the initial rate of hydrolysis of poly[(chloromethyl)thiirane] in a 9:1 dioxane:water mixture was found to be much greater than that of the polyether analogue poly(epichlorohydrin). This suggests anchimeric assistance of the hydrolysis by the backbone sulfur atom (Scheme I), in a mechanism analogous to the known mechanism of solvolysis of β-chloroethyl sulfides of low molecular weight (BARTLETT AND SWAIN, 1949).

Scheme I



A more striking demonstration of the importance of the backbone sulfur atom in poly[(chloromethyl)thiirane] was the observation that the polymer undergoes a structural rearrangement on standing at room temperature in the absence of solvent. On the basis of the observed changes in the ^1H and ^{13}C nuclear magnetic resonance spectra, we suggested that the rearrangement should proceed via a mechanism similar to that in Scheme I: nucleophilic attack of the backbone sulfur atom on the pendant chloromethyl group, followed by return of chloride to either of the thiiranium ring carbons, giving a copolymer of (chloromethyl)thiirane and 3-chlorothietane repeating units (Scheme II).

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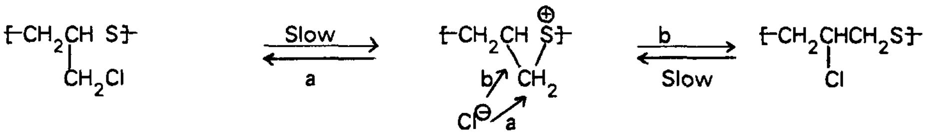
Scheme II



In this paper, we report the direct preparation of poly(3-chlorothietane) by polymerization of 3-chlorothietane monomer. We confirm that the rearrangement of poly[(chloromethyl)thiirane] does indeed produce 3-chlorothietane repeating units, and we show that virtually identical products may be obtained by rearrangement either of poly[(chloromethyl)thiirane] or of poly(3-chlorothietane).

EXPERIMENTAL

3-Chlorothietane. 3-Chlorothietane was prepared from epichlorohydrin in two steps. Thietan-3-ol was synthesized by treatment of epichlorohydrin (Aldrich 99+%, as received) with alkaline aqueous H_2S, according to the procedure of LAMM AND GUSTAFSON (1974). Thietan-3-ol (19.4g, 0.22 mol) and N,N-dimethylaniline (1 ml, dist. from CaH_2) dissolved in 200 ml benzene (dist. from P_2O_5), were added over 3 hr to a solution of $SOCl_2$ (22 ml, 0.30 mol, dist. from cottonseed oil) in 200 ml dry benzene at 0°C. The evolved HCl was flushed out of the reactor with a stream of N_2 as the reaction mixture was stirred for an additional 2 hr at room temperature. The benzene and $SOCl_2$ were distilled off at 30 mm Hg, and the remaining volatiles were transferred under high vacuum to a chilled receiver. Distillation of this fraction gave 10 g (42%) of 3-chlorothietane (bp 43°C/15 mm Hg (lit. bp 41°C/16 mm Hg, CHRISTY (1961))). 3-Chlorothietane was redistilled from CaH_2 prior to use.

Initiators. Boron trifluoride etherate (BF_3OEt_2, Aldrich) and ethyl trifluoromethanesulfonate (ethyl triflate, Fluka AG, purum) were distilled under N_2 before use. Trifluoromethanesulfonic anhydride (triflic anhydride, Aldrich) was distilled from P_2O_5 under N_2 (bp 83-83.5°C). Trifluoromethanesulfonic acid (triflic acid, Aldrich) and sulfuric acid (J. T. Baker, reagent) were used as received. $CdCO_3$ (Alfa-Ventron, ultrapure) was flamed under vacuum prior to use.

Polymerization of 3-Chlorothietane. 3-Chlorothietane was added to dry pyrex vials containing teflon coated magnetic stir bars. Polymerization vessels were then evacuated and purged with nitrogen repeatedly. Initiators were added portionwise via syringe to ice cold monomer with intermittent mixing on a vortex mixer. Reaction mixtures were then stirred at -10 to 0°C; polymerizations at long times (>12 hr) were allowed to proceed at room temperature. Polymerizations were quenched by precipitating the contents of the reaction vessel (assisted by some CH_2Cl_2) into MeOH followed by removal of solvent under vacuum. Poly(3-chlorothietane) was found to be soluble in CH_2Cl_2, THF and dioxane, but only slightly soluble in $CHCl_3$.

Rearrangement of Poly(3-chlorothietane). Poly(3-chlorothietane) (0.05 g, sample 1, Table) was dissolved in 0.5 ml CD_2Cl_2 (Stohler isotope chemicals, 99.5%D) and transferred to an NMR tube. After degassing, the tube was sealed and placed in a constant temperature bath at 35°C. 60 MHz NMR spectra were recorded intermittently. The extent of rearrangement was determined by integration (cut-and-weigh method) of the chloromethine (δ 4.0-4.5) (area A), chloromethyl (δ 3.75-4.0) (B), and thiomethylene, thiomethine (δ 2.8-3.75) (C) signals. The fraction of 3-chlorothietane units was calculated as $A/(A+B/2)$, or as $2 - [5(A+B)/C]/[1+(A+B)/C)]$; the reported value is the average of these results.

Measurements. Infrared spectra were recorded as films on NaCl, using a Perkin-Elmer 580 infrared spectrophotometer. ^1H NMR spectra were obtained at 60 MHz on a Hitachi Perkin-Elmer R24B spectrometer; chemical shifts are reported in parts per million from tetramethylsilane.

RESULTS AND DISCUSSION

Preparation of Poly(3-chlorothietane). The Table summarizes the results of our experiments concerning the preparation of poly(3-chlorothietane). Our initial experiments (not shown in the Table) were run in sealed tubes, with initiation at low temperature (-40°C) followed by warming to room temperature -- conditions which we had found most useful for polymerization of (chloromethyl)thiirane (ZUSSMAN AND TIRRELL, 1981). Polymerization of 3-chlorothietane under these conditions, however, gave insoluble polymers, with H_2SO_4, triflic acid or triflic anhydride as initiator.

Far more successful was polymerization at 0°C under N_2, with vigorous agitation of the reaction mixture during initiation and constant stirring of the polymerizing mixture. In particular, treatment of 3-chlorothietane with 5 mol-% of ethyl triflate in bulk at 0°C afforded a 37% yield of soluble poly(3-chlorothietane) of inherent viscosity 0.18 dl/g.

TABLE

Polymerization of 3-Chlorothietane

Sample	Initiator	Initiator Conc.(mol%)	Time (hr)	Temperature (°C)	Yield(%)	η_{inh}[a] (dl/g)
1	$EtOSO_2CF_3$	5	3.5	0	58[b]	0.08
2	$EtOSO_2CF_3$	5	8.5	0	37[b,c]	0.18
3[e]	$EtOSO_2CF_3$	5	22	0→R.T.[f]	21[d]	0.07
4	$EtOSO_2CF_3$	3	8.5	0	35[b]	0.07
5	$EtOSO_2CF_3$	1	11	0	13[b]	0.09
6	$EtOSO_2CF_3$	1	26	0→R.T.	22[d]	0.06
7	BF_3OEt_2	5	24	0→R.T.	8	0.10
8	BF_3OEt_2	5	24	0	8	
9	$(CF_3SO_2)_2O$	5	24	-10	Gel	--
10	$CdCO_3$	5	9 days	R.T.	24	0.04

[a] CH_2Cl_2, 25°C
[b] After two precipitations from CH_2Cl_2 into CH_3OH
[c] Some CH_2Cl_2-insoluble material also formed
[d] After one precipitation from CH_2Cl_2 into CH_3OH
[e] 20% monomer in CH_2Cl_2; all others in bulk
[f] Held at 0°C for 8 hr, then warmed to R.T.

Effective mixing of monomer and initiator seems to be essential to the formation of soluble products; we assume that polymers formed at low conversion in unstirred systems are subject to high local concentrations of initiator and are crosslinked as a result of cationation at the backbone sulfur atom followed by attack on the sulfonium ion by a second polymer chain. A similar mechanism has been advanced as the cause of gel formation in the dimethylsulfate-initiated polymerization of thietane (PRICE AND BLAIR, 1967). The trialkylsulfonium ions formed in this step would be expected to be quite stable (GOETHALS AND DRIJVERS, 1973). A second possibility is that crosslinking occurs via intermolecular attack of a backbone sulfur atom on the secondary carbon-chlorine bond, with formation of a sulfonium chloride branch point. Such a process would not be directly sensitive to the local initiator concentration, but would be expected to increase in importance if the local polymer concentration were high.

Experiments 1-9 in the Table all concern the cationic polymerization of 3-chlorothietane. We also examined the use of cadmium carbonate as an initiator of coordinate polymerization of this monomer (experiment 10, Table). Treatment of 3-chlorothietane with 5 mol-% of $CdCO_3$ at room temperature afforded a 24% yield of poly(3-chlorothietane) of low inherent viscosity (0.04 dl/g). Thus coordinate polymerization appears less useful than the cationic route. The use of anionic initiators for the polymerization of 3-chlorothietane was not investigated, due to the known tendency of the monomer to undergo attack at the ring sulfur atom in the presence of thiolate nucleophiles (MARITA AND OAE, 1977).

Structural Rearrangement of Poly(3-chlorothietane). An important objective of this work was the confirmation that the spectral changes observed upon rearrangement of poly[(chloromethyl)thiirane] could indeed be ascribed to the formation of 3-chlorothietane repeating units. Figure 1 provides such confirmation. The ^1H NMR spectrum of poly(3-chlorothietane) consists of a 4-proton doublet at 3.18 ppm and a 1-proton quintet at 4.25 ppm; these are precisely the signals which "grow into" the spectrum of poly[(chloromethyl)thiirane] in the course of the structural rearrangement (ZUSSMAN AND TIRRELL, 1981).

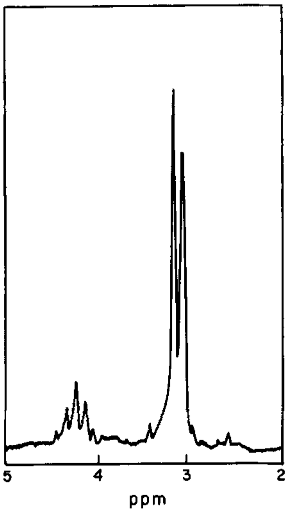


Figure 1. 60 MHz ^1H NMR spectrum of freshly-prepared poly(3-chlorothietane) in CD_2Cl_2.

A second objective of this work was the determination of the reversibility of the structural rearrangement shown in Scheme II. We have observed that the rearrangement of poly[(chloromethyl)thiirane] becomes very slow beyond ca. 50% isomerization, and it is interesting to determine the origin (kinetic or thermodynamic) of this effect. Figure 2 shows ^1H NMR spectra of the rearrangement products obtained at and from poly(3-chlorothietane) (Figure 2b). The spectra are virtually identical, suggesting that each represents a true equilibrium copolymer structure. Integration of each spectrum suggests that the equilibrium copolymer contains 58 ± 4% of 3-chlorothietane repeating units. The free energies of the isomeric repeating units are thus very similar. We have not calculated the free energy difference from these data, since they were obtained in different solvents. A more complete analysis of the kinetics and thermodynamics of this reaction will be published in due course.

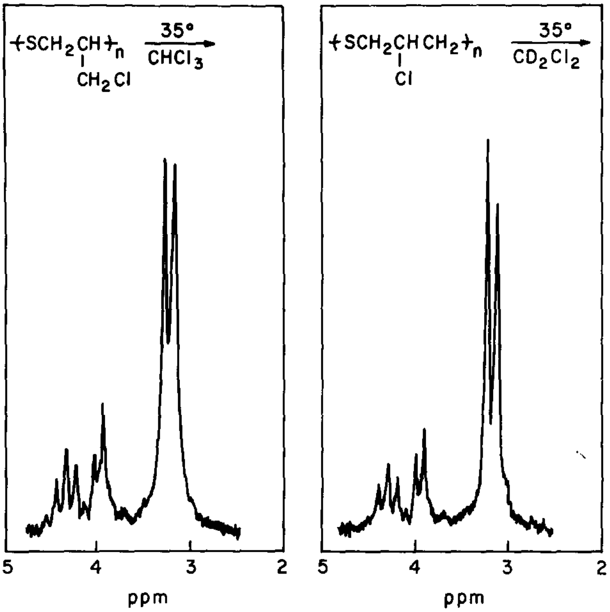


Figure 2a. (left) 60 MHz ^1H NMR spectrum of the product of rearrangement of poly[(chloromethyl)thiirane]; (35°C, $CHCl_3$, 105 days). **Figure 2b.** (right) 60 MHz ^1H NMR spectrum of the product of rearrangement of poly(3-chlorothietane); (35°C, CD_2Cl_2, 64 days).

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