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 CD2Cl2, 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 13C 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 thiranium ring carbons, giving a copolymer of (chloromethyl)thiirane and 3-chlorothietane repeating units (Scheme III).
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 \( \text{H}_2\text{S} \) according to the procedure of LAMM AND GUSTAFSON (1974). Thietan-3-ol (19.4 g, 0.22 mol) and \( \text{N,N-dimethylaniline} \) (1 ml, dist. from \( \text{CaH}_2 \)) dissolved in 200 ml \( \text{benzene} \) (dist. from \( \text{P}_2\text{O}_5 \)), were added over 3 hr to a solution of \( \text{SOCl}_2 \) (22 ml, 0.30 mol, dist. from cottonseed oil) in 200 ml dry benzene at \( 0^\circ\text{C} \). The evolved HCl was flushed out of the reactor with a stream of \( \text{N}_2 \) as the reaction mixture was stirred for an additional 2 hr at room temperature. The benzene and \( \text{SOCl}_2 \) 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 \( \text{CaH}_2 \) prior to use.

Initiators. Boron trifluoride etherate (BF\(_3\)OEt\(_2\), Aldrich) and ethyl trifluoromethanesulfonate (ethyl triflate, Fluka AG, purum) were distilled under \( \text{N}_2 \) before use. Trifluoromethanesulfonic anhydride (triflic anhydride, Aldrich) was distilled from \( \text{P}_2\text{O}_5 \) under \( \text{N}_2 \) (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 \(0^\circ\text{C}\); 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\(_2\)Cl\(_2\)) into MeOH followed by removal of solvent under vacuum. Poly(3-chlorothietane) was found to be soluble in CH\(_2\)Cl\(_2\), 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\(_2\)Cl\(_2\) (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 (\( \delta \) 4.0–4.5) (area A), chloromethyl (\( \delta \) 3.75–4.0) (B), and thiomethylene, thiomethine (\( \delta \) 2.8–3.75) (C) signals. The fraction of 3-chlorothietane units was calculated as \( A/(A+B)/2 \), or as \( 2-\left[5(A+B)/C\right]/\left[1+(A+B)/C\right] \); the reported value is the average of these results.