Backbone-Assisted Reactions of Polymers. 2. Poly[(chloromethyl)thiirane]

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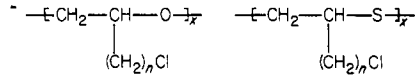
ABSTRACT: The conversion of (chloromethyl)thiirane to poly[(chloromethyl)thiirane] of molecular weight ca. 20 000 was accomplished by using boron trifluoride etherate as initiator. Initiators based on cadmium, zinc, or aluminum were less effective, and the anionic initiators KOH and $NaNH_2$ produced no polymer. Poly[(chloromethyl)thiirane] was found to undergo an unusual structural rearrangement at room temperature in the absence of solvent and to hydrolyze in a dioxane/water mixture at a rate much greater than that observed for poly(epichlorohydrin). These results suggest important anchimeric assistance by the backbone sulfur atom in the reactions of poly[(chloromethyl)thiirane].

The concept of "backbone-assisted" reactions of polymers was introduced in a recent preliminary communication from this laboratory.[1] This is the idea that functional groups or atoms which are part of the polymer chain backbone can participate in a reaction at a neighboring site, resulting in significant and potentially useful rate enhancement. It was suggested that the chloroalkyl-substituted polyethers (I) and polysulfides (II) might serve as model systems for an investigation of this effect.

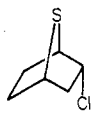


I, n = 1-5 II, n = 1-5

Polymers I and II were selected as model systems because of the striking neighboring group effects observed in the solvolyses of substituted alkyl sulfides of low molecular weight. The high reactivity of the β-chloroethyl sulfides ("sulfur mustards") is due to anchimeric assistance by sulfur; solvolysis proceeds through a rate-determining cyclization followed by a rapid ring-opening by attacking nucleophile (Scheme I). The magnitude of this effect is illustrated by the data of Bohme and Sell in Table I.[2]

A β-sulfur atom accelerates the solvolysis nearly 3000-fold compared to the simple chloroalkane and approximately 15 000-fold compared to the β-chloroethyl ether. The effect disappears when the heteroatom is γ to Cl, as this would require the formation of an intermediate four-membered cyclic sulfonium ion—a very slow process.

In conformationally restricted systems, the effect of a β-sulfur atom can be even more striking: Tabushi and co-workers found the acetolysis of *endo*-2-chloro-7-thiabicyclo[2.2.1]heptane (III) to be at least 4.7×10^9 times



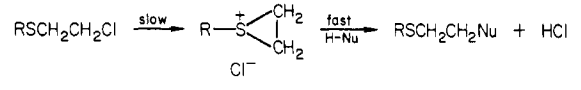
III

as rapid as that of the exo isomer.[3] Formation of the intermediate sulfonium ion from the exo isomer requires an unfavorable front-side attack of sulfur on the C_2–Cl bond.

Extension of the mechanism shown in Scheme I to the solvolysis of chloroalkyl-substituted polysulfides suggests that poly[(chloromethyl)thiirane] (PCMT) should exhibit enhanced reactivity as compared to poly(epichlorohydrin) (PECH), its polyether analogue (Scheme II).

In addition to its possible practical consequences, this mechanism provides three criteria for the demonstration of anchimeric assistance by the backbone sulfur atom: (i) the enhanced reactivity just mentioned, (ii) a strong dependence of polysulfide reactivity on the ring size of the intermediate sulfonium ion (i.e., on the length of the pendant chloroalkyl chain), and (iii) the possible formation of rearranged chain units.

Scheme I



Scheme II

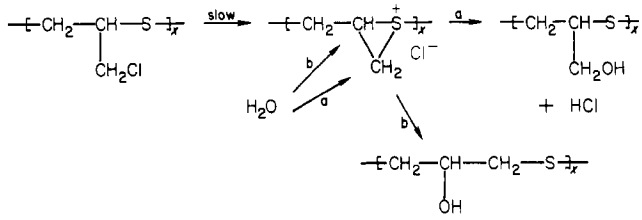


Table I
Relative Rate Constants for Hydrolysis of Chloroalkanes[a]

compound	relative rate constant[b]
$CH_3CH_2CH_2CH_2Cl$	1.00
$CH_3CH_2OCH_2CH_2Cl$	0.18
$CH_3CH_2SCH_2CH_2Cl$	2750
$CH_3CH_2OCH_2CH_2CH_2Cl$	0.77
$CH_3CH_2SCH_2CH_2CH_2Cl$	1.00

[a] Aqueous dioxane, $[H_2O]$ = 20 M, 100 °C. [b] 1-Chlorobutane as standard.

The present paper describes in detail the preparation of poly[(chloromethyl)thiirane]. Although this polymer has been reported in the literature,[4] previous work produced materials which were of low molecular weight and which were not well characterized. We report herein the synthesis of higher molecular weight PCMT, as well as preliminary observations concerning its chemical reactivity. These observations support the idea of anchimeric assistance by backbone sulfur.

Experimental Section

Monomers. Propylene oxide (PO, bp 34 °C), propylene sulfide (PS, bp 74 °C), and epichlorohydrin [ECH, bp 75 °C (140 mm)] were purchased from Aldrich Chemical Co. and distilled over CaH_2. (Chloromethyl)thiirane (CMT) was prepared by ECH and thiourea (Aldrich 99+%) after the method of Tabushi.[5] We found that increasing time to 15 h decreased the ECH fraction in the product. CMT was distilled [bp 78 °C (97 mm)] from CaH_2 prior to use; purified yields were typically 35%: ^{13}C NMR δ 48.67, 33.53, 25.53; ^1H NMR δ 3.8 (1 H, m), 3.1 (2 H, m), 2.5 (1 H, m), 2.2 (1

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H, m). All monomers had purity by gas chromatography in excess of 99.5%.

Initiators. Cadmium carbonate (Alfa-Ventron, ultrapure) and cadmium acetate (Alfa-Ventron, ultrapure hydrate) were dried overnight at $T > 100$ °C under reduced pressure prior to use.

Cadmium tartrate was prepared from cadmium acetate and DL-tartaric acid hydrate (Aldrich 98%) by adapting the procedure of Krylov and Livshits.[6]

Sulfuric acid (J. T. Baker reagent), trifluoromethanesulfonic acid (Aldrich), and sodium amide (Fisher Scientific, gray powder) were used as received. Boron trifluoride etherate (Aldrich) was distilled prior to use. Potassium hydroxide (Baker reagent) was activated by drying in a furnace at $T > 350$ °C for 3 days.

The Pruitt-Baggett catalyst[7] was prepared by slow addition of 6 cm^3 of PO to 2 g of $FeCl_3$ (Aldrich, anhydrous 98%) in a chilled tube under Ar. The resulting red-brown slurry was stored at 3 °C in a tightly stoppered tube.

Cadmium diallylthiolate was prepared from cadmium chloride (Alfa-Ventron, ultrapure hydrate) and allyl mercaptan (Aldrich, technical, 70+%, fractionally distilled) by the method of Cooper, Morgan, and Wragg.[8]

The preparation of diethylcadmium from cadmium bromide (Alfa-Ventron, 98% anhydrous) and ethylmagnesium bromide (Aldrich, 3.2 M in diethyl ether) followed the procedure of Thompson and Linnett.[9] The purified product [bp 66 °C (18 mm)] was distilled onto frozen toluene.

Butanethiol-modified diethylcadmium was prepared by dropwise addition of a solution of 0.97 cm^3 of *n*-butanethiol (Aldrich 98%, distilled) in 7 cm^3 of toluene to 7 cm^3 of chilled 1.3 M diethylcadmium in toluene with vigorous stirring under N_2.

Slow addition of 1.43 g of 3,3-dimethylbutane-1,2-diol (DMBD) in 6 cm^3 of toluene to 10 cm^3 of diethylzinc in toluene (Aldrich, 15 g/100 cm^3) with cooling in dry ice/2-propanol yielded the 1:1 modified catalyst. The toluene was removed under vacuum from the resultant sludge to give a white solid. DMBD was synthesized from 3,3-dimethyl-1-butene (Aldrich 95%), formic acid (Aldrich, 95–97%), and 30% stabilized hydrogen peroxide (J. T. Baker reagent) following the procedure of Brändström.[10] The low-melting solid was purified by distillation [bp 50 °C (0.5 mm)].

Diethylzinc initiators modified with equimolar amounts of methanol (purified as described by Riddick and Bunger[11]) and butanethiol (*n*-BuSH, distilled) were similarly prepared. In these cases the initiator suspensions were used directly, without evaporation of toluene.

A solution of 1.76 cm^3 of *n*-BuSH in 3.24 cm^3 of dry toluene was added dropwise to a solution of triethylaluminum in toluene (5 cm^3, Aldrich 25 g/100 cm^3) in a chilled, dry Schlenk tube under N_2. The resultant 1:1.5 Al-*n*-BuSH initiator was a clear, colorless, homogeneous solution.

A modified diethylmercury initiator was prepared by dropping a solution of 0.52 cm^3 of *n*-BuSH in 4.5 cm^3 of dry toluene into a stirred solution of 0.52 cm^3 of diethylmercury (Alfa-Ventron, used as received) in 4.5 cm^3 of toluene in a cooled (0 °C) Schlenk tube under N_2.

Polymerizations. Polymerization tubes were prepared from Pyrex tubing. Homopolymerizations of all four monomers, as well as copolymerization of CMT with PS, PO, and ECH, were carried out with the initiators described above. Copolymerizations were examined at monomer mole ratios of 9:1 and 1:1 ([comonomer]/[CMT]). In all cases, a total of 1 g of monomer was polymerized using an initiator concentration of 4 mol %.

The procedure varied slightly with initiator. Solid initiators were weighed into desiccated reaction tubes. The tubes were then flushed with N_2 or Ar and the appropriate volume(s) of monomer(s) was added by syringe under N_2. Liquid initiators were added via syringe to the N_2-flushed tube containing the monomer(s). The more vigorous initiators—BF_3·OEt_2, H_2SO_4, CF_3SO_3H, $ZnEt_2$–*n*-BuSH—required freezing of the monomer during initiator addition. In all cases tubes were attached to a vacuum line, frozen in liquid N_2, evacuated, and sealed. Polymerizations were carried out at room temperature; the more reactive systems were first kept cooled in dry ice/2-propanol overnight.

After a reaction time ranging from a few days to several weeks, the polymerization tubes were opened and the contents placed in dioxane. The dioxane-soluble fractions were filtered and freeze-dried. Acid initiators were removed by passing the dioxane solutions over a column of basic alumina or over a 4-vinylpyridine/divinylbenzene resin (Polysciences). The isolated products were then examined by ^{1}H NMR, ^{13}C NMR, IR, size exclusion chromatography, and/or measurement of inherent viscosity (0.5 g/100 cm^3, dioxane).

Larger scale preparations were accomplished with BF_3·OEt_2 as initiator. CMT (8 cm^3, 10 g) was placed in a polymerization tube, degassed by two freeze–pump–thaw cycles, and frozen in liquid nitrogen during addition of 0.3 cm^3 of BF_3·OEt_2. The frozen sample was evacuated, sealed, and allowed to warm slowly in dry ice/2-propanol. After 28 h the tube was opened and the product worked up as above.

Hydrolyses of PCMT and PECH. Precisely weighed quantities of polymer (ca. 0.5 g) were placed in 50-cm^3 volumetric flasks and dissolved in dioxane which had been purified according to Eigenberger.[12] After dissolution was complete, 5 cm^3 of distilled H_2O was added to each flask, and the mixtures were diluted to the mark with dioxane. The flasks were stoppered and placed in a constant-temperature bath at 75 °C. At desired intervals, flasks were removed and cooled rapidly to room temperature, and the contents was titrated with 0.1 N ethanolic KOH, and rosolic acid as indicator.[2] The titer of a blank dioxane/water mixture was subtracted from each measurement, and the concentration [C] of unreacted chloromethyl groups at time t was calculated from the amount of HCl released. Titration of dioxane/water/HCl mixtures confirmed the accuracy of the method for reaction times up to ca. 10 h at 75 °C. At longer times, we found the blank titer to be unreliable, as has been observed by others.[13]

Measurements. Infrared spectra were recorded as films on NaCl, using a Perkin-Elmer 580 infrared spectrophotometer. ^{1}H NMR spectra were obtained in solution ($CDCl_3$) on a Hitachi Perkin-Elmer R-24 spectrometer. ^{13}C NMR spectra were measured on a Varian CFT-20 with broad-band proton decoupling (4500 transients, 25% solution in $CDCl_3$). Chemical shifts are reported in parts per million from tetramethylsilane as internal standard. Gel permeation chromatography was performed on a Waters Associates Model 200 gel permeation chromatograph equipped with a differential refractive index detector, using either of two sets of Styragel columns (set A, 60, 100 Å; set AB, 60, 100, 1000, 10^4 Å). The solvent was THF and the flow rate 1 cm^3/min. Column set AB was used for determination of polymer molecular weights and calibrated by using a set of seven polystyrene standards (Pressure Chemical Co.). Molecular weight determined by GPC is reported as the molecular weight of polystyrene of equivalent elution volume.

Results and Discussion

Preparation of (Chloromethyl)thiirane. (Chloromethyl)thiirane was prepared by a portionwise addition of solid thiourea to a chilled (0–5 °C) methanolic solution of epichlorohydrin. Optimum yields were obtained with a reaction time of 15 h, and we found that (chloromethyl)thiirane could be distilled safely from CaH_2 at ca. 100-mm pressure, without loss of chlorine.

Polymerization of (Chloromethyl)thiirane. The objective of our preparative work was the identification of reaction conditions suitable for the synthesis of poly[(chloromethyl)thiirane] of high molecular weight. After an initial screening of potential polymerization initiators (described below), we succeeded in preparing PCMT as a tacky solid, with a GPC peak molecular weight of 20 000, using boron trifluoride etherate as initiator. We also examined the copolymerization of CMT with PS under similar conditions. These results are summarized in Table II.

All of these polymerizations were very rapid, and cooling of the monomer to −78 °C before addition of initiator was necessary in order to avoid a violent exotherm. Cooling also allowed the preparation of PCMT of increased molecular weight: room-temperature initiation provided polymer of GPC peak molecular weight 8000, initiation at −78 °C a product of peak molecular weight 20 000. Bulk polymerization was found to be superior to solution polymerization in CH_2Cl_2, and reaction times of less than ca.

Table II
Polymerization of CMT with $BF_3 \cdot OEt_2$ as Initiator

experiment	[CMT]/[PS] in feed	reaction time, h	[CMT]/[PS] in product	η_{inh},[a] 100 cm^3/g
1[b]	1/0	28		0.15
2[b]	1/1	43	60/40	0.09
3[b]	1/9	43	10/90	0.10
4[b]	0/1	43		0.16
5[c]	1/0	26		0.04
6[c]	1/1	26	45/55	0.09
7[c]	1/9	26	<5/>95	0.08
8[c]	0/1	26		0.12

[a] 0.5 g/100 cm^3 in dioxane, 30 °C. [b] Initiator added to cooled (−78 °C) monomer(s) in bulk; tube sealed under vacuum and allowed to warm to room temperature over a period of ca. 8 h; held at room temperature until completion of reaction. [c] Conditions same as in (b) except monomer diluted 4:1 with CH_2Cl_2.

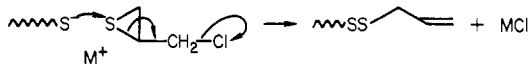
24 h, or continued cooling to −78 °C, also produced PCMT of reduced molecular weight. The ^1H and ^{13}C NMR spectra, as well as the infrared spectrum of PCMT, were consistent with the expected ring-opened structure of the polymer, although small amounts of defect structures were observed. The NMR spectra are discussed in detail in the following section.

Copolymers of CMT with PS were found (by ^1H NMR) to be very similar in composition to the monomer feed mixture. We did not pursue the determination of copolymer microstructure, nor did we prove rigorously that the products were indeed copolymers rather than mixtures of homopolymers.

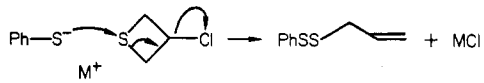
The use of $BF_3 \cdot OEt_2$ to prepare high molecular weight PCMT was the result of a careful, though rather qualitative, evaluation of potential polymerization initiators. The homopolymerization of CMT and its copolymerizations with PS, PO, and ECH were examined by using the sealed-tube techniques described in the Experimental Section. In each case, the homopolymerization of PS was run as a control in order to check catalyst activity and polymerization technique. We found the polymerization of CMT to be rather difficult in that many initiators which rapidly converted PS into high polymer afforded only oily polymers of CMT. Table III is a compilation of these qualitative results, based on visual examination of the polymerization products.

The initiators listed in Table III may be divided into three general classes: (i) the purely anionic (nucleophilic) initiators KOH and $NaNH_2$, (ii) those with some coordinative reactivity, based on cadmium, zinc, aluminum, or mercury, and (iii) the purely cationic (electrophilic) initiators H_2SO_4 and $BF_3 \cdot OEt_2$. We will consider each class in turn.

The anionic initiators were completely ineffective in polymerization of CMT; we recovered almost quantitatively unreacted monomer from these attempts. In our hands, as in others,[14] both of these initiators polymerized PS very well. It is possible that the nucleophilic species involved in the initiation and/or propagation of polymerization attack the chloromethyl group of CMT to give products which are unreactive with respect to polymerization. A second possibility is that the anionic polymerization of CMT may suffer effective termination through formation of allylic disulfide end groups:



This suggestion is based on the observation of Morita and Oae that 3-chlorothietane yields up to 72% of allyl phenyl disulfide upon treatment with thiophenoxide anion:[15]



Initiators based on compounds of cadmium, zinc, and aluminum were found to be more effective than KOH or $NaNH_2$ but still provided PCMT of rather low molecular weight, even after long reaction times (weeks to months at room temperature). Most effective among the organometallic initiators investigated was a 1:1.5 mixture of triethylaluminum and butanethiol, which afforded PCMT of η_{inh} 0.08 dL/g. This polymer was isolated as a colorless, highly viscous oil.

The cationic initiators H_2SO_4 and $BF_3 \cdot OEt_2$ were found to be most useful. As described above, these initiators were most effectively used in bulk polymerizations, with initiation at −78 °C followed by polymerization at room temperature. In some preliminary experiments using room-temperature initiation, polymerization for 24 h in sealed tubes afforded PCMT of GPC peak molecular weights as follows: 4900 (CF_3SO_3H), 5500 (H_2SO_4), and 7700

Table III
Evaluation of Initiators for Polymerization of CMT[a]

initiator[b]	monomers: CMT	CMT + PS	CMT + PO	CMT + ECH	PS
KOH	D	D	D	D	A (0.85)[c]
KOH[d]	D	D	D	D	A
$NaNH_2$	D	D			A
$CdCO_3$	B[e]	B	D	D	A (1.0)
$Cd(OAc)_2$	B	A	C	C	A
$CdC_4H_4O_6$	B	B	D	D	A
$CdEt_2$	C	C	C	C	A
$CdEt_2$-*n*-BuSH	C (0.01)	C	D	C	B (0.04)
$Cd(SCH_2CHCH_2)_2$	B	B	D		A (0.17)
$ZnEt_2$-CH_3OH	B		D	D	A
$ZnEt_2$-*n*-BuSH	B	C	C		C
$ZnEt_2$-DMBD	B	B	D	C	A
$HgEt_2$-*n*-BuSH	D				
$AlEt_3$-*n*-BuSH	B (0.08)				
H_2SO_4	A	A	C	C	A
$BF_3 \cdot OEt_2$	cf. Table II				

[a] Results reported on the basis of visual examination of polymerization products: A = tacky solid, B = viscous oil, C = fluid oil, D = no visible increase in viscosity. [b] 4 mol % based on monomer; no solvent unless indicated. [c] Figures in parentheses are η_{inh} (100 cm^3/g). [d] In CH_2Cl_2 as solvent. [e] GPC peak molecular weight 5000.

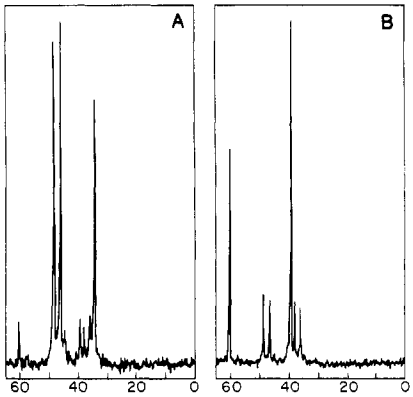
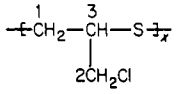


Figure 1. ^{13}C NMR spectra of PCMT: (A) immediately after isolation; (B) ca. 3 months after isolation.

Table IV
Calculated and Observed ^{13}C Chemical Shifts for PCMT



carbon	chem shift, ppm from ^{13}C Me_4Si calcd	obsd
C-1	38.6,[a] 35.0[b]	34.96
C-2	50.6,[a] 52.0[b]	46.88
C-3	54.1,[a] 51.0[b]	49.28

[a] Propane as model compound. [b] Poly(propylene sulfide) as model compound.

(BF_3·OEt_2). Polymerizations with BF_3·OEt_2 were more readily reproducible than those with the protonic acids, so it was this system which was selected for optimization.

The following discussion concerns PCMT prepared with BF_3·OEt_2 initiator (experiment 1, Table II).

Structural Rearrangement of PCMT. The proton-decoupled ^{13}C NMR spectrum of PCMT, recorded 3 days after initiation of polymerization (i.e., immediately after workup and solvent removal), is shown in Figure 1A. The three major lines of the spectrum—at 34.96, 46.88, and 49.28 ppm—are consistent with the expected ring-opened structure for PCMT. Table IV gives the line assignments and lists the line positions calculated using additive substituent parameters, with propane or poly(propylene sulfide) as the model compound.[16] These assignments were confirmed by off-resonance decoupling experiments.

The ^{13}C spectrum in Figure 1B was recorded approximately 3 months after completion of polymerization; the solid, isolated polymer had been stored at room temperature in a desiccator for this period. The spectrum has clearly changed: The major lines in Figure 1A are much diminished in intensity and are replaced by intense signals at 39.93 and 60.92 ppm. Off-resonance decoupling allows assignment of the former line to CH_2 groups and the latter to a CH structure.

The ^1H NMR spectra of the same samples also reveal structural changes (Figure 2). The spectrum of the freshly isolated sample shows two broad signals at δ 3.10 (3 H, $CHCH_2$) and 3.85 (2 H, CH_2Cl); again, this is consistent with the structure shown in Table IV. After 3 months, a new multiplet (quintet?) has appeared at δ 4.28, and the upfield resonance is an apparent doublet centered at δ 3.18. Double-resonance experiments show that these two signals are coupled with J = 6 Hz. In addition, a broad signal remains at δ 3.90. Integration of the spectrum gives the following relative signal intensities (in order of increasing field strength): 7:8:36.

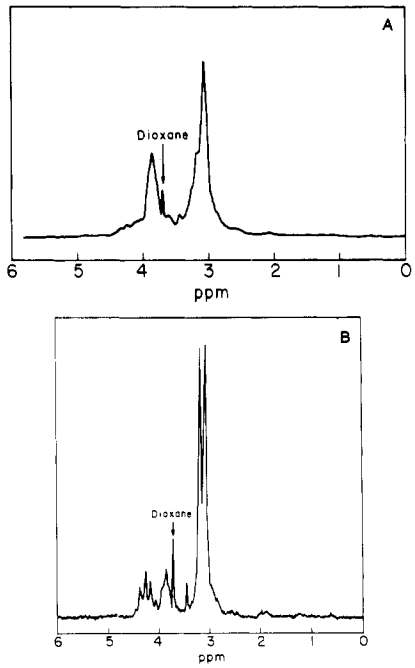
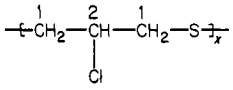


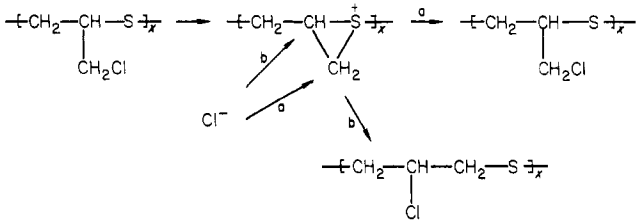
Figure 2. ^1H NMR spectra of PCMT: (A) immediately after isolation; (B) ca. 3 months after isolation.

Table V
Calculated and Observed ^{13}C Chemical Shifts for Rearranged PCMT Units



carbon	chem shift, ppm from ^{13}C Me_4Si calcd	obsd
C-1	43.6	39.93
C-2	61.1	60.92

We believe all of these spectral features to be consistent with a room-temperature rearrangement of PCMT *in the absence of solvent*, according to the following mechanism:



Nucleophilic attack of backbone sulfur on the pendant chloromethyl group yields the cyclic sulfonium chloride, which in the absence of added nucleophile reacts by internal return to yield either starting material (path a) or a 3-chlorothietane repeat unit (path b). It is the latter route which gives rise to the observed changes in the ^1H and ^{13}C NMR spectra.

The ^1H NMR spectrum of fully rearranged polymer would consist of a 1 H quintet and a 4 H doublet. Assuming that the multiplet at δ 4.28 is a 1 H quintet due to 3-chlorothietane units, integration of the spectrum suggests 60–65% rearrangement of this sample. The ^{13}C NMR spectrum of the rearranged polymer is assigned as in Table V. The calculated line positions are based on propane as the model compound.

This unusual rearrangement of PCMT may provide new insight into the chemical behavior of bulk polymers. The

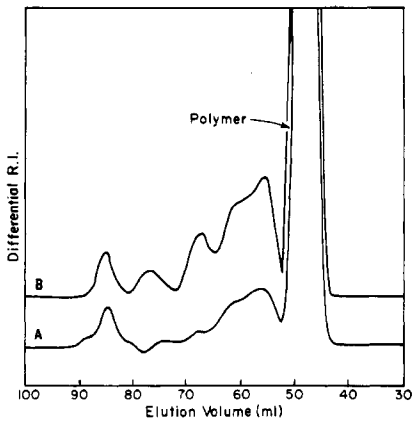


Figure 3. GPC traces (column set A, Experimental Section) of PCMT, showing oligomer fraction: curve A, 5 days after isolation; curve B, ca. 3 months after isolation.

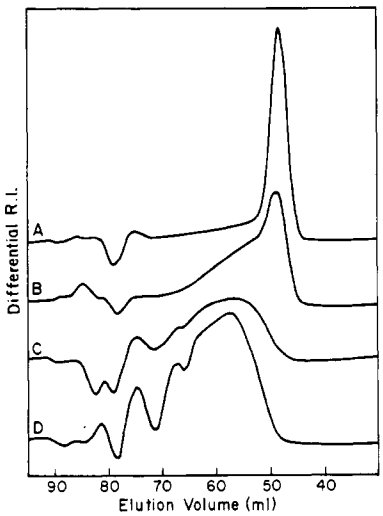


Figure 4. GPC traces (column set A, Experimental Section) of PCMT treated with triethyloxonium tetrafluoroborate (TEFB) or with BF_3·OEt_2: (A) as polymerized (Table II, experiment 1); (B) after 2 days at room temperature with TEFB; (C) after 8 days at room temperature and 3 days at 65 °C with TEFB; (D) polymerization mixture (BF_3·OEt_2) allowed to stand at room temperature for 15 days.

results of an ongoing study of this reaction will form the basis of a future paper.

Formation of Oligomers from PCMT. The observation of the rearrangement of PCMT was a surprising one. It is tempting to ascribe the observed spectral changes to the formation of oligomers, which are known to form following the introduction of sulfonium ions into polythiiranes.[17-22] In fact, the oligomer fraction in PCMT does increase on standing at room temperature, as shown in the GPC traces in Figure 3. However, this oligomer fraction is far too small to account for the intensities of the NMR signals due to rearranged chain units.

We have also observed in preliminary experiments that PCMT can be converted to oligomers upon treatment with triethyloxonium tetrafluoroborate in CH_2Cl_2 or upon extended treatment with BF_3·OEt_2 (Figure 4). This is consistent with the extensive work of Goethals et al. on the depolymerization of polythiiranes.[17-22] We are now attempting to isolate and identify the oligomeric products from PCMT.

Hydrolyses of PCMT and PECH. The rates of hydrolysis of PCMT and PECH were determined at 75 °C in a 90:10 dioxane/water mixture. The HCl evolved in the hydroysis was titrated with 0.1 N alcoholic KOH, using

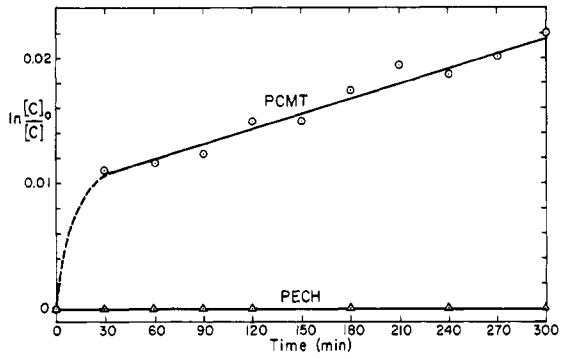


Figure 5. First-order kinetic plot of hydrolysis of PCMT (○) and PECH (△) at 75 °C in 90:10 (v/v) dioxane/water. $[C]_0$ is the initial molar concentration of PCMT repeat units; $[C] = [C]_0 - [HCl\ evolved]$.

rosolic acid as indicator, according to the method of Bohme and Sell.[2] Figure 5 shows the results.

PECH is completely unreactive under these conditions; no HCl was detected in up to 7 h at 75 °C. The hydrolysis of PCMT, on the other hand, shows a rapid initial burst of HCl, followed by an apparent first-order release. A least-squares fit of the linear portion of the curve yields a first-order rate constant of 7×10^{-7} s^{-1}.

The major conclusion to be drawn from this result is that PCMT is considerably more reactive than PECH under these conditions. Thorough interpretation of this observation must await a detailed examination of the solvolysis—including determination of its temperature coefficient, extension to higher conversion, and analysis of reaction products—but it is plausible that the enhanced reactivity of PCMT is a result of anchimeric assistance by backbone sulfur. Should this be so, the initial burst of HCl in the hydrolysis of PCMT may represent the rapid decomposition of a steady-state concentration of sulfonium ions present in bulk polymer, and the linear portion of the curve should provide the rate constant for ring closure to the sulfonium ion. Information of this kind is not readily available for polymer systems. We are currently extending our solvolysis experiments.

Conclusions

(Chloromethyl)thiirane may be converted to poly[(chloromethyl)thiirane] of molecular weight ca. 20 000 through ring-opening polymerization with boron trifluoride etherate as initiator. Anionic initiators are completely ineffective in this reaction, and various derivatives of cadmium, zinc, or aluminum afford—at best—polymers of molecular weight ca. 5000.

Poly[(chloromethyl)thiirane] exhibits unusual reactivity in bulk and in solution. A room-temperature rearrangement in the absence of solvent converts the (chloromethyl)thiirane chain unit to a structure which may be regarded as derived from ring-opening of 3-chlorothietane. The solvolytic reactivity of poly[(chloromethyl)thiirane] is significantly enhanced as compared to that of poly(epichlorohydrin). These observations are consistent with the idea of anchimeric assistance by the chain backbone of poly[(chloromethyl)thiirane], and continuing investigation of the reactivity of this and related polymers may be expected to provide new insight into the chemical properties of high polymer chains.

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Oxygenation of Iron(II) Picket-Fence Porphyrin Bound to Amphiphilic Block Copolymer in Water

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ABSTRACT: Several *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[*o*-(alkylamido)phenyl]porphyrin–iron(II) complexes were prepared and their NEI (*N*-ethylimidazole) or PSI [styrene (84 mol %)–*N*-vinylimidazole (16 mol %) copolymer] complexes were observed with respect to the oxygenation reaction in dry toluene. In H_2O-saturated toluene, the Fe(II) picket-fence porphyrin (alkyl = tert-butyl)–PSI complex formed a more stable oxygen complex than the NEI complex did, probably due to the hydrophobicity of PSI. The Fe(II) picket-fence porphyrin coordinately bound to a water-soluble polymer ligand, such as *N*-vinyl-2-pyrrolidone (80 mol %)–*N*-vinylimidazole (20 mol %) copolymer, was rapidly oxidized upon exposure to oxygen gas, while amphiphilic ABA-type block copolymer ligands, such as PEO–PSI–PEO [PEO = poly(ethylene oxide)], gave oxygen complexes which were observed even at pH 7.0 in aqueous solution at room temperature. Further attempts to bind the complex units covalently to the hydrophobic B block of such ternary block copolymers also produced a stable oxygen complex in water at room temperature.

Introduction

A naked heme or related iron(II) complexes free from apoprotein are known to be rapidly oxidized in homogeneous solution at room temperature due to the oxidation side-reactions shown below:[1-4]

Oxygenation

$$\mathrm{B\text{–}Fe^{II}P + O_2 \rightleftarrows [B\text{–}Fe^{II}P\text{–}O_2 \leftrightarrow B\text{–}Fe^{III}P\text{–}O_2^{-}*]}$$
$$\mathrm{B\text{–}Fe^{II}P\text{–}B + O_2 \rightleftarrows [B\text{–}Fe^{II}P\text{–}O_2 \leftrightarrow B\text{–}Fe^{III}P\text{–}O_2^{-}*] + B} \quad (1)$$

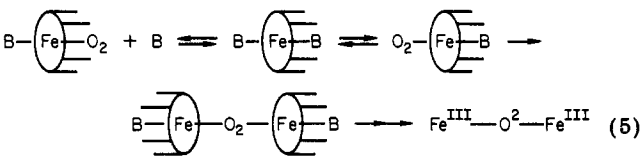
Oxidation

$$\mathrm{[B\text{–}Fe^{II}P\text{–}O_2 \leftrightarrow B\text{–}Fe^{III}P\text{–}O_2^{-}*] \rightarrow B\text{–}Fe^{III} + O_2^{-}*} \quad (2)$$
(monomeric aprotic)

$$\mathrm{[B\text{–}Fe^{II}P\text{–}O_2 \leftrightarrow B\text{–}Fe^{III}P\text{–}O_2^{-}*] + B\text{–}Fe^{II}P \rightarrow}$$
$$\mathrm{[B\text{–}Fe^{III}P\text{–}O_2^{2-}\text{–}Fe^{III}P\text{–}B] \xrightarrow[-2B]{} 2[Fe^{IV}{=}O] \xrightarrow[-2B]{2B\text{–}Fe^{II}P}}$$
$$\mathrm{2Fe^{III}P\text{–}O^{2-}\text{–}Fe^{III}P} \quad \text{(dimeric)} \quad (3)$$

$$\mathrm{[B\text{–}Fe^{II}P\text{–}O_2 \leftrightarrow B\text{–}Fe^{III}P\text{–}O_2^{-}*] \xrightarrow{H^+}}$$
$$\mathrm{B\text{–}Fe^{III}P + HO_2^{*}} \quad \text{(monomeric protic)} \quad (4)$$

Here $Fe^{II}P$ and $Fe^{III}P$ indicate iron(II)- and iron(III)–porphyrin complexes, respectively, and B represents a given axial base, such as an imidazole derivative. In an initial attempt to minimize oxidation process 3, Baldwin et al.[5,6] obtained an oxygen complex in aprotic organic solvents at room temperature. Collman et al. also succeeded in reversible oxygenation, using the Fe(II) picket-fence porphyrin *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[[*o*-(pivalamido)phenyl]porphyrinato]iron(II), or Fe^{II}TpivPP, in aprotic solvents at room temperature.[1,7-13] Its reversible oxygenation is attributed to the fact that the bulky *tert*-butyl groups attached to one side of the porphyrin plane prevent oxidation process 3 and that (4) is negligible in aprotic solvents. Collman et al. assumed an intramolecular solvation effect of the tetrapivalamide groups at the sixth coordination sphere,[1,10] to which an oxygen molecule was ligated, caused oxidation process 5 to be suppressed.



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