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Reactive Polymers and Oligomers from Cyclic Ethers and Cyclic Sulfides

Jenn S. Shih and David A. Tirrell

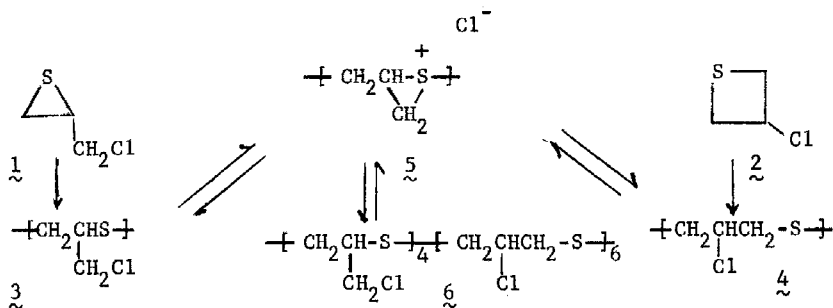
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ABSTRACT

(2-Bromoethyl)oxirane is converted in 39% yield to poly[(2-bromoethyl)oxirane] of inherent viscosity 1.99 dL/g. The $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$ system is a very effective initiator for the polymerization of (2-bromoethyl)oxirane. Poly[(2-bromoethyl)oxirane] is a white elastomer, soluble in CHCl_3 and insoluble in CH_3OH . Polyether-urethane hydrogels are prepared by the room temperature crosslinking of poly[(3-hydroxypropyl)oxirane] with aliphatic or aromatic diisocyanates. These networks absorb 100-200% of their weights in water, and can be prepared in transparent form with potential application as biomaterials or contact lenses.

INTRODUCTION

We have for some time been interested in the design of synthetic polymers which undergo "backbone-assisted" reactions: chemical transformations which are accelerated by functional groups located in the polymer's main chain. Our primary objective has been the development of an understanding of the scope and limitations of such reactions, but we are interested also in developing new reactive polymers which may be applied in areas such as adhesives or biomaterials.



Scheme I

Reactive polysulfides (Scheme I) may be prepared by ring-opening polymerization of chloromethylthiirane (CMT, 1) or 3-chlorothietane (3CT, 2) (1-3). The polymers so obtained contain reactive β -chlorosulfide structures, and would be expected to combine rapidly with nucleophiles under ionizing conditions. In preliminary experiments (4), we have observed a rapid insolubilization of poly(chloromethylthiirane) (3) in aqueous dioxane solutions. We suggest that this may be a result of crosslinking via the formation of ether links by displacement of reactive chloride functions, and we are currently exploring the nature and applications of this reaction. A second manifestation of the high reactivity of these polymeric β -chlorosulfides is the facile interconversion of CMT and 3CT repeating units (3 and 4, respectively). Either homopolymer is converted spontaneously, through the sulfonium ion (5), to a copolymer (6) which contains the isomeric repeating units in a ratio of approximately 4 to 6.

In an attempt to extend this approach to the preparation of reactive polyethers, we prepared the poly[(ω -chloroalkyl)oxirane]s (7) (5).



These polymers showed no tendency to rearrange via a route analogous to that shown in Scheme I. On the other hand, the increased separation of the leaving group from the polymer

backbone increased approximately sevenfold the S_N2 reactivity of these new elastomers, as compared to polyepichlorohydrin ($\bar{M}_n=1$). Thus quantitative substitution of the pendant chloride by tetrabutylammonium benzoate was accomplished in only 6 hr in DMAc at 50°C without significant loss of inherent viscosity (5,6). This reaction, and subsequent methanolysis, allowed us to prepare the poly[(ω -hydroxyalkyl)oxirane]s (8),



which are of interest as precursors for polyethers bearing reactive sulfonate leaving groups. But these hydroxylated polyethers are interesting materials in their own right: they form tough, clear films when cast from hydroxylic solvents, and they are either water-soluble or water-swellaable, depending on the length of the pendant hydroxyalkyl chain (6).

In this paper, we report two new developments in the area of reactive heterochain polymers: i). the preparation of poly-[(2-bromoethyl)oxirane], and ii). the preparation of polyether-urethane hydrogels based on poly[(3-hydroxylpropyl)oxirane].

EXPERIMENTAL

(2-Bromoethyl)oxirane. 4-Bromo-1-butene (Aldrich, bp. $98-100^\circ\text{C}$; 50g, 0.37 mol) was dissolved in 800 ml of CH_2Cl_2 in a 2-liter 3-necked round-bottom flask fitted with a mechanical stirrer and condenser. The mixture was cooled in ice, and 85 g (0.49 mol) of m-chloroperoxybenzoic acid were added, with stirring, over 0.5 hr. After stirring for 18 hr at room temperature, the reaction mixture was filtered and the filtrate was washed with 10% aqueous sodium sulfite until the color reaction with KI/starch paper was no longer observed. The mixture was then further washed with 5% aqueous NaHCO_3 (twice), water and brine. After drying (MgSO_4) and removal of the solvent on the rotary evaporator, 40.7 g (73%) of (2-bromoethyl)oxirane was isolated by fractional distillation

(bp. 150°C). ^1H NMR (80 MHz, CDCl_3): δ : 1.9-2.1 (m, 2H), 2.55 (m, 1H), 2.8 (m, 1H), 3.0 (m, 1H), 3.55 (t, 2H). IR(neat): 3050, 2980, 1490, 1440, 1330, 1270, 1230, 1150, 1000, 960, 920, 860 cm^{-1}

Polymerization of (2-Bromoethyl)oxirane:Initiator. To a carefully dried, N_2 -filled Schlenk tube that contained a small magnetic stir bar was added via syringe 4.5 mL (9.87 mmol) of triethylaluminum solution (25% in toluene, Aldrich, or 25% in heptane, Texas Alkyls). The tube was cooled in a dry ice/isopropanol bath and 90 μL (5.00 mmol) of doubly distilled water was added dropwise with stirring under strong N_2 flow. After 15 min 0.50 mL (4.88 mmol) of 2,4-pentanedione (AcAc) (Aldrich 99+, redistilled) was added in similar fashion. The mixture was then stirred overnight at room temperature before use. Initiators prepared in this way contain ca. 2 mmol of Al/mL.

Polymerization. Polymerization was performed in bulk in sealed glass tubes. A polymerization tube was flushed with dry N_2 and the monomer and initiator (5 mol% Al with respect to monomer) were added via dry syringes. The tube was then attached to a vacuum line, the contents frozen in liquid N_2 , and the tube evacuated and sealed. After 8 days at room temperature the tube contents were dissolved in benzene. Dropwise addition of the benzene solution to methanol containing 0.5% (by volume) of concentrated HCl caused precipitation of the polymer, which was collected by filtration and dried at room temperature at ca. 0.1 mm Hg. This procedure afforded a 39% yield of poly[(2-bromoethyl)-oxirane] of inherent viscosity 1.99 dL/g (0.5% w/v, CHCl_3 , 35°C). ^1H NMR (60 MHz, CDCl_3) δ 1.8-2.3 (broad, 2H), 3.2-3.8 (broad, 5H). IR(neat): 2900, 1370, 1270, 1150, 1090, 910 cm^{-1} .

Preparation of Poly[(3-hydroxypropyl)oxirane]. Poly-[(3-hydroxypropyl)oxirane] was prepared from poly[[3-(m-chlorobenzyloxy)propyl]oxirane] via methanolysis (6), or from poly-

[(3-chloropropyl)oxirane] (5), via treatment with tetrabutylammonium benzoate (TBAB) and subsequent methanolysis (6). Recently we have prepared several samples of a related polymer, poly[2-hydroxyethyl]oxirane], via a similar procedure which employs sodium benzoate in the first step; although this reaction is heterogenous and slower than that with TBAB, quantitative replacement of chloride is achieved in 4 days. The simplicity of this procedure recommends it for the majority of preparations.

Preparation of Polyether-urethane Hydrogels. Poly[(3-hydroxypropyl)oxirane] [η_{inh} (0.5% w/v in CH_3OH , 35°C) = 0.68 dL/g; 0.06 g, 0.6 mmol of repeating units] was dissolved in 2 ml of pyridine. A measured amount of 1,6-diisocyanatohexane or tolylenediisocyanate was added, and the mixture stirred rapidly and cast on an aluminum pan. The mixture was allowed to cure overnight at room temperature, and then immersed in water. The hydrogel was washed with water for several hours to remove residual pyridine, and then dried at 50°C in air.

Measurements. ^1H NMR spectra were recorded at 60 MHz on a Hitachi-Perkin Elmer R24B spectrometer, or at 80 MHz on an IBM-Bruker NR80 instrument. Infrared spectra were taken on a Perkin Elmer Model 700 spectrophotometer. Water absorption of polyether-urethane hydrogels was determined by weighing carefully dried films, and then reweighing, after immersion in distilled water and blotting of the film surface, until constant weight was attained.

RESULTS AND DISCUSSION

Polymerization of (2-Bromoethyl)oxirane. (2-Bromoethyl)oxirane was prepared in 73% yield by epoxidation of 4-bromo-1-butene with m-chloroperoxybenzoic acid. Polymerization of this monomer was readily accomplished by using the $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$ initiator system developed by Vandenberg (7,8). Polymerization in bulk at room temperature produced after 8 days a 39% yield of

poly[(2-bromoethyl)oxirane] of inherent viscosity 1.99 dL/g. Poly[(2-bromoethyl)oxirane] is a slightly tacky, white elastomer which displays good elasticity even without crosslinking. The work of Oae (9) on solvolysis of bromoalkylethers of low molecular weight suggests that poly[(2-bromoethyl)oxirane] might be prone to structural isomerization under ionizing conditions; this prospect is now under investigation in continuing studies of the chemical reactivity of poly[(2-bromoethyl)oxirane].

Preparation of Polyether-urethane Hydrogels. The reactions of polyols with difunctional isocyanates provide a standard method of producing polyurethane networks. The elasticity and water solubility of poly[(3-hydroxypropyl)oxirane] make this polymer an attractive intermediate for the synthesis of flexible, hydrophilic networks by this route. Hydrogels have been investigated with some intensity because of their potential value as biocompatible materials. In addition, films of poly[(3-hydroxypropyl)oxirane] are very nearly transparent, so that these hydrophilic networks might be considered as candidate materials for the production of contact lenses. We report herein the first preparation of polyether-urethane hydrogels based on poly[(3-hydroxypropyl)oxirane].

In these experiments, pyridine solutions of poly[(3-hydroxypropyl)oxirane] were treated with 1,6-diisocyanatohexane or with tolylene diisocyanate, and cured in film form at room temperature. The resulting films were insoluble in water, but were water-swellaible to a degree which depended upon the amount of the added diisocyanate. The Table presents water absorption results for several networks produced in this way. As expected, equilibrium water absorption is depressed as the concentration of the crosslinker is increased.

These hydrophilic networks can, under appropriate conditions, be made transparent. The Figure shows a network prepared from poly[(3-hydroxypropyl)oxirane] and tolylene diisocyanate ($[-OH]/[-NCO] = 2.5/1$). The development of transparent networks of varying hydrophilicity and crosslink density is underway.

TABLE
Water Absorption of Polyether-urethane Networks

<u>Crosslinker</u>	<u>[-OH]/[-NCO]</u>	<u>Equilibrium Water Absorption (%)</u>
1,6-Diisocyanatohexane	5/1	270
1,6-Diisocyanatohexane	2.5/1	115
Tolylene diisocyanate	2.5/1	120

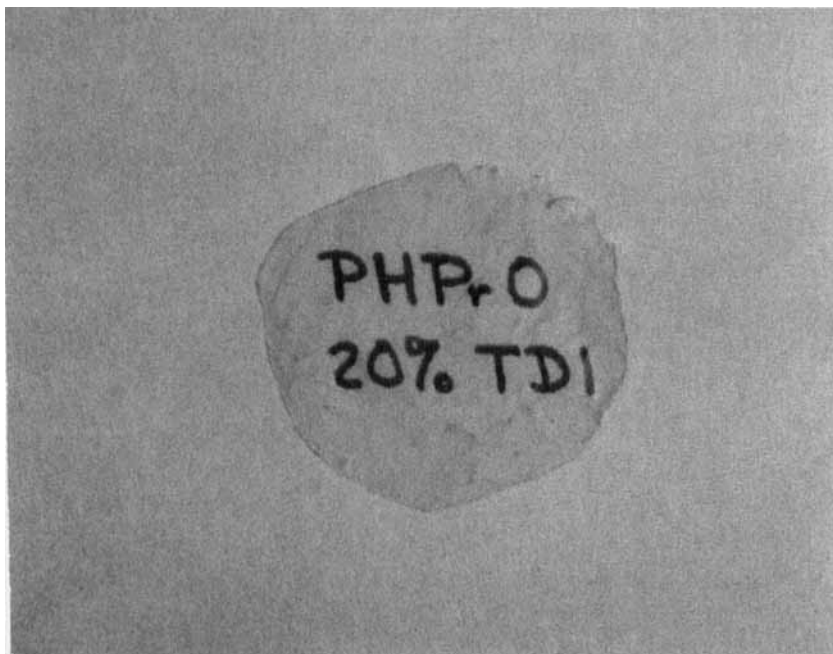


Figure. Polyether-urethane hydrogel (dried) prepared from poly[(3-hydroxypropyl)oxirane] and tolylene diisocyanate $[-OH]/[-NCO] = 2.5/1$. Lettering on surface behind the polymer film illustrates the transparency of the network.

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