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Shigetaka Shimada and Ffrancon Williams*

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37916

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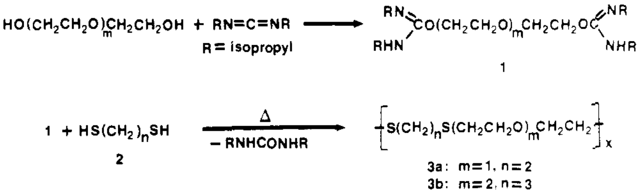
Sequential Copolymers of Oxyethylene Oligomers and α,ω-Poly(methylenedithiols)

Poly(oxyethylene) $(CH_2CH_2O)_n$, poly(thioethylene) $(CH_2CH_2S)_n$, and their homologues and copolymers are currently under widespread investigation. One main area of interest involves theoretical and experimental conformational analysis. Dielectric measurements[1] and viscosity[2] determinations are two techniques applicable to such studies. A few examples of the polymers recently examined include poly(1,3-dioxolane), $[CH_2OCH_2CH_2O]_n$,[2] poly(thiodiethylene glycol), $[CH_2CH_2OCH_2CH_2S]_n$,[3] and poly(1,3-dioxa-6-thiocane), $[CH_2CH_2OCH_2OCH_2CH_2S]_n$.[1]

A second area being explored involves the crystallinity and thermal behavior of these polymers. While poly(oxyethylene) (POE) melts around 66 °C, poly(thioethylene) (PTE) has a melting point of 210 °C.[4] We are interested in the effect on the thermal behavior of PTE of nonrandom replacement of thioethylene units with oxyethylene moieties. From a different perspective, the nonrandom substitution of oxyethylene units in POE with dithio(polymethylene) groups poly(1,3-dioxa-6-thiocane), also attractive. Related work with low molecular weight alkoxy-end-capped POE indicated significant changes in crystallinity and fusion properties with increases in the length of the alkyl groups.[5] The crystallinity of a series of sequential copolymers with increasing polymethylene chain length between thioether groups would, thus, be of fundamental interest.

A more recent development in the chemistry of POE and its derivatives lies in their similarity to the macrocyclic crown ethers. The cation binding ability of the crown ethers has led to widespread application as phase-transfer catalysts (PTC).[6] We recently reviewed the use of crown ethers and PTC in polymer chemistry.[7] One important discovery is the ability of POE to act as an efficient PTC in a manner similar to crown ethers. This suggests a potential of oxy–thio copolymers, for example, to function as PTC and cation-complexing agents. Thio-containing polymers should interact especially well with certain transition-metal ions. We are currently developing a program involving synthesis of such sequential copolymers for examination of their physical and catalytic behavior.

Scheme I



The poly(thiodiethylene glycol) and poly(1,3-dioxa-6-thiocane) mentioned above were obtained by condensation methods which gave only low molecular weight polymer. In a recent review of the chemistry of isoureas,[8] we had suggested the use of bisisoureas derived from oligo(oxyethylenes) for polymer synthesis by condensation with appropriate difunctional nucleophiles. We find that this method appears to be generally applicable to the synthesis of oxy–thio copolymers. The synthesis (Scheme I) involves initial formation of the bisisourea **1** (as previously described[8]) from the simple, high-yield addition of the oligo(oxyethylene) to excess *N*,*N*′-diisopropylcarbodiimide. Purification of **1**[8] is followed by thermal condensation with an α,ω-dithioalkane **2** to give the copolymer **3**.

A typical procedure involves the bisisourea of diethylene glycol (**1**, $m = 1$) prepared and purified as previously described[8] and ethanedithiol (**2**, $n = 2$; freshly distilled at 0.2 mmHg and 30 °C). The reagents **1** (3.58 g, 0.01 mol) and **2** (0.94 g, 0.01 mol) were mixed together with anhydrous KF (0.93 g, 0.016 mol) in a polymerization tube which was then sealed under nitrogen. The tube was placed in an oil bath and the temperature gradually brought to 140 °C, where it was held for 3 days. The cooled mixture was then separated into several fractions by sequential extraction with benzene, tetrahydrofuran, methanol, water, and finally chloroform. The polymer was recovered in fair-to-good yield from the chloroform extract by rotary evaporation. Reprecipitation from chloroform into methanol gave pure polymer **3a** with a melting point of 87–91 °C and an intrinsic viscosity of 0.22 dL/g in chloroform at 30.0 °C. Anal. Calcd for $C_6H_{12}S_2O$: C, 43.87; H, 7.36. Found: C, 44.60; H, 7.72.

Essentially the same procedure was used for condensation of triethylene glycol bisisourea (**1**, $m = 2$) and 1,3-propanedithiol (**2**, $n = 3$) to give polymer **3b** with an intrinsic viscosity of 0.96 dL/g. No melting point was obtainable for this tacky, soft material.

The ^1H and ^{13}C NMR spectra of polymers **3a** and **3b** are given in Figure 1. The ^1H integration ratios and chemical shifts are entirely consistent with the expected product structures. The ^{13}C NMR shifts, intensities, and T_1 relaxation parameters are similar to those of POE and a new class of polyureas recently synthesized in this laboratory containing a structurally related macrocycle in the polymer backbone.[9]

The generality of this procedure is being further explored for a series of oligo(oxyethylene) bisisoureas with several additional alkane and aromatic dithiols. The full paper will contain additional synthetic details and complete physical and spectroscopic characterization of these now readily available sequential copolymers.

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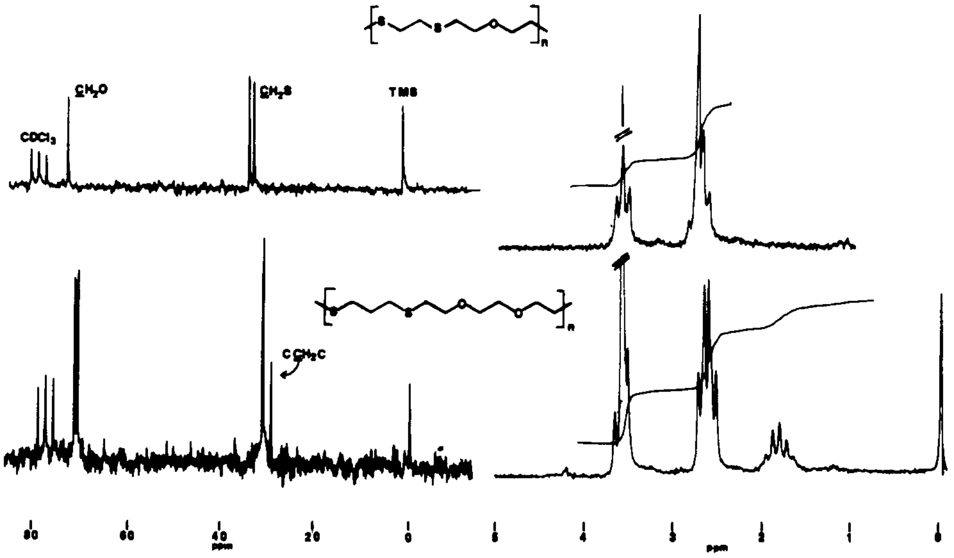

Figure 1. Partial ^{13}C NMR spectra (left) and ^{1}H NMR spectra (right) of polymers **3a** (upper) and **3b** (lower) in $CDCl_3$.

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Lon J. Mathias* and J. B. Canterberry

Department of Chemistry
Auburn University
Alabama 36849

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