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Polyethers with Reactive Side Chains—Hydroxy Polyethers

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Polyethers with Reactive Side Chains—Hydroxy Polyethers

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ABSTRACT

The author's work on preparing polyethers with reactive side chains is reviewed with emphasis on hydroxy polyethers. High molecular weight hydroxy polyethers were prepared by polymerizing epoxides containing a hydroxyl group protected with an appropriate group such as $SiMe_3$ and then removing it by hydrolysis.

Atactic and isotactic polyglycidol were made in this way using coordination catalysts. The isotactic polymer was found to be unusual since it did not crystallize readily from the melt and was relatively low melting (60°C). Poly(cis-1,4-dihydroxy-2,3-epoxybutane), PDHEB, was prepared, preferably from the cyclic acetone ketal which polymerized with $i\text{-}Bu_3Al\text{-}0.7H_2O$ cationic catalyst at -78°C to a moderate molecular weight (η_{inh} up to 0.7) atactic polymer. This polymer is readily hydrolyzed with aqueous HCl treatment to atactic, amorphous, water-soluble PDHEB with a T_g of 80°C. PDHEB is melt stable to 200°C and can be molded to

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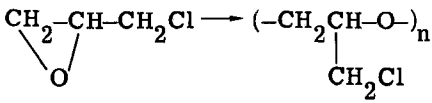
give brittle, clear films which readily pick up 5-10% H_2O from the atmosphere to give properties like plasticized poly(vinyl chloride). The bis(trimethylsilyl) ether of cis-1,4-dihydroxy-2,3-epoxybutane was polymerized cationically with the i-Bu_3Al-0.7H_2O catalyst at -78°C to a fairly tactic, presumably racemic diisotactic, amorphous polymer, with η_{inh} of 0.16. A mechanism is proposed for this stereoregular polymerization based on a complexation of the Si side group of the last chain unit with the propagating oxonium ion. Hydroxy polyethers, in general, merit extensive future study since they are analogues of the biochemically important polysaccharides.

INTRODUCTION

The author previously reported a wide variety of organometallic coordination catalysts, particularly those based on aluminum, for preparing high molecular weight polyethers from epoxides [1] and oxetanes [2]. These new catalysts led to the discovery and commercial development [3] of a new class of unusual elastomers [4], the epichlorohydrin elastomers, as typified by amorphous, atactic polyepichlorohydrin:



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High molecular weight polyethers with reactive side chains could be especially useful in many areas. However, the organometallic catalysts often do not work well or very little with epoxides having such groups. We have reported successful polymerizations with epoxides containing ester groups, such as in ethyl glycidate and in glycidyl methacrylate, with our Al catalysts, particularly with our organoaluminum-H_2O-acetylacetonate catalyst ("chelate" catalyst), and with tert-amino groups as in 3-diethylamino-1,2-epoxypropane using some of our modified organomagnesium catalysts [5]. Tucker [6] and Cantor et al. [7] have reported the preparation of high molecular weight homopolymer and copolymers from cyanoethyl glycidyl ether using our chelate catalyst. Vogl et al. [8] have recently reported preparing a variety of polyethers with ester groups using our chelate catalyst.

An alternate method of preparing polyethers with reactive side chains is to react polyepichlorohydrin with various nucleophiles. The author has used this method to introduce carboxyl, carboxylate, sulfoxide, amino, isothiuronium, thioether, thiosulfate, azide, and phosphonate [4]. Diverse applications have been reported for these modified

polyethers, including flame retardants, photosensitive materials, and a variety of applications for water systems such as thickeners, flocculating agents, semipermeable membranes for reverse osmosis, drainage aids for paper manufacturing, de-emulsifiers, and shrink-proofing agents for wool [4].

Polyethers with reactive hydroxyl side chains could be especially interesting, but are particularly difficult to prepare with organometallic catalysts. In this case such polyethers can be prepared by using a blocking group such as the trimethylsilyl group which is easy to remove after polymerization. This method has proved especially useful for the preparation and study of atactic and isotactic polyglycidol, and of its disubstituted analogue, poly(cis-1,4-dihydroxy-2,3-epoxybutane), PDHEB. These studies are summarized below.

HYDROXY POLYETHER STUDIES

Polyglycidol

Some years ago we made a high polymer from glycidol by blocking the hydroxyl groups with trimethylsilyl groups, polymerizing this trimethylsilyl glycidyl ether (TMSGE) with the chelate catalyst to a very high molecular weight polymer and then converting it by methanolysis to a new polymer, high molecular weight polyglycidol, an interesting water-soluble elastomer [9] (Fig. 1). This product was amorphous by

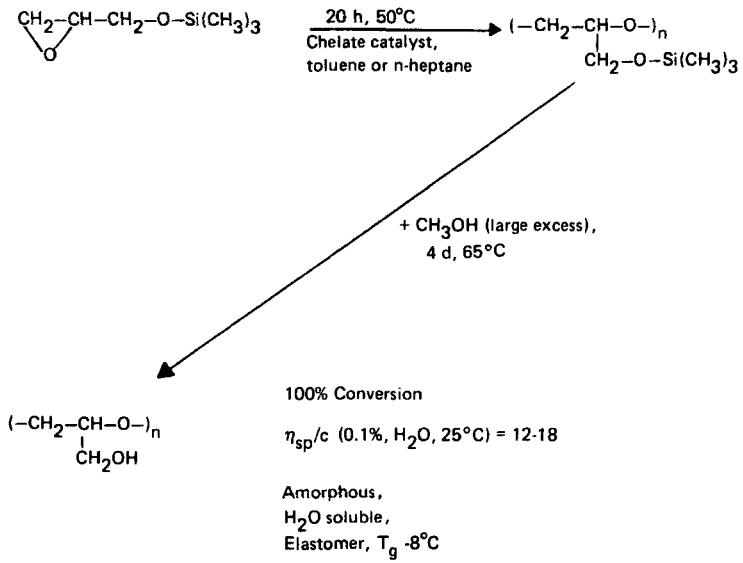
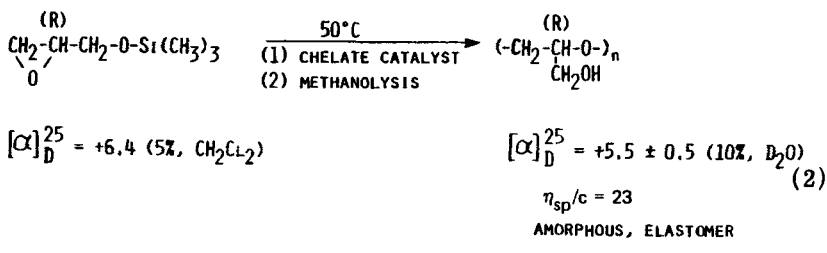


FIG. 1. Synthesis and properties of polyglycidol.

x-ray, presumably atactic, with a T_g of -8°C. Subsequently, some related work on glycidol and TMSGE polymerization has appeared in the literature. Sandler and Berg reported obtaining a liquid polyglycidol of very low molecular weight (445) by polymerizing glycidol with various base catalysts [10]. Tsuruta et al. reported polymerizing glycidol and TMSGE with various organometallic catalysts and then methanolyzing the TMSGE polymer to polyglycidol [11]. With Et_3Al-0.7H_2O and n-Bu_2Mg as catalysts, glycidol gave the low molecular weights ($[\eta]$, intrinsic viscosity, up to 0.07 in CH_3OH) reported by Sandler, and TMSGE gave somewhat higher viscosity polyglycidol ($[\eta]$ up to 0.4). In a study of other organometallic catalysts on TMSGE, the Et_2Zn-H_2O catalyst gave the highest molecular weight polyglycidol with $[\eta]$ in CH_3OH of 1.8. The viscosity of Tsuruta's polyglycidol is thus an order of magnitude lower than we obtained with the chelate catalysts. Rates of polymerization and conversion also appear lower. Tsuruta also reports that the polyglycidol from glycidol polymerization has the same IR spectra as that obtained via TMSGE.

Our polyglycidol as well as that reported in the literature appeared to be atactic. Presumably, the isotactic form should be a high melting crystalline polymer since its hydrocarbon analog, isotactic poly(propylene oxide), is a crystalline polymer with a melting point of about 70°C. Over the years we have made numerous attempts with different catalysts to make this crystalline isotactic polyglycidol without a great deal of success. Recently, we have explored this problem further and used two approaches to the synthesis of isotactic polyglycidol [5]. In the first approach we prepared the pure R-enantiomer of TMSGE from the well-known R-glycidol in order to utilize the method first used by Price [12] to make isotactic poly(propylene oxide), i.e., the base-catalyzed polymerization of R-propylene oxide. The second approach was to make isotactic poly(tert-butyl glycidyl ether) and then convert it to polyglycidol.

In our work on polymerizing R-TMSGE, we quickly found that a simple base catalyst such as the KOH used by Price [12] could not be utilized because of the reactivity of the trimethylsilyl ether group. The side reactions are complex and have been discussed in detail [13]. We then polymerized R-TMSGE with our chelate catalyst under our usual conditions for racemic TMSGE. The polyglycidol obtained was an optically active polymer but it was still an amorphous elastomer:



(2)

The ^{13}C-NMR of the poly(R-glycidol) (Fig. 2) shows clearly that it is indeed isotactic polyglycidol with mainly three sharp, equal peaks at the expected locations for the three carbons of polyglycidol. Contrast this with the ^{13}C-NMR of the poly(RS-glycidol) made under the same conditions where there are peaks due to other than isotactic sequences. The CH group shows three peaks due to isotactic (δ 79.71), heterotactic (δ 79.59), and syndiotactic (δ 70.50) triads, and the chain CH_2 shows two peaks due to isotactic (δ 68.88) and syndiotactic (δ 68.60) dyads, as expected for an amorphous, atactic polymer. However, the ^{13}C-NMR of our products from racemic and R-enantiomer monomer show minor peaks around δ 78.2, 70.3, 70.8, and 61.2 which are due to some head-to-head and tail-to-tail polymerization– ~6 to 10%–in addition to the usual head-to-tail polymerization. The chelate catalyst was previously found to give substantial amounts–20 to 30%– of these abnormal units in propylene oxide polymerization. This poly(R-glycidol) does, however, crystallize on stretching, relaxing, restretching, and then holding it taut. In this way we have obtained a highly crystalline, highly-oriented x-ray pattern which loses most of its crystallinity on relaxing. Atactic polyglycidol does not crystallize on stretching. We have made pure (99%) head-to-tail poly(R-glycidol) by catalyst and polymerization modifications and found that it exhibits the same reluctance to crystallize [5].

The second method of preparing isotactic poly(RS-glycidol), based on preparing isotactic poly(RS-tert-butyl glycidyl ether) and hydrolyzing it [5], gave lower molecular weight (η_{sp}/c = 2.1), isotactic polymer which crystallized somewhat better but still reluctantly (mp 60°C).

Small amounts of H_2O (6-12%) in isotactic polyglycidol markedly influences its glass transition, lowering it to -30 to -40°C from the usual -8 to -12°C in the dry state, based on DSC studies. This effect of H_2O on T_g and the reluctance of isotactic polyglycidol to crystallize may be due to the ready formation of intramolecular hydrogen bonds via 5- or 6-membered rings as shown in Fig. 3 [5].

Poly(cis-1,4-dihydroxy-2,3-epoxybutane)

The properties of polyglycidol and the importance of hydroxy-substituted polyethers in nature prompted the preparation of a poly(ethylene oxide) with a hydroxymethyl group on every chain carbon, i.e., poly(cis-1,4-dihydroxy-2,3-epoxybutane), $(-CH(CH_2OH)-CH(CH_2OH)-O-)_n$, PDHEB. The author previously reported the synthesis and unusual properties of the chlorine-substituted analogues, poly(cis- or trans-1,4-dichloro-2,3-epoxybutane) [14]. Complete details on the synthesis and properties of PDHEB are being reported separately [15]. The important results are summarized below.

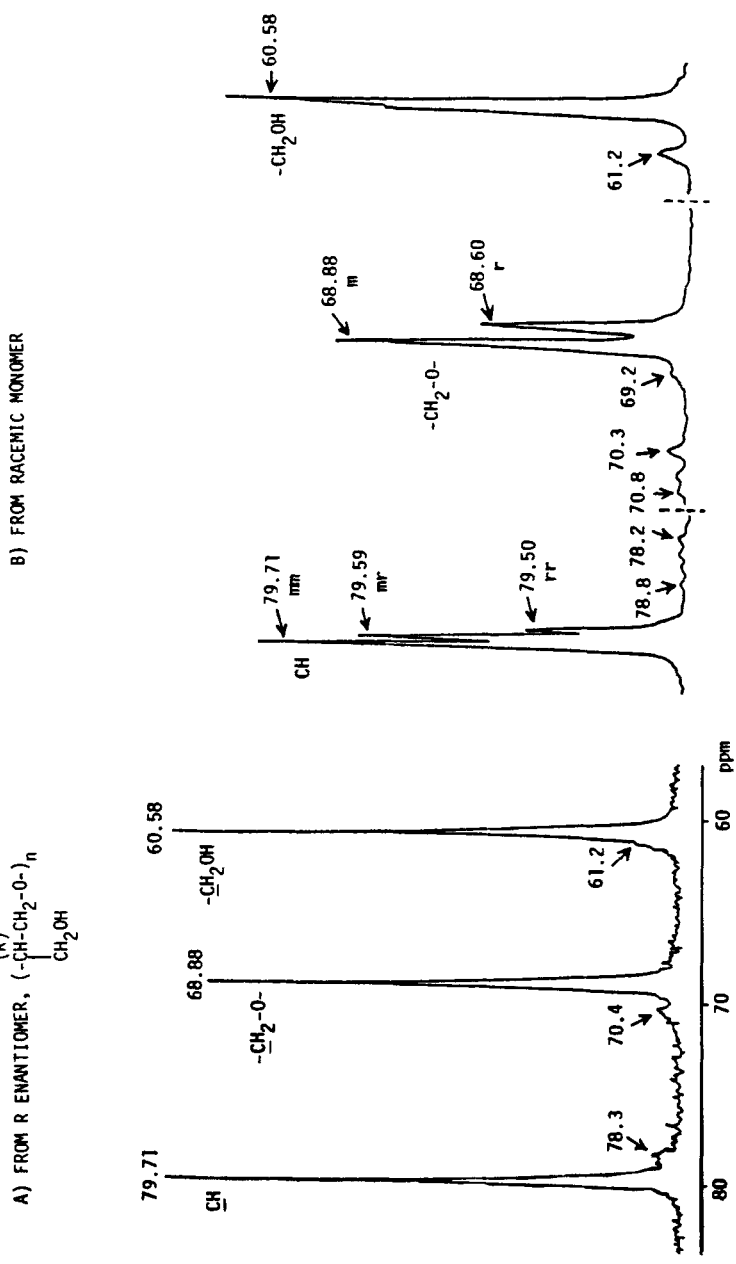


FIG. 2. ^{13}C-NMR of polyglycidols prepared in toluene at 50°C with chelate catalyst. D_2O, 62.9 MHz.

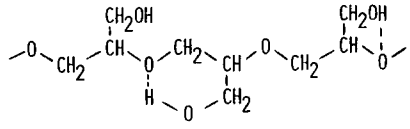


FIG. 3. Intramolecular hydrogen bonding in polyglycidol.

Monomer Syntheses

As in the prior synthesis of polyglycidol [5], the hydroxyl was blocked with an acid labile group either as the trimethylsilyl ether (TMS-DHEB) [13, 16] or as the cyclic acetone ketal, 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (DMTO) [17, 18]. The high yield syntheses from the commercial (GAF) cis-2-butene-1,4-diol are given in Figs. 4 and 5.

These monomers gave the best results in cationic polymerizations at -78°C in toluene diluent (10% monomer) with i-Bu_3Al-0.7H_2O (in heptane) catalyst to give high yields of soluble polymer with η_{inh} ($CHCl_3$) of 0.16 (TMS-DHEB) and up to 0.7 (DMTO). These polymers were converted to PDHEB by treatment in toluene solution with 3% aqueous HCl for 6-24 h at 65°C and recovered by dialysis and freeze drying of the aqueous phase.

An investigation of other polymerization catalysts and conditions indicated that TMS-DHEB was much more difficult to polymerize—giving only low molecular weight polymer (η_{inh} 0.04) in bulk at 65°C

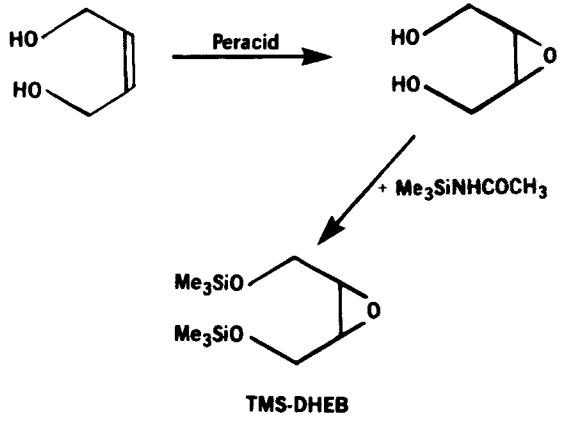


FIG. 4. Synthesis of bis(trimethylsilyl) ether of cis-1,4-dihydroxy-2,3-epoxybutane.

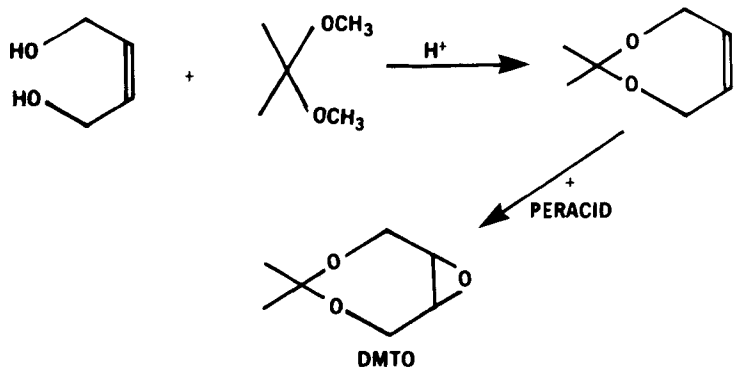


FIG. 5. Synthesis of cyclic acetone ketal of cis-1,4-dihydroxy-2,3-epoxybutane.

with our coordination chelate catalyst [5]. On the other hand, the chelate catalyst worked better in bulk on DMTO at 65°C (η_{inh} 0.13). It appears probable that improved coordination catalysts can be devised. The cationic i-Bu_3Al-0.7H_2O catalyst when used in bulk at higher temperature (0°C) on DMTO gave η_{inh} 0f 0.28 and up to 14% crosslinked polymer as a result of epoxide and ketal ring-opening. Et_3Al and i-Bu_3Al were fairly good catalysts for DMTO in bulk at 0-50°C (η_{inh} up to 0.27). Since ether addition is detrimental with these R_3Al catalysts, these polymerizations are presumed to be cationic.

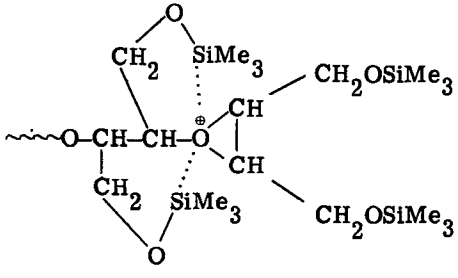
Properties

PDHEB from the complete hydrolysis of PDTMO is amorphous, water-soluble, forms brittle, clear films when dry, with a T_g of 77°C (from DSC and rheological data), and has η_{inh} (H_2O) of 0.43 [15]. Water solutions of PDHEB (2%) do not precipitate on heating up to 150°C in a sealed vessel whereas polyglycidol precipitates at about 120-140°C. The polymer recovered by freeze drying usually contains 5-10% H_2O and in this state is tough and flexible. Similar water levels are quickly obtained when dry polymer is handled in ambient air. PDHEB containing a small amount of H_2O can be compression molded at about 100-120°C with some difficulty to give clear flexible films with mechanical properties much like plasticized poly(vinyl chloride). Rheological studies indicate that the unstabilized polymer is very

stable at 200°C under nitrogen. Dynamic shear rate data on dry polymer under nitrogen at 120, 150, and 200°C indicates that it changes from the rubbery state to the melt at about 150°C. Thus, the polymer should be melt processable above 150°C. Compression molding studies indicate that 200°C may be needed for good flow in the dry state. This result is surprising in view of the relatively low molecular weight of PDHEB. A plasticizer such as 15% water reduces the required molding temperature to 150°C. Treatment of a PDHEB film with electron beam radiation degraded it with only a trace of crosslinking. PDHEB was readily crosslinked with acetal links by treating with 0.4% gyloxal plus 0.7% toluene sulfonic acid in a 25% aqueous solution, followed by drying at 80°C.

Stereochemistry

The ^{13}C-NMR of PDHEB from DMTO or TMS-DHEB has two main peak areas (Fig. 6), one being the multiplet due to the chain CH carbons from 79.5 to 77.0 ppm and the other due to the side chain CH_2OH at 59.1 ppm. Based on prior work on the 2,3-epoxybutanes and related symmetrical disubstituted epoxides [14, 19], the CH peaks of stereoregular polymer should be a singlet for the expected units, i.e., either racemic diisotactic polymer with all R or S carbons or the meso disyndiotactic polymer with RR-SS chain carbon sequences. It is, of course, expected that ring opening occurs with complete inversion of configuration of the ring-opening carbon as shown previously [1] for epoxide polymerization. Atactic polymer should have four peaks based on prior work [19], and this appears to be the case for the polymer from DMTO (Fig. 6). However, the PDHEB made from TMS-DHEB is largely tactic (~80-90%), probably racemic diisotactic with chains having largely R or S carbons. Previously, with cis-1,4-dichloro-2,3 epoxybutane [14] and cis-butene-2-episulfide [20], such tacticity was explained by chain-end control. We propose the same mechanism here, i.e., the Me_3Si of the chain end interacts with the growing oxonium ion to promote attack on the same carbon in each propagation step:



(3)

The interaction shown by the β substituent with the oxonium ion to form a six-membered ring appears more likely and is similar to the

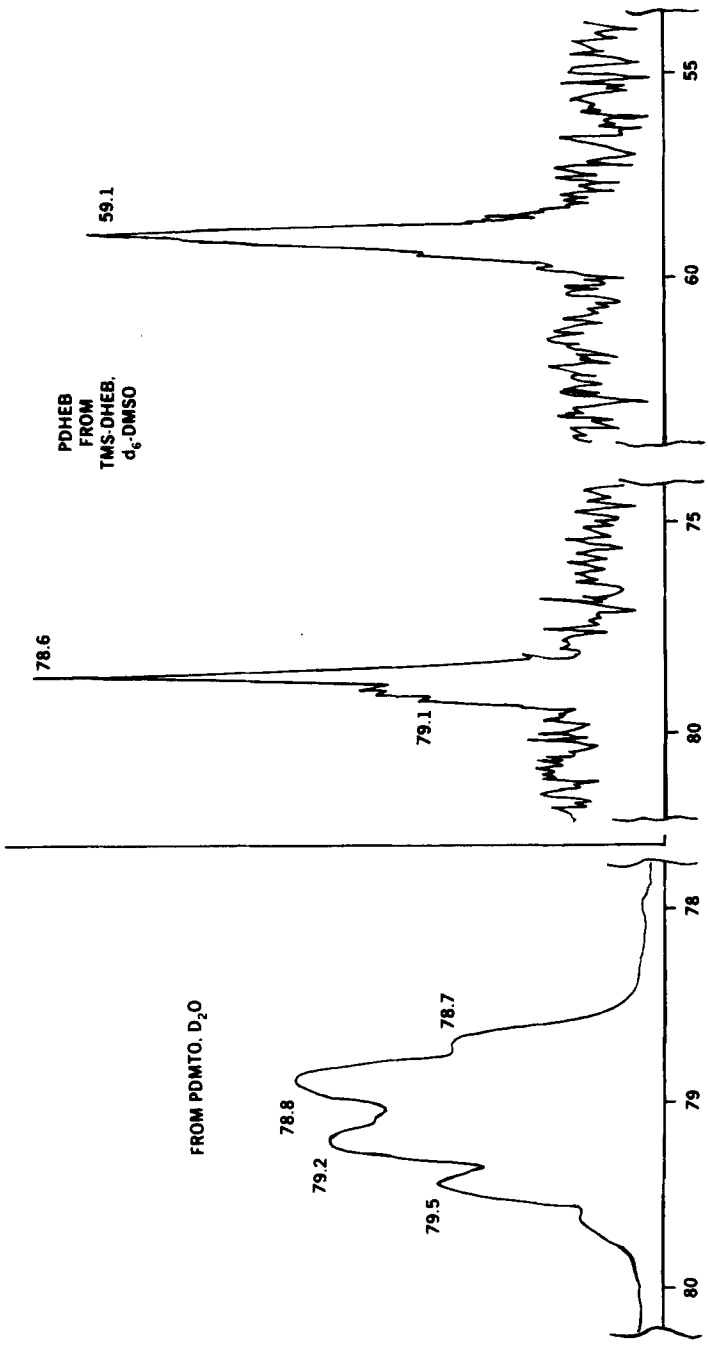


FIG. 6. ^{13}C-NMR of PDHEB prepared with i-Bu_3Al-0.7H_2O catalyst at -78°C. D_2O and d_6DMSO, 90 MHz.

mechanism previously proposed [14]. We recently reported a similar interaction of the $SiMe_3$ group with a growing oxonium ion in the cationic polymerization of trimethylsily glycidyl ether which influenced head-to-tail vs head-to-head polymerization [13].

The finding that DMTO yields atactic polymer appears reasonable since the side-chain ring structure minimizes freedom of motion of the side chain of the last chain unit and prevents these groups from facilitating stereoregular polymerization as previously reported [14].

CONCLUSIONS

Polyglycidol and PDHEB are interesting water-soluble polymers with some unusual properties which merit further study, particularly with regard to utility. In the case of PDHEB, higher molecular weights are desirable and can probably be achieved by catalyst, particularly coordination catalyst, studies. The stereoregular PDHEB needs further study and a better synthesis. Hydroxy polyethers, in general, merit extensive future study since they are analogues of the biochemically-important polysaccharides.

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