

# Reactions of Glycerol with Poly(Ethylene Ether Carbonate) Polyols

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## SYNOPSIS

Poly(ethylene ether carbonate) polyols can be modified by chemical reactions with polyglycol modifiers under conditions of elevated temperatures and reduced pressures. The modifier becomes chemically incorporated into the modified polyol and is used to control properties such as moisture sensitivity, CO<sub>2</sub> content,  $T_g$ , density, etc. in the resultant polyol. However, glycerol cannot be used as a modifier for poly(ethylene ether carbonate) polyols under the same conditions since it reacts with poly(ethylene ether carbonate) polyols by a transesterification reaction sequence to form glyceryl carbonate. As the temperature is increased, the glyceryl carbonate decomposes to yield glycidol and carbon dioxide. These reactions are conveniently followed by <sup>13</sup>C-NMR. The preparation of glyceryl carbonate by this process has not been previously reported.

## INTRODUCTION

Poly(ethylene ether carbonate) polyols are polymers that contain alternating blocks of carbon dioxide units and poly(ethylene glycol) units in their backbones. When these polyols are prepared from ethylene carbonate (or ethylene oxide and carbon dioxide) and diethylene glycol (DEG), backbone hydrolysis studies<sup>1</sup> and <sup>13</sup>C-NMR studies<sup>2</sup> have shown that the backbone structure is highly dependent on the catalyst employed. When a sodium stannate trihydrate–potassium carbonate mixed catalyst system is used, these polyols contain predominantly DEG, triethylene glycol (TriEG), and tetraethylene glycol (TetraEG) backbone units with smaller quantities of higher units, and the polyols have largely —OC(O)OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH end groups. When heated to elevated temperatures (> 180°C) at reduced pressures, volatile impurities are removed from the polyols, followed by molecular weight advancement and formation of DEG.<sup>3–6</sup> As

DEG (and lesser amounts of TriEG) is removed as distillate, molecular weight builds in a controllable manner. This is thought to be a transesterification process in which —OC(O)CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH end groups on one molecule react with carbonate moieties on a second molecule with loss of DEG. These molecular weight advanced polyols form rapidly with high CO<sub>2</sub> retention, relatively low polydispersity, and high purity.

Poly(ethylene ether carbonate) polyols can be modified by chemical reactions with polyglycol modifiers under these molecular weight advancement conditions.<sup>7–11</sup> The modifier becomes chemically incorporated into the modified polyol and is used to control properties such as moisture sensitivity, CO<sub>2</sub> content,  $T_g$ , density, etc. in the resultant polyol. Since unmodified poly(ethylene ether carbonate) polyols have predominately polyester polyol properties, modification with polyether polyols can be used to adjust properties between those of polyether and polyester polyols. These polyols are useful in polyurethane applications.<sup>12–15</sup>

When glycerol was evaluated as a modifier for poly(ethylene ether carbonate) polyols, it was found to be an anomaly. This work discusses the chemistry that occurs when glycerol is used as a modifier.

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## EXPERIMENTAL

Glycerol and glycidol were obtained from Aldrich Chemical Co. Diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TetraEG), and Voranol 2025 [glycerol-initiated propylene oxide (PO) adduct; 2.8 PO,  $\bar{M}_n = 255$ , 20% OH] were manufactured by Dow Chemical Company. Glyceryl carbonate was obtained from City Chemical Corporation. The molecular weights and distribution were determined by size exclusion chromatography (SEC) on Waters Ultrastyrigel 500-, 1000-, and 10,000-Å columns, in series, using tetrahydrofuran (THF) as the mobile phase and calibrated with narrow molecular weight poly(ethylene glycols) using a refractive index detector. NMR spectra were obtained on a Varian Gemini 300 NMR instrument (300 MHz for proton and 75 MHz for carbon) using DMSO- $d_6$  as solvent. The CO<sub>2</sub> content of the poly(ethylene ether carbonate) polyols was measured by quantitative proton NMR in CDCl<sub>3</sub> using dimethylsulfoxide as the internal standard.

### Poly(Ethylene Ether Carbonate) Polyol Synthesis

All work was done using the same poly(ethylene ether carbonate) diol. It was prepared from ethylene oxide, CO<sub>2</sub>, and DEG using a sodium stannate trihydrate-potassium carbonate mixed catalyst system.<sup>16</sup> The catalysts were removed by dissolving the polyol in acetone, stirring with Florisil, filtering, and acetone stripping.<sup>17</sup> The polyol was a colorless liquid having the following properties:  $\bar{M}_n = 779$ ,  $\bar{M}_w = 1291$ ,  $\bar{M}_w/\bar{M}_n = 1.66$ , 20.2 wt % CO<sub>2</sub>.

### Polyol Modification-Molecular Weight Advancement Procedure

A given amount of poly(ethylene ether carbonate) diol, modifier (when used), and boiling stones were placed in a boiling flask equipped with a thermometer, heating mantle, and attached to a water chilled, down draft condenser and trap ( $\sim 15^\circ\text{C}$ ), dry ice-isopropanol trap ( $-78^\circ\text{C}$ ), and a vacuum source. A simple take off head was used (no column). The system was heated to 60–80°C to reduce viscosity and outgassed at about 50 mm Hg. The vacuum was then adjusted to 10 mm Hg pressure and heating increased to affect fractionation. The distillate was weighed and analyzed. In experiments where samples were collected at various pot temperatures, the reaction setup was modified to include a syringe port where pot samples could be removed without disturbing the system vacuum.

### Transesterification Procedure

The poly(ethylene ether carbonate) diol (catalyst removed) and modifier were weighed into a reactor equipped with overhead stirring, thermometer, condenser, heating control system, and maintained under a nitrogen atmosphere. The reaction temperature was established and small samples were removed from the reactor at appropriate times and analyzed.<sup>18,19</sup>

## RESULTS AND DISCUSSION

### Glycerol as a Modifier under Molecular Weight Advancement Conditions

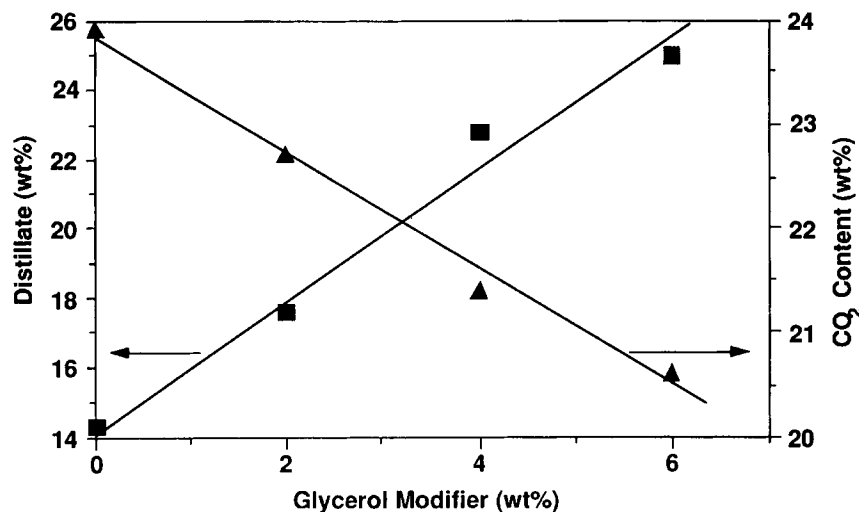
When poly(ethylene ether carbonate) polyols and polyol modifiers are heated to elevated temperatures ( $> 180^\circ\text{C}$ ) at reduced pressures, volatile impurities are removed from the polyols, followed by molecular weight advancement and formation of DEG. Removal of the DEG from the system controls the molecular weight build. The modifier is chemically incorporated into the product and modifies its properties (Fig. 1). However, when glycerol is used as modifier under the same reaction conditions, gas is evolved during the process and the resultant product does not contain any glycerol moieties and has the same <sup>13</sup>C-NMR spectrum obtained in the absence of modifier. Since the glycerol has a higher boiling point (167°C at 10 mm Hg) than DEG (134°C at 10 mm Hg), the DEG should be removed selectively under the distillation process, while the glycerol should remain with the product in the flask.

Table I summarizes the results of experiments where 2, 4, and 6 wt % glycerol was added to the poly(ethylene ether carbonate) diol prior to the advancement process. Results are also presented where the poly(ethylene ether carbonate) diol alone was subjected to the advancement process to produce a series of products in the same molecular weight range. Several differences are apparent. There is an approximately linear increase in the weight of distillate formed and a linear decrease in the CO<sub>2</sub> content of the product as the glycerol level is increased (Fig. 2). In addition, there is a systematic increase in the amount of material unaccounted for (passing through the  $-78^\circ\text{C}/10$  mm Hg trap).

### <sup>13</sup>C-NMR Study Using Glycerol as Modifier under Molecular Weight Advancement Conditions

An experiment was run in which glycerol (6 wt %) was added initially to the poly(ethylene ether car-





**Figure 2** Effect of glycerol modifier level on amount of distillate formed and product carbon dioxide content.

of glycerol with a carbonate moiety on the poly(ethylene ether carbonate) diol (Fig. 5). Glyceryl carbonate (**6**) was further confirmed by an NMR of the pure material and by a mixed NMR at ambient temperature.

As heating is continued, the first drop of distillate is removed at a pot temperature of 168°C. Additional samples are removed and analyzed by <sup>13</sup>C-NMR at pot temperatures of 175 and 185°C. These samples have essentially the same components as the 166°C sample. Samples removed at pot temperatures of 195 and 215°C were essentially only advanced poly(ethylene ether carbonate) diol (Figs. 3 and 4).

The distillate was analyzed by <sup>13</sup>C-NMR and found to be essentially a seven-line pattern (Fig. 6). The bulk of the distillate was DEG (61.2 and 72.8 ppm) and TriEG (61.2, 70.5, and 72.9 ppm). A small amount of ethylene carbonate was present (65.6 ppm). Glycidol (**7**) was present as a three-line pat-

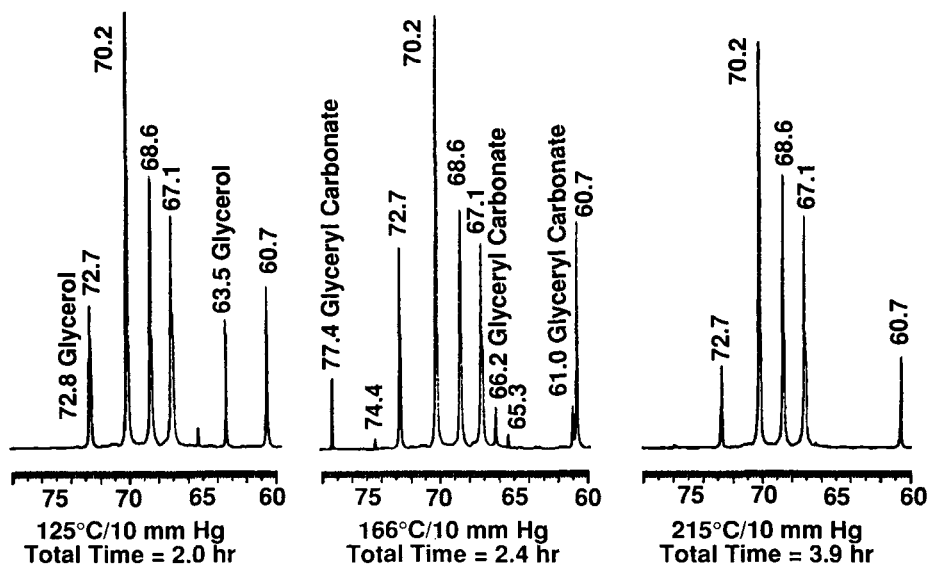
tern (44.2, 52.8, and 62.6 ppm) and was further confirmed by an NMR of the pure material and by a mixed NMR at ambient temperature. Loss of CO<sub>2</sub> accounts for the systematic increase in unaccounted for material when glycerol is used as modifier (Table I).

### Proposed Reaction Sequence

The proposed reaction sequence is given in Figure 5. A hydroxyl moiety on glycerol reacts with a carbonyl moiety of the poly(ethylene ether carbonate) diol (**1**) to yield a transient intermediate that can either (a) release DEG to form linear carbonate (**4a**) or (b) release a poly(ethylene ether carbonate) diol fragment (**5**) to form linear carbonate (**4b**). Both (**4a**) and (**4b**) can undergo an intramolecular cyclization to yield transient intermediates, which release glyceryl carbonate (**6**). At the same time, the

**Table II** Reactor Conditions and Carbon-13 NMR Analysis of Product

Sample Number	Reaction Time (h)	Temperature		Pressure (mm Hg)	Components in Reactor by <sup>13</sup> C-NMR
		Pot (°C)	Head (°C)		
1	1.6	75	25	10	<b>1</b> , glycerol
2	2.0	125	25	10	<b>1</b> , glycerol
3	2.4	166	70	10	<b>1</b> , <b>4a</b> and/or <b>4b</b> ; glyceryl carbonate ( <b>6</b> )
4	2.7	175	129	10	<b>1</b> , <b>4a</b> and/or <b>4b</b> ; glyceryl carbonate ( <b>6</b> )
5	3.0	185	130	10	<b>1</b> , <b>4a</b> and/or <b>4b</b> ; glyceryl carbonate ( <b>6</b> )
6	3.3	195	131	10	<b>1</b> , glyceryl carbonate (trace)
7	3.9	215	131	10	<b>1</b>



**Figure 3** Reaction of glycerol with a poly(ethylene ether carbonate) diol followed by  $^{13}\text{C}$ -NMR of methylene and methine carbon atoms.

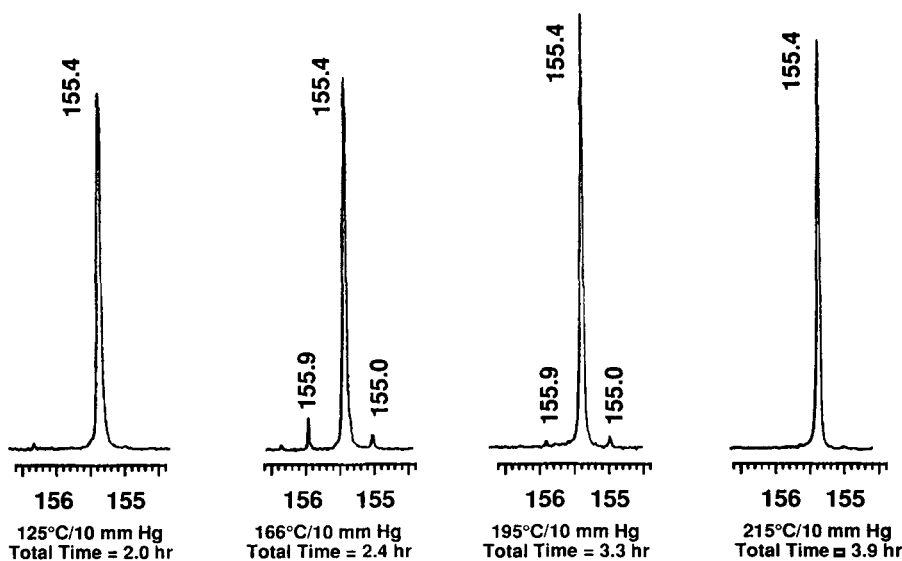
poly(ethylene ether carbonate) diol (**1**) and the linear carbonates (**4a**, **4b**) undergo a series of transesterification reactions to form the molecular weight advanced, unmodified poly(ethylene ether carbonate) diol product, while DEG and TriEG are removed as distillate.<sup>3-5</sup>

The transesterification reactions of glycerol with simple carbonates to form glyceryl carbonate (**6**) is well known.<sup>20-23</sup> However, the corresponding transesterification reactions of glycerol with poly(ethylene ether carbonate) polyols has not been

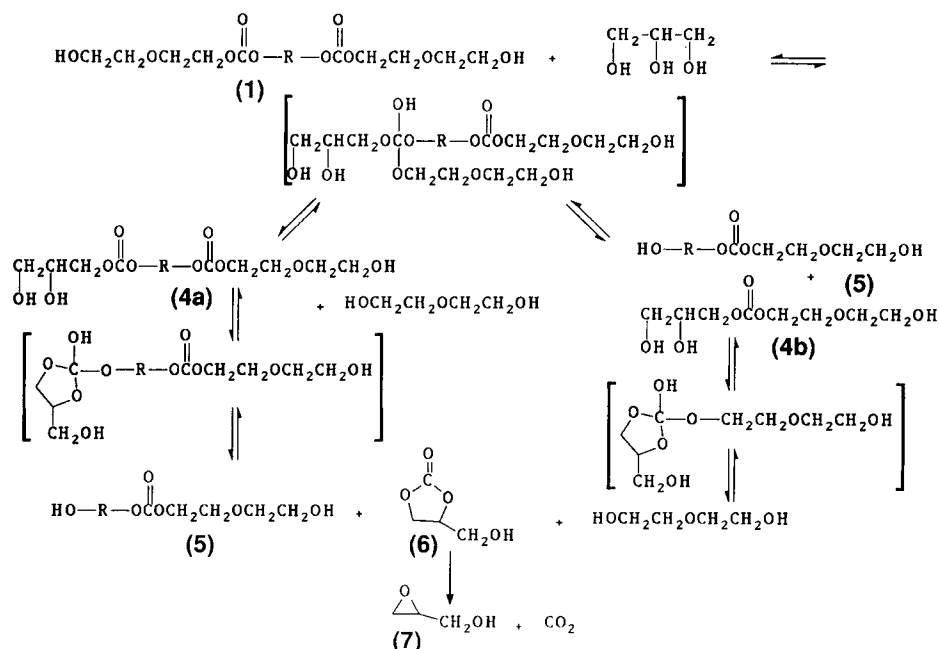
previously reported. The decomposition of glyceryl carbonate (**6**) to glycidol (**7**) and carbon dioxide is known to occur thermally at about 200°C<sup>20,21,24,25</sup> and can be easily followed by  $^{13}\text{C}$ -NMR (Fig. 7).

#### $^{13}\text{C}$ -NMR Study Using Glycerol as Modifier under Transesterification Conditions

A second experiment was run in which glycerol (6 wt %) was added initially to the poly(ethylene ether carbonate) diol (**1**) and the mixture was heated to



**Figure 4** Reaction of glycerol with a poly(ethylene ether carbonate) diol followed by  $^{13}\text{C}$ -NMR of carbonyl carbon atoms.



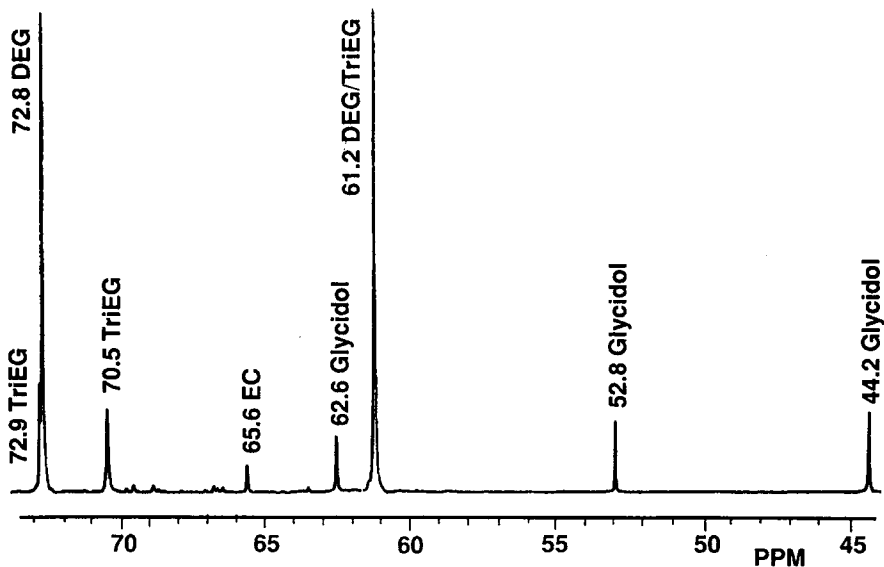
**Figure 5** Sequence for the reactions of glycerol with a poly(ethylene ether carbonate) diol.

175°C at atmospheric pressure. Samples were removed for  $^{13}\text{C}$ -NMR analysis at various stages during the transesterification process. The glycerol was completely converted to glyceryl carbonate (**6**) and the linear carbonates (**4a**, **4b**) by the time the mixture reached 175°C. After 2 h at 175°C, only glyceryl carbonate (**6**) and poly(ethylene ether carbonate) diol (**1**) were present. Therefore, the same reaction

sequence occurs under transesterification conditions.

#### Voranol 2025 as Modifier under Transesterification Conditions

The problem with using glycerol as a modifier is due to hydroxyl moieties on adjacent carbon atoms with



**Figure 6** Reaction of glycerol with a poly(ethylene ether carbonate) diol followed by  $^{13}\text{C}$ -NMR of distillate.

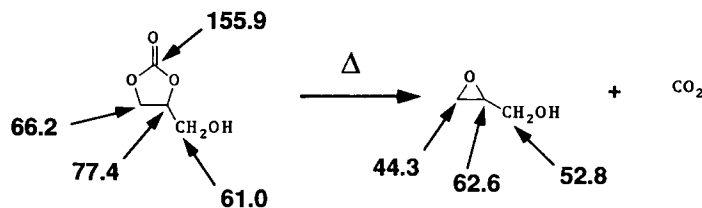


Figure 7 Thermal decomposition of glyceryl carbonate studied by  $^{13}\text{C}$ -NMR.

resultant five-membered ring formation in the presence of carbonate moieties at elevated temperatures. This situation is circumvented by using Voranol 2025, a glycerol-propylene oxide adduct (1 : 2.8 molar ratio).

The poly(ethylene ether carbonate) diol and Voranol 2025 (20 wt %) were combined and heated to  $175^\circ\text{C}$  under nitrogen. Reaction was easily followed by  $^{13}\text{C}$ -NMR of the methyl and carbonyl carbon atoms. Line assignments for related systems have been reported.<sup>11</sup> The poly(ethylene ether carbonate) diol starting material has only one kind of carbonyl carbon (155.4 ppm). However, since Voranol 2025 has secondary hydroxyl end groups, its reaction with carbonate carbonyl moieties produces a different kind of carbonyl moiety—a carbonate connected to both methylene and methine carbon atoms (155.0 ppm). Figure 8 illustrates these structures and gives the associated line spectra.

There are no methyl moieties in the poly(ethylene ether carbonate) diol starting material. Voranol 2025 has two different kinds of methyl moi-

eties: the methyl groups attached to a carbon atom adjacent to a hydroxyl end group (20.0/20.1 ppm) and the methyl groups attached to a carbon atom adjacent to an ether oxygen moiety (17.1 ppm). The modification reaction produces an additional kind of methyl group: methyl groups on the methine carbon atom attached to carbonyl moieties (16.2 ppm). Figure 9 illustrates these structures and gives the associated line spectra.

#### Voranol 2025 as Modifier under Molecular Weight Advancement Conditions

The poly(ethylene ether carbonate) diol and Voranol 2025 (20 wt %) were combined and heated slowly under reduced pressure (10 mm Hg) with distillate removal to a pot temperature of  $230^\circ\text{C}$ . The product was a light amber liquid and represented 80.7 wt % of the reactants charged.  $^{13}\text{C}$ -NMR analysis of the product showed the expected line spectrum consistent with Figures 8 and 9.

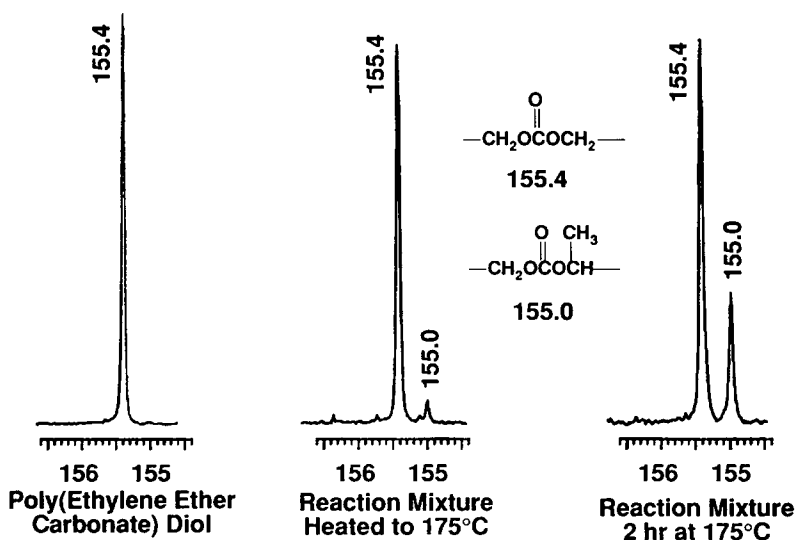
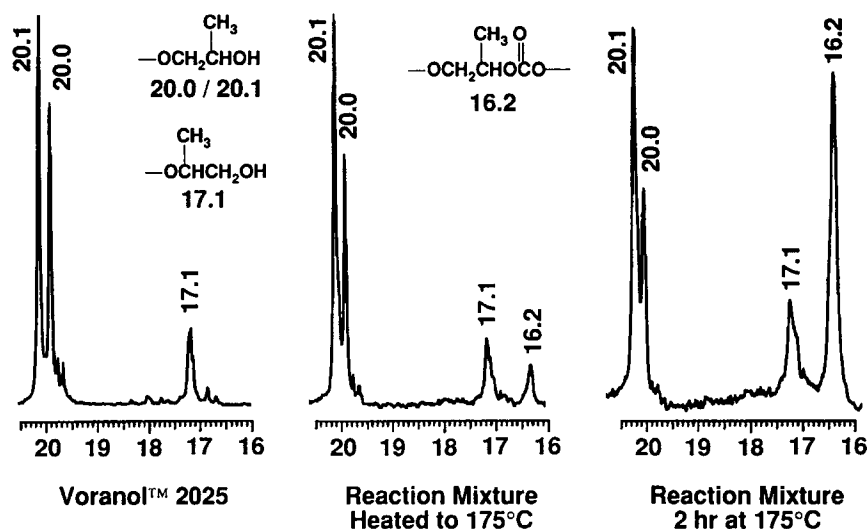


Figure 8 Reaction of Voranol 2025 with a poly(ethylene ether carbonate) diol followed by  $^{13}\text{C}$ -NMR of carbonyl carbon atoms.



**Figure 9** Reaction of Voranol 2025 with a poly(ethylene ether carbonate) diol followed by  $^{13}\text{C}$ -NMR of methyl carbon atoms.

## CONCLUSIONS

Glycerol cannot be used as a modifier for poly(ethylene ether carbonate) polyols since it reacts with poly(ethylene ether carbonate) polyols at elevated temperatures by a transesterification reaction sequence to form glyceryl carbonate. As the temperature is increased, the glyceryl carbonate decomposes to yield glycidol and carbon dioxide. These reactions are conveniently followed by  $^{13}\text{C}$ -NMR. The preparation of glyceryl carbonate by this process has not been previously reported.

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