

Structural Features of Poly(alkylene Ether Carbonate) Diol Oligomers by Capillary Gas Chromatography

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Synopsis

A series of poly(ethylene ether carbonate) diol oligomers were synthesized from ethylene carbonate (EC) using various catalysts and low EC: initiator molar ratios. The structures of these oligomers have been studied by alkaline degradation to the poly(ethylene glycol)s, which make up their backbone, followed by capillary gas chromatographic (CGC) analysis. Comparisons of CGC traces before and after hydrolysis indicate which volatile components contain carbonate moieties. Some poly(ethylene glycol)s were not chemically bound into the polymer backbone and were analyzed directly by CGC. Based on the combination of analytical techniques developed in this study, it is possible for the first time to establish the approximate composition of a given poly(ethylene ether carbonate) diol. A typical composition made using a sodium stannate trihydrate catalyst consists of (1) an oligomeric portion which is a copolymer of carbon dioxide and poly(ethylene glycol)s and (2) a monomeric portion which consists mostly of diethylene glycol with lesser quantities of monoethylene glycol, triethylene glycol, 1,4-dioxane and unreacted ethylene carbonate.

INTRODUCTION

Poly(alkylene ether carbonate) polyols are the reaction products of an alkylene carbonate or an alkylene oxide and carbon dioxide with an alcoholic initiator in the presence of an appropriate catalyst.¹⁻¹⁷ These materials are valuable as polyols in polyurethanes and as chemical intermediates.

There are many references to the preparation of these polyols using a variety of catalysts and to their utility as polyols. However, there has been very little definitive work directed toward the detailed structural features of these materials.

Since carbonate moieties are rather labile, especially under alkaline conditions, backbone hydrolysis is one approach toward probing the backbone structure of poly(alkylene ether carbonate) polyols. Soga et al.¹⁰ hydrolyzed some materials of this type with 0.6*N* KOH in ethanol. Gas chromatographic analysis of the resulting liquid product showed only one peak, with a retention time corresponding to diethylene glycol. Sakai et al.¹⁶ hydrolyzed structures related to poly(alkylene ether carbonate) polyols which were made from *n*-octanol initiated ethylene carbonate reactions using mixed tin alkoxides as catalysts. This procedure involved dilute alkaline hydrolysis followed by neutralization with acid and ether extraction. Analysis indicated diethylene glycol at 80% of the anticipated level. Vogdanis and Heitz¹⁷ recently reported hydrolysis work which gives more detailed structural information when certain catalysts are employed.

The current work details the backbone hydrolysis of several poly(ethylene ether carbonate) diol oligomers and discusses the structural units present in the backbone prior to hydrolysis as a function of the catalyst used in their preparation. Some glycols which do not contain carbonate moieties are also present with the oligomers.

EXPERIMENTAL

Materials

Ethylene carbonate (EC, distilled prior to use), 1,6-hexanediol (99 + %) and all catalysts were obtained from Aldrich. All poly(ethylene glycol)s were produced at the Dow Chemical Company. Dimethylsulfoxide (DMSO) was obtained from Burdick & Jackson and dried over molecular sieves.

Synthesis of Poly(ethylene Ether Carbonate) Diols

Poly(ethylene ether carbonate) diol oligomers were synthesized by reacting an initiator (monoethylene glycol, MEG or diethylene glycol, DEG) with ethylene carbonate (EC) in the presence of a catalyst. Low EC: initiator molar ratios (5 to 15) were used to make low molecular weight products. The reaction conditions employed and the CO₂ content of each material are given in Table I.

Hydrolysis Procedure

A standard solution of diols and 1,6-hexanediol (internal standard) was prepared in acetone at the approximate relative concentrations expected after hydrolysis and was used to develop relative response factors. The poly(ethylene ether carbonate) diol sample to be analyzed (about 4.0 g) and 1,6-hexanediol (about 0.4 g) were weighed to four significant figures into a 125 mL, single-necked flask equipped with a condenser and drying tube. A solution of 1.25*N*

TABLE I
Reaction Conditions and Carbon Dioxide Content of Poly(Ethylene Ether Carbonate) Diols Synthesized

Sample number	Initiator	EC: initiator molar ratio	Catalyst (0.5 wt%)	Time (h)	Temperature (°C)	CO ₂ ^a retained (mol%)	Wt% ^b CO ₂
1	MEG	5	Na ₂ SnO ₃ · 3H ₂ O	4	150	39.9	23.7
2	MEG	5	Na ₃ VO ₄	7	150	28.4	18.4
3	MEG	5	KF	2	175	9.8	7.5
4	MEG	5	K ₂ CO ₃ ^c	2	175	9.9	7.7
5	DEG	5	Na ₂ SnO ₃ · 3H ₂ O	7	150	44.1	23.1
6	DEG	15	Na ₂ SnO ₃ · 3H ₂ O	8	150	34.2	21.8
7	DEG	5	Na ₃ VO ₄	1.5	175	31.2	17.5
8	DEG	5	Na ₂ WO ₄	4.5	175	25.8	15.0
9	DEG	5	Na ₂ B ₂ O ₂	6	175	20.6	12.5
10	DEG	5	K ₂ MoO ₄	4	175	27.2	16.2

^aMol% of CO₂ present in EC charged which is present in product.

^bDetermined by NMR.

^c1.0 wt% catalyst.

NaOH in methanol (25 mL) was added and the resultant solution was stirred magnetically at reflux for 1 h. After cooling, the solution was diluted with about 50 mL of methanol and the pH adjusted to about 4.5 with HCl gas using a pH meter and a combination electrode. The resultant sample was further diluted with methanol. The precipitated NaCl was allowed to settle and the clear supernatant was analyzed for diols by capillary gas chromatography.

Analysis of Diols Not Chemically Bound

A standard solution of diols, DMSO (internal standard), EC and 1,4-dioxane was prepared in acetone at the approximate concentrations expected and used to develop relative response factors. The poly(ethylene ether carbonate) diol to be analyzed (about 3.0 g) and DMSO (about 0.4 g) were weighed to four significant figures into a small vial. The sample was diluted with acetone and analyzed for diols by capillary gas chromatography.

Capillary Gas Chromatography Analysis

Gas chromatograms were obtained on a Hewlett-Packard 5840A unit with a J & W Scientific Co. DB-1 fused silica capillary column (30 m \times 0.25 μ m). Helium carrier gas; flow rate, 0.5 ml/min; column pressure, 10 psig; initial temperature, 90°C; final temperature, 300°C; heating rate, 25°C/min; time at initial temperature, 3.0 min; time at final temperature, 20 min; flame ionization detection. The instrument was calibrated with known quantities of diols in acetone solution using the calibrate mode: MEG, 3.54 min; 1,4-dioxane, 3.65 min; DMSO, 4.05 min; EC, 5.14 min; DEG, 5.45 min; 1,6-hexanediol, 7.05 min; tri(ethylene glycol) (TriEG), 8.24 min; tetra(ethylene glycol) (TetraEG), 10.75 min; penta(ethylene glycol) (PentaEG), 13.20 min; hexa(ethylene glycol) (HexEG), 15.55 min and hepta(ethylene glycol) (HeptaEG), 17.85 min. Unknowns in acetone solution were analyzed in wt% using the internal standard mode. Results are given in Table II.

RESULTS AND DISCUSSIONS

Poly(ethylene ether carbonate) diols are copolymers containing carbonate moieties and polyoxyethylene moieties. Alkaline hydrolysis can result in quantitative cleavage of the carbonate moieties followed by loss of carbon dioxide and formation of the corresponding poly(ethylene glycol)s (Scheme 1). Since some of the poly(ethylene glycol)s are also present prior to hydrolysis, they must be determined independently and subtracted from the total poly(ethylene glycol)s present after hydrolysis. By quantifying the poly(ethylene glycol)s formed from a poly(ethylene ether carbonate) diol produced using a given catalyst, insight is gained into the structural control that the given catalyst plays.

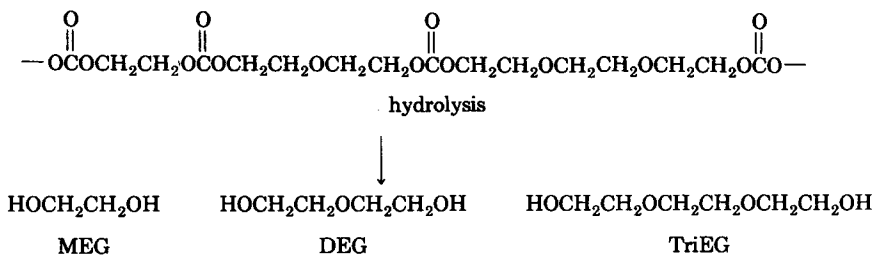
Capillary Gas Chromatographic Analysis of Poly(ethylene Glycols)

The poly(ethylene glycol)s of importance in this study were analyzed directly by capillary gas chromatography. Under the conditions employed, it

TABLE II
Analysis of Hydrolysis Products of Selected Samples Using the Internal Standard Method

Sample number	Initiator	EC: init molar ratio	Reaction conditions				Diols after hydrolysis (wt%)							Total diols (wt%)		
			Catalyst (0.5 Wt%)	Time (h)	Temp (°C)	MEG	DEG	TriEG	TetraEG	PentaEG	HexaEG	HeptaEG				
													Na ₂ SnO ₃ · 3H ₂ O		Na ₃ VO ₄	KF
1	MEG	5	Na ₂ SnO ₃ · 3H ₂ O	4	150	2.80	73.83	10.30	0.35	—	—	—	—	—	—	87.28
2	MEG	5	Na ₃ VO ₄	7	150	1.32	48.84	30.29	8.57	0.86	—	—	—	—	—	89.88
3	MEG	5	KF	2	175	Tr	9.09	24.00	29.20	20.61	7.68	Tr	—	—	—	90.58
4	MEG	5	K ₂ CO ₃ ^a	2	175	0.26	7.99	23.67	31.19	21.66	9.69	2.34	—	—	—	96.80
5	DEG	5	Na ₂ SnO ₃ · 3H ₂ O	7	150	1.64	73.19	11.15	0.53	—	—	—	—	—	—	86.51
6	DEG	15	Na ₂ SnO ₃ · 3H ₂ O	8	150	3.14	61.09	11.13	1.08	—	—	—	—	—	—	76.44
7	DEG	5	Na ₃ VO ₄	1.5	175	0.20	43.90	33.24	11.76	1.69	—	—	—	—	—	90.79
8	DEG	5	Na ₃ WO ₄	4.5	175	—	30.80	36.68	21.76	5.56	Tr	—	—	—	—	94.80
9	DEG	5	Na ₂ B ₂ O ₄	6	175	Tr	26.10	39.96	25.30	7.10	Tr	—	—	—	—	98.46
10	DEG	5	K ₂ MoO ₄	4	175	—	21.81	36.40	28.56	9.36	1.18	—	—	—	—	97.31

^a 1.0 wt% catalyst.



Scheme 1.

was possible to obtain baseline to baseline resolution from monoethylene glycol through hepta(ethylene glycol). Procedural modifications should permit detection of even higher polyglycols, however this was not necessary in this study. Under hydrolysis conditions any ethylene carbonate is converted to monoethylene glycol. Variations in the gas chromatographic technique can provide information about: (a) the extent of the reaction of EC with diols versus time, (b) the poly(ethylene glycol)s formed which do not contain carbon dioxide moieties, and (c) the poly(ethylene glycol)s formed after alkaline hydrolysis.

Capillary Gas Chromatography as a Means of Following Poly(ethylene Ether Carbonate) Diol Chemistry

Capillary gas chromatography is a very useful tool for following the reactions of EC with polyglycols at low molar ratios. The EC and DEG are readily resolved. This allows one to follow the disappearance of reactants with time and the formation of volatile intermediates and products. The less volatile components are not eluted and therefore cannot be studied by this technique.

Reaction of a 5 : 1 Molar Ratio of EC : DEG at 150°C Using 0.5 Wt% Na₂SnO₃ · 3H₂O as Catalyst (Sample 5)

Figure 1 shows a series of GC traces from the reactions of a 5 : 1 molar ratio of EC : DEG at 150°C using 0.5 wt% sodium stannate trihydrate as catalyst. The left trace shows the volatile components present when the reactor first reaches 150°C. The middle trace shows the composition after 3 h at 150°C, while the right trace shows the composition after 7 h. The EC (5.08 to 5.22 minutes depending on concentration) clearly changes from a high value to a very low value after 7 h. However, the DEG (5.46 min) does not change by anything close to the EC change. MEG (3.49 min) is present early in the reaction. TriEG (8.15 min) is formed in low quantities as reaction proceeds. Several other volatile components are formed with time. Major products are present at 14.04 and 16.27 min in the 7-h sample.

The carbonate moieties in the polymer backbone are quantitatively degraded to give the corresponding polyglycols under alkaline conditions. By the comparison of traces before and after hydrolysis, it is very easy to see which volatile components in the reaction mixture contain carbonate moieties. Figure 2 shows such a comparison for the reaction product described above. The

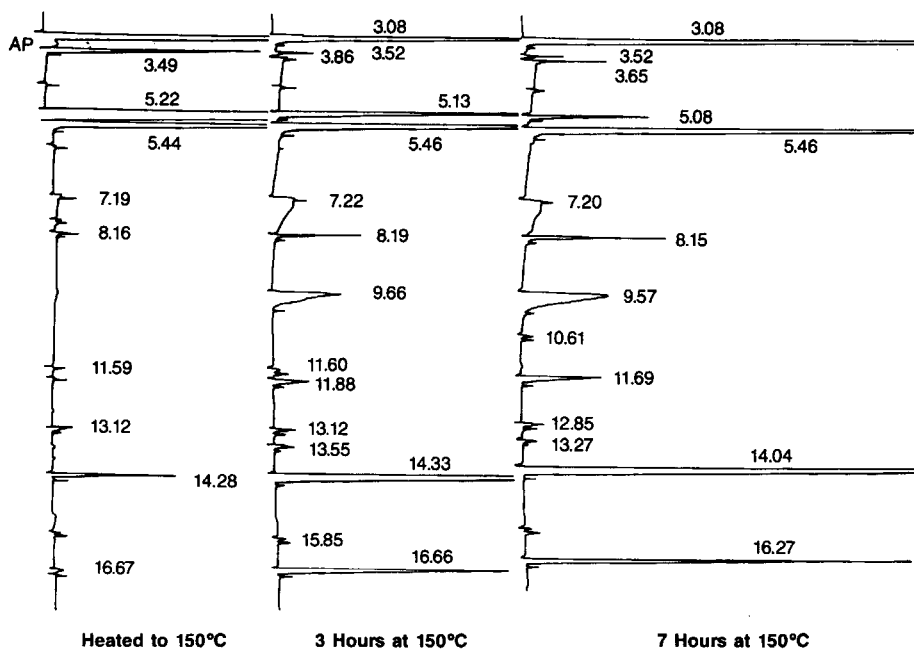


Fig. 1. Capillary GC traces of a 5 : 1 molar ratio product of EC : DEG at 150°C using 0.5 wt% $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ as catalyst.

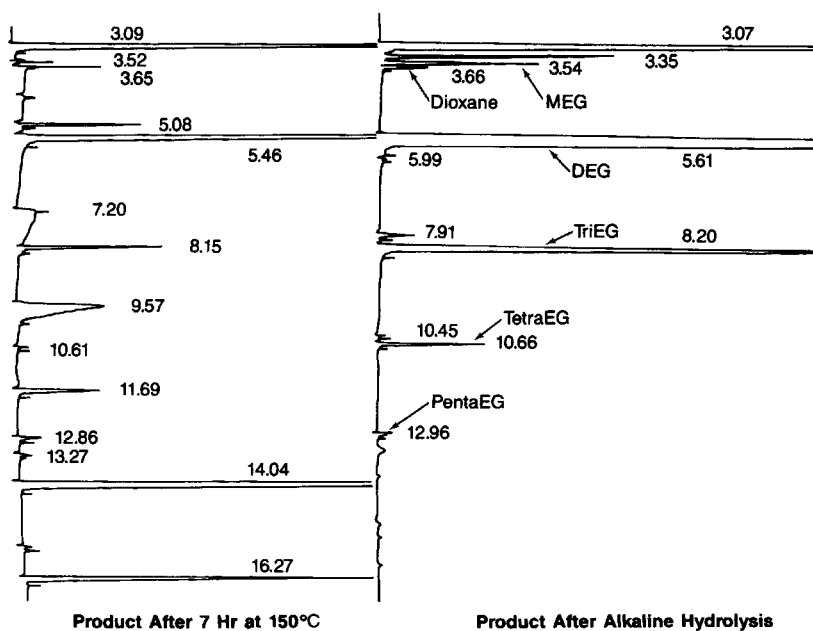


Fig. 2. Effect of hydrolysis on a 5 : 1 molar ratio product of EC : DEG at 150°C using 0.5 wt% $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ as catalyst.

left trace shows the volatile products after 7 h at 150°C. The right trace shows the same material after alkaline hydrolysis. The diol hydrolysis products are clearly evident in the hydrolyzed product: MEG (3.54 min), DEG (5.61 min), TriEG (8.20 min), TetraEG (10.66 min), and PentaEG (12.96 min). 1,4-Dioxane (a decomposition product) is also present (3.66 min). Several peaks (7.20, 9.57, 11.69, 14.04 and 16.27 min) present in the product are absent in the hydrolyzed sample indicating that these peaks contain carbonate moieties. These volatile carbonate-containing components have not yet been fully characterized.

DEG is the major hydrolysis product. It is important to understand that not all of the diols are linked by carbonate moieties. Clearly diols are present, as such, before hydrolysis. However, much larger quantities of diols are present after hydrolysis. Unreacted EC is converted to MEG by hydrolysis.

Reaction of a 5 : 1 Molar Ratio of EC : MEG at 175°C Using 1.0 Wt% Potassium Carbonate as Catalyst (Sample 4)

Figure 3 shows a series of traces from the reactions of a 5 : 1 molar ratio of EC : MEG at 175°C using 1.0 wt% K_2CO_3 as catalyst. The left trace shows the volatile components present when the reactor first reaches 175°C. The middle trace shows the composition after 1 h at 175°C, while the right trace shows the composition after 2 h. The MEG (3.51 min) and EC (5.14 min) are quickly reduced to low concentrations. EC conversion is 100% in less than 2 h. DEG (5.36 min) is formed rapidly and is still present after 2 h. TriEG, TetraEG, and PentaEG are also present.

Figure 4 shows traces of this product before and after hydrolysis. DEG, TriEG, TetraEG, PentaEG, HexaEG, and HeptaEG are all present in the hydrolyzed sample. Several peaks (9.61, 11.80, 14.17, 16.48, and 18.78 min)

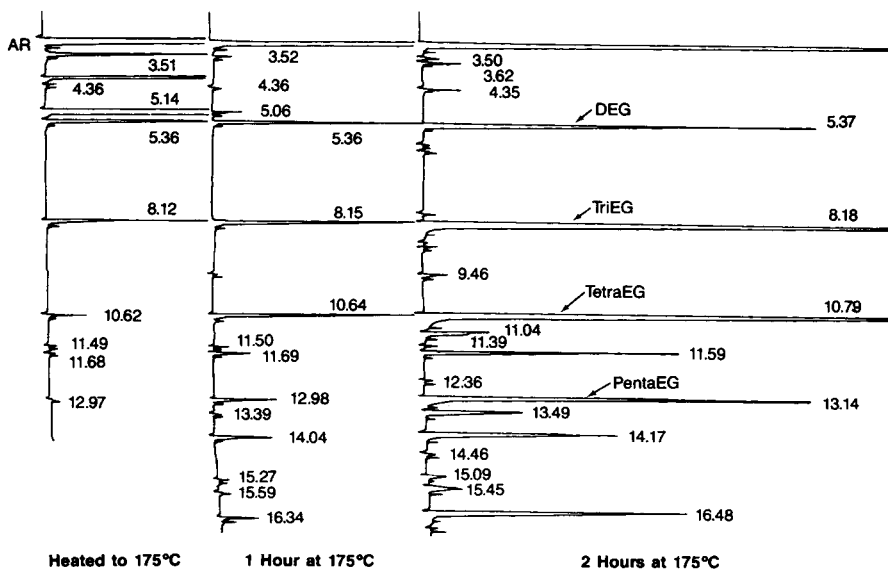


Fig. 3. Capillary GC traces of a 5 : 1 molar ratio product of EC : MEG at 175°C using 1.0 wt% potassium carbonate as catalyst.

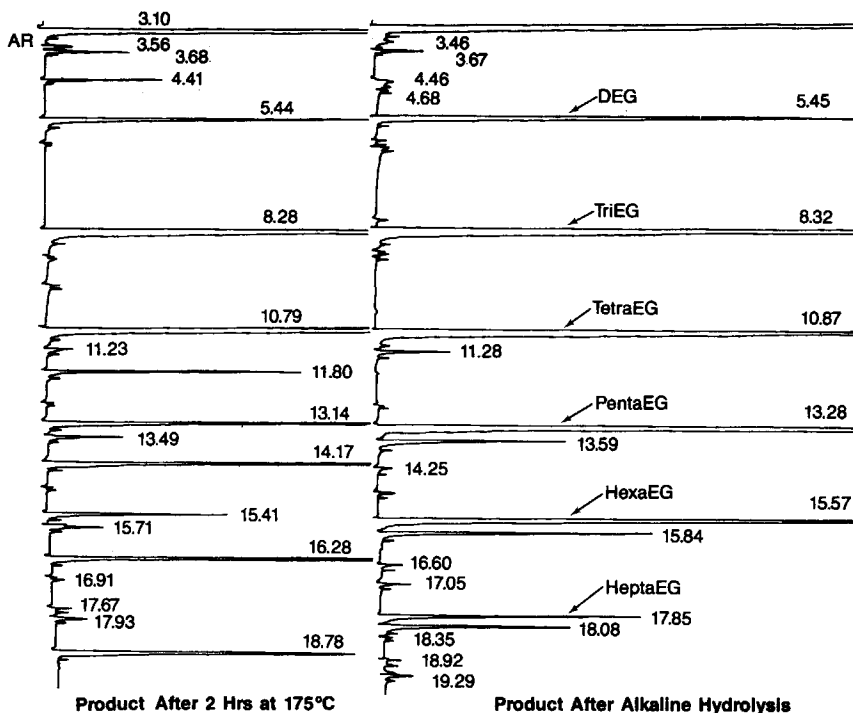


Fig. 4. Effect of hydrolysis on a 5:1 molar ratio product of EC:MEG at 175°C using 1.0 wt% potassium carbonate as catalyst.

present in the product are absent in the hydrolyzed sample indicating that each peak contains carbonate moieties.

Quantification of Hydrolysis Products

Analysis of Selected Samples

A series of selected reaction products are hydrolyzed using 1,6-hexanediol as the internal standard. The results are given in Table II. Sodium stannate has the highest selectivity to DEG units in the poly(ethylene ether carbonate) diol backbone. Potassium carbonate and potassium fluoride give a broad distribution of diol units in the backbone. The other catalysts studied are intermediate between these extremes.

Ethylene Oxide Equivalents Balance

Once the weight percent of each diol in a hydrolysis sample is known, it is possible to calculate the ethylene oxide equivalents of each component and compare to the ethylene oxide equivalents in the initiator and the ethylene carbonate charged. This calculation is given in Table III for the reaction of a 5:1 molar ratio of EC:MEG at 150°C using 0.5 wt% Na_3VO_4 as catalyst (Sample 2). The moles of each diol present can be calculated from the wt%

TABLE IV
 Ethylene Oxide Equivalents Balance of Selected Samples

Sample number	Initiator	EC: initiator molar ratio	Reaction conditions						Diols after hydrolysis (mol%)							% EO equivalents	
			Catalyst (0.5 wt%)	Time (h)	Temp (°C)	MEG	DEG	TriEG	TetraEG	PentaEG	HexaEG	HeptaEG					
1	MEG	5	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	4	150	5.5	85.8	8.5	0.2	—	—	—	—	—	—	—	101.9
2	MEG	5	Na_2VO_4	7	150	2.9	63.0	27.6	6.0	0.5	—	—	—	—	—	—	98.3
3	MEG	5	KF	2	175	Tr	16.8	31.4	29.5	17.0	5.3	Tr	—	—	—	—	88.8
4	MEG	5	K_2CO_3^a	2	175	0.8	14.2	29.7	30.5	17.1	6.5	1.4	—	—	—	—	93.2
5	DEG	5	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	7	150	3.3	87.0	9.4	0.3	—	—	—	—	—	—	—	98.1
6	DEG	15	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	8	150	6.9	81.0	11.2	0.9	—	—	—	—	—	—	—	94.7
7	DEG	5	Na_3VO_4	1.5	175	0.4	58.6	31.4	8.6	1.0	Tr	—	—	—	—	—	97.3
8	DEG	5	Na_2WO_4	4.5	175	—	43.3	36.5	16.7	3.5	Tr	—	—	—	—	—	101.7
9	DEG	5	$\text{Na}_2\text{B}_2\text{O}_4$	6	175	Tr	36.6	39.6	19.4	4.4	Tr	—	—	—	—	—	101.2
10	DEG	5	K_2MnO_4	4	175	—	32.1	38.0	23.0	6.2	0.7	—	—	—	—	—	103.0

^a1.0 wt% catalyst.

TABLE V
Analysis of Selected Samples for Free Diol Content

Sample number	Initiator	Catalyst	EC: init molar ratio	Mol% ^a CO ₂ retained	Wt% ^b CO ₂	Wt% free diol products	Normalized distribution of free diols (wt%)						
							MEG	DEG	TriEG	TetraEG	PentaEG	HexaFG	
1	MEG	Na ₂ SnO ₃	5/1	39.9	23.7	25.9	1.6	87.4	11.0	Tr	—	—	—
2	MEG	Na ₃ VO ₄	5/1	28.4	18.4	33.8	0.9	65.8	28.2	5.1	—	—	—
4	MEG	K ₂ CO ₃	5/1	9.9	7.7	71.8	0.2	9.7	32.4	39.2	14.8	—	3.7
3	MEG	KF	5/1	9.8	7.5	88.2	0.2	11.0	33.7	37.7	13.8	—	3.6
6	DEG	Na ₂ SnO ₃	15/1	34.2	21.8	10.3	1.7	87.4	10.8	—	—	—	—
5	DEG	Na ₂ SnO ₃	5/1	44.1	23.1	22.7	1.2	86.7	12.1	—	—	—	—
7	DEG	Na ₃ VO ₄	5/1	31.2	17.5	28.4	0.6	60.8	32.5	6.0	—	—	—
8	DEG	Na ₂ WO ₄	5/1	25.8	15.0	37.4	0.4	46.7	40.7	12.2	Tr	—	—
9	DEG	Na ₂ B ₂ O ₄	5/1	20.6	12.5	37.3	0.5	40.3	44.1	15.1	Tr	—	—
10	DEG	K ₂ MoO ₄	5/1	27.2	16.2	43.3	1.8	35.7	43.4	16.9	2.2	—	—

^aMol% of CO₂ present in EC charged which is present in product.

^bDetermined by NMR.

diol, the molecular weight of the diol and the total amount of product formed. This can then be converted to the equivalent number of moles of ethylene oxide in each diol. The equivalent number of moles of ethylene oxide units found in diol products can then be compared to the equivalent number of moles of ethylene oxide units charged to the reactor to obtain an ethylene oxide equivalents balance. In the example cited above, 98.3% of the ethylene oxide equivalents charged were accounted for as diol products after hydrolysis. This indicates that very little of the ethylene oxide equivalents are going to other kinds of products (such as 1,4-dioxane).

Similar calculations were made for each of the samples listed in Table II and the results are given in Table IV. The diols are given in mol% in Table IV; they are given in wt% in Table II. The ethylene oxide equivalents balance is close to 100% in all cases studied.

Quantification of Diols Present Prior to Hydrolysis

As previously discussed, not all of the diols are chemically bound to the poly(ethylene ether carbonate) diol backbone. Some diols are present as such. The amount of diols which are not bound to carbonate moieties (free diols) can have an adverse effect on certain properties in various applications. Therefore, a quantitative capillary gas chromatographic method was developed. The results from a series of selected samples are given in Table V.

Comparison of Diols Before and After Hydrolysis

Total Diols

The amount of diol bound into the poly(ethylene ether carbonate) diol backbone through carbonate moieties can be determined by subtracting the wt% of free diols (Table V) from the wt% of total diols (Table II). These calculations are tabulated in Table VI. The amount of bound diol varies from 8.9 to 86.5% of the total diol present and correlates with the amount of carbonate present. When sodium stannate trihydrate is used as catalyst, the

TABLE VI
Total, Free and Bound Diols in Selected Poly(Ethylene Ether Carbonate) Diol Samples

Sample number	Reaction Conditions									
	EC :		Catalyst (0.5 wt%)	Time (h)	Temp (°C)	Wt% CO ₂	Diols (wt%)			Bound diol as percent of total
	Initiator molar ratio	Initiator					Total	Free	Bound	
1	MEG	5	Na ₂ SnO ₃ · 3H ₂ O	4	150	23.7	87.3	25.9	61.4	70.3
2	MEG	5	Na ₃ VO ₄	7	150	18.4	89.9	33.8	56.1	62.4
3	MEG	5	KF	2	175	7.5	90.6	71.8	18.8	20.8
4	MEG	5	K ₂ CO ₃	2	175	7.7	96.8	88.2	8.6	8.9
5	DEG	5	Na ₂ SnO ₃ · 3H ₂ O	7	150	23.1	86.5	22.7	63.8	73.8
6	DEG	15	Na ₂ SnO ₃ · 3H ₂ O	8	150	21.8	76.4	10.3	66.1	86.5
7	DEG	5	Na ₃ VO ₄	1.5	175	17.5	90.8	28.4	62.4	68.7
8	DEG	5	Na ₂ WO ₄	4.5	175	15.0	94.8	37.4	57.4	60.5
9	DEG	5	Na ₂ B ₂ O ₄	6	175	12.5	98.6	37.3	61.2	62.1
10	DEG	5	K ₂ MoO ₄	4	175	16.2	97.3	43.3	54.0	55.5

TABLE VII
Calculation of Total, Free and Bound Moles of Diols in 5 : 1 Molar Ratio Product
of EC : DEG at 150°C Using 0.5 wt% Na₂SnO₃ · H₂O Catalyst (Sample 5)

Component	Free diol (wt%)	Product (g)	Grams component	Mol wt	Free diol (mol)	Total diol (mol)	Moles linked by CO ₂	Normalized
MEG	0.27	318	0.86	62.07	0.014	0.084	—	—
Dioxane	0.75	318	2.39	88.1	0.027	ND	—	—
EC	2.16	318	6.87	88.1	0.078	—	—	—
DEG	19.68	318	62.58	106.12	0.590	2.193	1.603	89.6
TriEG	2.75	318	8.75	150.17	0.058	0.236	0.178	9.9
TetraEG	Tr	318	—	194.23	—	0.009	0.009	0.5
	<u>25.61</u>					<u>1.790</u>	<u>1.790</u>	<u>100.0</u>
97.8%								
EC Conversion								

carbon dioxide content of the poly(ethylene ether carbonate) diol is highest and the percent of bound diol is highest. The highest value of bound diol is obtained with the highest EC : DEG molar ratio¹⁵ using sodium stannate trihydrate as catalyst. Low carbon dioxide contents and low percent bound diols are obtained when potassium carbonate or potassium fluoride are used as catalysts. Other catalysts give values intermediate between these extremes.

Distribution of Diols

Additional information can be obtained by comparing the distribution of the free and bound diols. The calculations involved are given in Table VII for the case of a 5 : 1 molar ratio of EC : DEG at 150°C using sodium stannate trihydrate as catalyst (Sample 5). The total moles of each diol are calculated from the wt% diol, the molecular weight, and weight of product. The number of moles of each diol bound in the oligomer backbone is obtained by subtracting the moles of free diol from the total moles of diol. The moles of MEG present after hydrolysis is totally accounted for by the free MEG present in the product before hydrolysis and the MEG formed by hydrolysis of EC. This indicates that there are few, if any, $-\text{OCO}_2\text{CH}_2\text{CH}_2\text{OCO}_2-$ units in the poly(ethylene ether carbonate) diol backbone of this product.

The distribution of bound diols was calculated for selected poly(ethylene ether carbonate) diols by the procedure given above. These values are tabulated for comparative purposes in Table VIII. Several conclusions can be drawn.

1. There is no bound MEG in any of these low molar ratio samples.
2. Due to the high selectivity of sodium stannate trihydrate, there is very little difference in the distribution of free and bound diols when this catalyst is used.
3. As catalyst selectivity decreases, there is a progressive change between the distribution of free diols and bound diols (see Fig. 5). The free diol content of each sample is DEG > TriEG > TetraEG > PentaEG regardless of the catalyst used. This is reasonable since the materials are formed in this

TABLE VIII
Distribution of Free and Bound Diols in Selected Poly(Ethylene Ether Carbonate) Diols

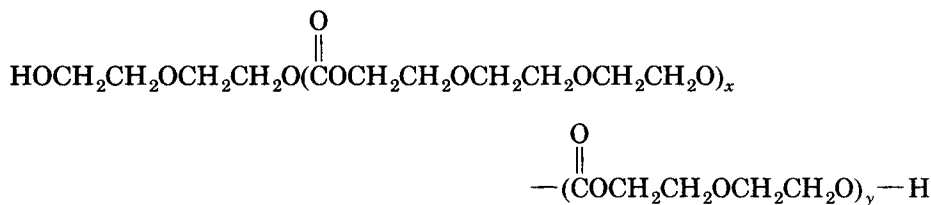
Sample number	Reaction conditions			Normalized diols (mol%)														
	Initiator	Molar ratio	Catalyst	MEG			DEG			TriEG			TetraEG			PentaEG		
				Free	Bound	—	Free	Bound	—	Free	Bound	—	Free	Bound	—	Free	Bound	—
1	MEG	5	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	2.8	—	—	89.3	90.4	7.9	9.3	—	Tr	0.3	—	—	—	—	
5	DEG	5	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	2.1	—	—	89.1	89.6	8.8	9.9	—	Tr	0.5	—	—	—	—	
6	DEG	15	$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	3.1	—	—	89.1	86.2	7.8	12.7	—	Tr	1.1	—	—	—	—	
2	MEG	5	Na_3VO_4	1.8	—	—	72.9	59.1	22.2	32.6	—	3.1	8.3	—	—	—	—	
7	DEG	5	Na_3VO_4	1.2	—	—	69.1	53.4	26.1	34.1	—	3.7	11.0	Tr	1.5	—	—	
8	DEG	5	Na_2WO_4	0.8	—	—	56.4	33.0	34.7	37.5	—	8.1	23.3	Tr	6.2	—	—	
9	DEG	5	$\text{Na}_2\text{B}_2\text{O}_4$	Tr	—	—	50.0	26.6	38.7	39.9	—	10.3	25.9	Tr	7.6	—	—	
10	DEG	5	K_2MoO_4	1.1	—	—	46.1	18.4	39.6	36.0	—	11.9	33.5	1.2	10.8	—	—	

order from EC. Relative differences reflect differences in catalyst selectivities. There is a shift to higher molecular weight bound diols with decreasing catalyst selectivity.

Poly(ethylene Ether Carbonate) Diol Composition

Based on the various analytical methods developed in this study, it is possible for the first time to establish the approximate composition of a given poly(ethylene ether carbonate) diol. This is illustrated below for the reaction product of a 5:1 molar ratio of EC:DEG using 0.5 wt% sodium stannate trihydrate as catalyst (Sample 5).

The oligomeric components have the following general structure:



From Table VIII, the normalized bound diols are:

89.6 mol% DEG
9.9 mol% TriEG
0.5 mol% TetraEG (ignore)

$$\text{Therefore: } \frac{\text{mol DEG bound}}{\text{mol TriEG bound}} = \frac{89.6}{9.9} = 9.05$$

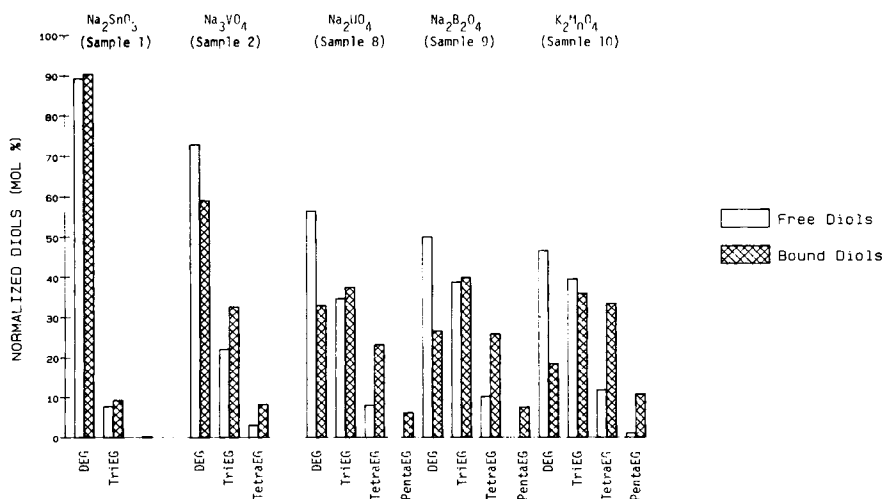


Fig. 5. Distribution of free and bound diols in poly(ethylene ether carbonate) diols as a function of catalyst; EC: initiator molar ratio of 5:1.

The weight average molecular weight, \bar{M}_w , determined by size exclusion chromatography is 998. If $x = 0.76$ and $y = 5.84$,

$$\bar{M}_w = 105 + 0.76(172) + 5.84(132) + 1 = 1007$$

On hydrolysis, this would give (per 1007 g oligomers):

6.84 mol DEG or 725.0 g DEG and
0.76 mol TriEG or 114.0 g TriEG

$$\frac{\text{mol DEG}}{\text{mol TriEG}} = \frac{6.84}{0.76} = 9.00$$

The total weight of diols formed from hydrolysis of 1007 g of oligomers is 725.0 + 114.0 = 839.0 g.

From Table VI,

$$\text{wt\% bound diols} = 63.8\%$$

$$\text{wt\% free diols} = 22.7\%$$

The total weight of poly(ethylene ether carbonate) diol that would yield 839.0 g of diols from oligomers on hydrolysis can be calculated.

$$\frac{839.0 \text{ g}}{0.638} = 1315 \text{ g total poly(ethylene ether carbonate) diol}$$

The weight percent oligomer present is

$$\frac{1007}{1315} \times 100 = 76.5 \text{ wt\% oligomer}$$

The weight of free diols is

$$(1315)(0.227) = 298.5 \text{ g}$$

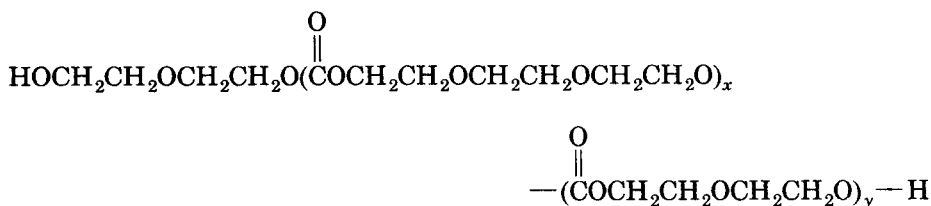
From Table V, the normalized distribution of free MEG, DEG, and TriEG is 1.2, 86.7, and 12.1 wt%, respectively. Therefore, 1315 g of poly(ethylene ether carbonate) diol product contains:

$$\begin{aligned} (298.5)(0.012) &= 3.6 \text{ g MEG (0.27 wt\%)} \\ (298.5)(0.867) &= 258.8 \text{ g DEG (19.67 wt\%)} \\ (298.5)(0.121) &= 36.1 \text{ g TriEG (2.74 wt\%)} \end{aligned}$$

This is in complete agreement with Table VII (column 3). Therefore, the calculated composition of the material is:

76.5 wt% oligomer
19.68 wt% DEG
2.75 wt% TriEG
2.16 wt% EC
0.75 wt% 1,4-dioxane
0.27 wt% MEG
102.1

The oligomer has the following average structure:



where $x = 0.76$ and $y = 5.84$

The calculated wt% carbon dioxide of this oligomer is

$$\text{wt\% CO}_2 = \frac{0.76(44) + 5.84(44)}{1315} \times 100 = 22.1 \text{ wt\%}$$

The experimental value is 23.1 wt%

The product consists of (1) an oligomeric portion which is a copolymer of carbon dioxide and poly(ethylene glycol)s and (2) a monomeric portion which consists mostly of diethylene glycol with lesser quantities of monoethylene glycol, triethylene glycol, 1,4-dioxane and unreacted ethylene carbonate. The distribution of poly(ethylene glycol)s both in the polymer backbone and as free glycols is dependent on the catalyst employed.

CONCLUSIONS

Poly(ethylene ether carbonate) diols are readily hydrolyzed and degraded under alkaline conditions to the poly(ethylene glycol)s which make up their backbone structure. When hydrolysis is carried out in the presence of 1,6-hexanediol as internal standard, the resultant poly(ethylene glycol)s can be quantified by direct capillary gas chromatographic analysis (derivatives are not necessary). Excellent material balances are obtained by comparing the poly(ethylene glycol)s obtained after hydrolysis to the equivalents of poly(ethylene glycol)s in the initiator and ethylene carbonate reactants.

Comparison of capillary gas chromatographic traces of samples before and after hydrolysis is a method for determining which components (volatile to GC conditions) contain carbonate moieties. Such carbonate-containing components are absent in the GC trace after hydrolysis.

Some of the poly(ethylene glycol)s present in the ethylene carbonate-initiator reaction products are not chemically bound into the polymer backbone. These materials can be analyzed directly by capillary gas chromatography using dimethylsulfoxide as internal standard. Larger quantities of free poly(ethylene glycol)s are produced by using catalysts which produce materials with lower carbon dioxide contents.

Based on the combination of analytical techniques in this study, it is possible for the first time to establish the approximate composition of a given poly(ethylene ether carbonate) diol. A typical composition made using a sodium stannate trihydrate catalyst consists of (1) an oligomeric portion which is a copolymer of carbon dioxide and poly(ethylene glycol)s and (2) a monomeric portion which consists mostly of diethylene glycol with lesser quantities of monoethylene glycol, triethylene glycol, 1,4-dioxane and unreacted ethylene carbonate. These techniques should also be applicable to poly(ethylene ether carbonate) polyols made from ethylene oxide and carbon dioxide.

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