

Structural Features of Poly(Alkylene Ether Carbonate) Diols and Intermediates Formed during Their Preparation

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Synopsis

Capillary vapor-phase chromatography and carbon-13 nuclear magnetic resonance (NMR) have been used to elucidate the structure of poly(ethylene ether carbonate) diols and certain intermediates produced by the oligomerization of ethylene carbonate (EC) using monoethylene glycol (MEG) or diethylene glycol (DEG) as initiator and catalyzed by sodium stannate trihydrate. These diols are alternating copolymers of carbon dioxide and DEG which also contain smaller amounts of higher glycols as determined by comparing their ^{13}C NMR spectra to the spectra of model compounds. Diethylene glycol is an important reaction intermediate and is present in steady-state concentrations. Although both 2-hydroxyethyl carbonate and 2-hydroxyethyl ether end groups are present at an intermediate stage in the reaction, only 2-hydroxyethyl ether end groups are present at high EC conversion. Molecular weight builds as a smooth function of conversion and time.

INTRODUCTION

Poly(alkylene ether carbonate) polyols are the reaction products of an aryl, alkyl, or alkylene carbonate or an alkylene oxide and carbon dioxide with an alcoholic initiator in the presence of an appropriate catalyst. 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.¹⁻¹⁷ However, there has been very little definitive work directed toward the detailed structural features of these materials.

A recent report described the backbone features of poly(ethylene ether carbonate) diol oligomers, made using various catalysts, by alkaline degradation to the corresponding poly(ethylene glycols) which make up their backbone.¹⁸ That study indicated that the poly(ethylene ether carbonate) diol oligomers consisted of (a) an oligomeric portion which is a copolymer of carbon dioxide and poly(ethylene glycols) and (b) a monomeric portion which consists mostly of diethylene glycol with lesser quantities of monoethylene glycol, triethylene glycol, 1,4-dioxane, and ethylene carbonate (sodium stannate catalyst). Other catalysts gave larger quantities of higher poly(ethylene glycols).

The current work extends the understanding of the structural features of poly(ethylene ether carbonate) diols by studying their carbon-13 nuclear magnetic resonance (NMR) spectra and making comparisons to model compounds. Some insight is also gained into the mechanism of formation of

poly(ethylene ether carbonate) diols by studying their reaction intermediates by capillary vapor-phase chromatography and their ^{13}C NMR spectra as a function of time during their preparation.

EXPERIMENTAL

Materials. Ethylene carbonate (EC, distilled prior to use), diethyl carbonate, diethylene glycol dibutylether, and sodium stannate trihydrate were obtained from Aldrich Chemical Company. Monoethylene glycol (MEG), all poly(ethylene glycols), and the monomethyl ether of diethylene glycol (Dowanol[®] DM) were produced by The Dow Chemical Company.

Dowanol DM Carbonate. Prepared by reacting Dowanol DM with diethyl carbonate in a 2 : 1 molar ratio using $\text{Ti}(\text{i-PrO})_4$ as catalyst. Reaction temperature was increased stepwise from 130°C to 185°C while byproduct ethanol was removed overhead. After reaction, catalyst was removed and the product was fractionated. The fraction distilling from 131–134°C at 0.4 to 0.5 mmHg was taken as product. Proton and ^{13}C NMR and infrared IR were consistent with the assigned structure.

Diethylene Glycol Bis(Ethyl Carbonate). Prepared by reaction of diethylene glycol with excess diethyl carbonate using $\text{Ti}(\text{i-PrO})_4$ as catalyst. Reaction temperature was increased stepwise from 128°C to 190°C while byproduct ethanol was removed overhead. After reaction, the catalyst was removed and the product fractionated. The fraction distilling at 121°C at 0.7 mmHg was taken as product. Proton and ^{13}C NMR and IR were consistent with the assigned structure.

Poly(Ethylene Ether Carbonate) Diol from DEG and Diethyl Carbonate. Prepared by reaction of diethylene glycol with diethyl carbonate (equal molar quantities) using $\text{Ti}(\text{i-PrO})_4$ as catalyst. Reaction temperature was increased stepwise from 130°C to 190°C while byproduct ethanol was removed overhead. After reaction, the catalyst was removed and the crude product was heated under vacuum to remove volatiles (mainly unreacted DEG).

Poly(Ethylene Ether Carbonate) Diol from DEG and EC. Prepared by reaction of ethylene carbonate with diethylene glycol (10 : 1 molar ratio; 7 h at 150°C) using sodium stannate trihydrate (0.5 wt%) as catalyst. The product was dissolved in acetone, treated with magnesium silicate, filtered to remove the magnesium silicate and catalyst, and stripped on a rotary evaporator to remove the acetone.¹⁹ The crude product was then heated under vacuum to remove volatiles (mainly DEG and EC).

Quantitative Studies of the Reactions of EC with Diol Initiators. All reactions were carried out by heating EC and the particular diol initiator of interest at the appropriate reactant molar ratio and temperature using sodium stannate trihydrate (0.5 wt%) as catalyst and diethylene glycol dibutylether (4 wt%) as internal standard. This internal standard was shown to be inert to the reaction conditions and to elute in an open region of the capillary vapor-phase chromatogram. Samples were removed from the reactor at various times for capillary vapor-phase chromatographic analysis and molecular weight analysis by size-exclusion chromatography.

^{13}C NMR Study of the Reactions of MEG with EC. All reaction product samples were prepared by heating MEG and EC (10 : 1 molar ratio; 135°C)

using sodium stannate trihydrate (0.5 wt%) as catalyst with periodic sample removal until EC conversion was essentially complete.

Capillary Vapor-Phase Chromatography Measurements. 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; 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; EC, 5.14 min; DEG, 5.45 min; tri(ethylene glycol) (TriEG), 8.24 min; diethylene glycol dibutylether, 10.38 min; tetra(ethylene glycol) (TetraEG), 10.75 min. Unknowns in acetone solution were analyzed in wt% using the internal standard mode.

TABLE I
Tabulation of Molecular Weight Data

Time (h)	EC : MEG = 10 : 1; 150°C		
	\bar{M}_n	\bar{M}_w	PDI
0	147	189	1.29
0.25	162	233	1.44
0.5	219	393	1.79
1.0	316	626	1.98
2.0	398	834	2.10
3.0	480	990	2.06
4.0	514	1070	2.08
5.0	533	1111	2.08
6.0	539	1124	2.09
	EC : MEG = 10 : 1; 175°C		
0.5	392	863	2.20
0.75	485	1145	2.36
1.0	548	1206	2.20
1.5	570	1220	2.14
1.75	580	1250	2.16
2.0	586	1302	2.22
	EC : DEG = 50 : 1; 175°C		
4.5	1065	3425	3.22
5.5	1239	3613	2.92
6.5	1460	4050	2.77
9.5	1700	4616	2.71
11.5	1735	4600	2.65
	EC : TriEG = 10 : 1; 150°C		
2.0	492	967	1.97
3.0	583	1165	2.00
4.0	622	1417	2.28
5.0	694	1440	2.07
6.0	701	1560	2.23
7.0	700	1530	2.19

Size-Exclusion Chromatography (SEC) Measurements. The molecular weights and distribution were determined by SEC on Waters Ultrastaygel® 1000 Å and 10,000 Å columns in series using tetrahydrofuran (THF) as the mobile phase, a refractive index detector and calibrated with narrow molecular weight poly(ethylene glycol) standards. Results are tabulated in Table I.

¹³C NMR Measurements. The spectra of samples dissolved in chloroform-*d* were obtained on a Bruker WM 360 MHz (90.5 MHz for carbon-13) instrument.

RESULTS AND DISCUSSION

¹³C NMR Studies of Model Systems

Ethylene Carbonate, Monoethylene Glycol, and Diethylene Glycol. The ¹³C NMR spectra of the starting materials (EC and MEG) used in this study and a suspected intermediate (DEG) were obtained as baseline data (Fig. 1).

Dowanol® DM Carbonate. Polymers derived from EC and MEG were anticipated to be, at least in part, copolymers of DEG and carbon dioxide. Therefore, the carbonate of Dowanol DM was chosen as a model compound since it consists of two DEG units linked together as a carbonate with the remaining two hydroxyls capped as methyl ethers (Fig. 2).

Diethylene Glycol Bis(Ethyl Carbonate). The *bis*(ethyl carbonate) of diethylene glycol is a good model compound since it consists of two carbonate moieties linked by a DEG unit with the two remaining parts of the carbonate moieties capped as ethyl esters (Fig. 3).

Poly(Ethylene Ether Carbonate) Diol from DEG and Diethyl Carbonate. This structure was obtained by linking DEG units together with diethyl carbonate. The backbone of this polymer should be a good model for copolymers of DEG and carbon dioxide, since it consists of alternating *bis*(ethyleneoxy) and carbonate moieties. However, the end groups could be somewhat different as both ethoxy and 2-(hydroxyethyl)ethyleneoxy end groups should

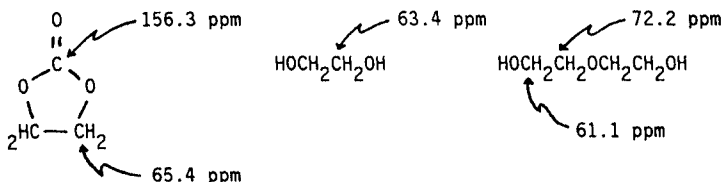


Fig. 1. ¹³C NMR structural assignments for starting materials and DEG.

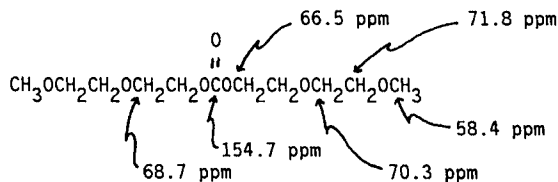


Fig. 2. ¹³C NMR structural assignments for Dowanol DM carbonate.

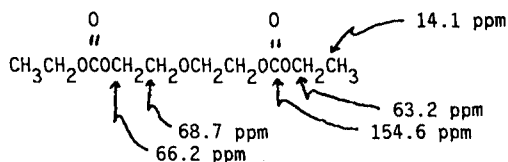
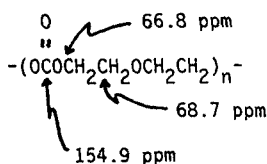


Fig. 3. ^{13}C NMR structural assignments for diethylene glycol bis(ethyl carbonate).

Backbone:



End Groups:

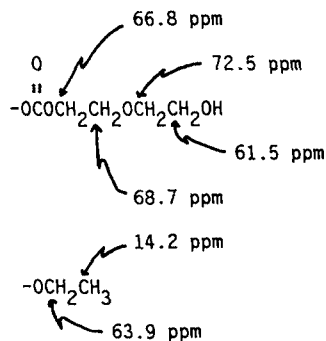
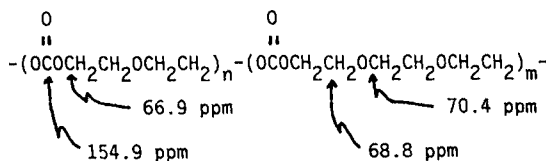


Fig. 4. ^{13}C NMR structural assignments for DEG/ CO_2 copolymer from DEG and diethyl carbonate.

be present (Fig. 4). Unreacted DEG and other volatiles were removed from the crude product by heating under vacuum prior to ^{13}C NMR studies.

Poly(Ethylene Ether Carbonate) Diol from DEG and EC. This structure was obtained by reacting EC with DEG using a 10:1 molar ratio of EC:DEG at 150°C with a sodium stannate trihydrate catalyst, followed by catalyst removal and volatiles removal (DEG, EC, etc.) by heating under vacuum (Fig. 5).

Backbone:



End Groups:

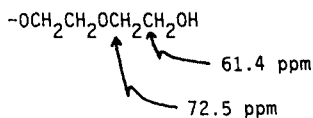


Fig. 5. ^{13}C NMR structural assignments for a polymer from EC and DEG.

Results from Model System Studies

It is possible to assign all ^{13}C NMR lines in the spectra of the model compounds. Results are given below:

The *bis*(ethyl carbonate) of diethylene glycol contains only two kinds of carbons which are not associated with end groups:

1. α to carbonate oxygen; β to ether oxygen; 66.2 ppm
2. β to carbonate oxygen; α to ether oxygen; 68.7 ppm

The polymeric reaction product of diethylene glycol with diethyl carbonate contains only the same two kinds of methylene carbons which are not associated with end groups:

1. α to carbonate oxygen; β to ether oxygen; 66.8 ppm
2. β to carbonate oxygen; α to ether oxygen; 68.7 ppm

The Dowanol DM carbonate contains the same two kinds of methylene carbons and one additional kind:

1. α to carbonate oxygen; β to ether oxygen; 66.5 ppm
2. β to carbonate oxygen; α to ether oxygen; 68.7 ppm
3. α to ether oxygen; β to ether oxygen; 70.3 ppm

The polymeric reaction product of diethylene glycol and ethylene carbonate contains the same three kinds of methylene carbons not associated with end groups:

1. α to carbonate oxygen; β to ether oxygen; 66.9 ppm
2. β to carbonate oxygen; α to ether oxygen; 68.8 ppm
3. α to ether oxygen; β to ether oxygen; 70.4 ppm

These results suggest that poly(ethylene glycols) higher than diethylene glycol are formed by the reactions of DEG with EC. These higher poly(ethylene glycols) can react with additional EC to form copolymers of poly(ethylene glycols) and carbon dioxide.¹⁸ The amount of carbon at 70.4 ppm can be used as a direct measure of the amount of these higher poly(ethylene glycols) present in a given reaction product.

These model system studies also indicate the kind of end groups present.

Location of Carbon Atoms	DEG	DEG/DEC Product	DEG/EC Product
a. α to ether oxygen; β to OH	72.2 ppm	72.5 ppm	72.5 ppm
b. β to ether oxygen; α to OH	61.1 ppm	61.5 ppm	61.5 ppm

Reactions of EC with MEG Using an EC : MEG Molar Ratio of 1 : 1 at 150°C

The reactions between EC and MEG using an EC : MEG molar ratio of 1 : 1 and sodium stannate trihydrate as catalyst were studied by capillary vapor-

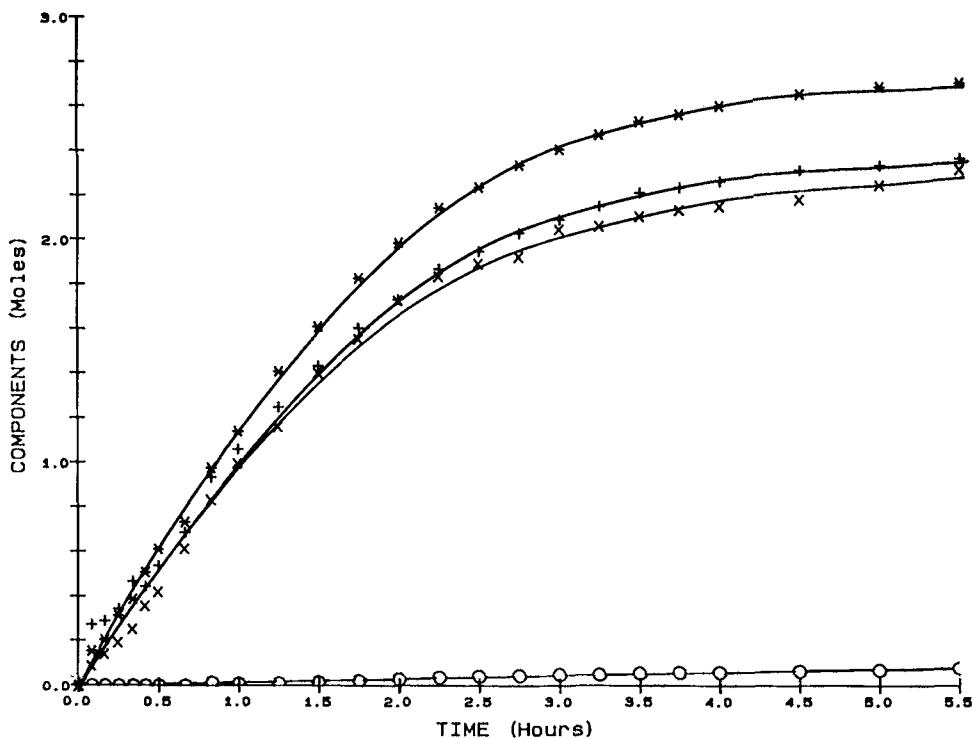
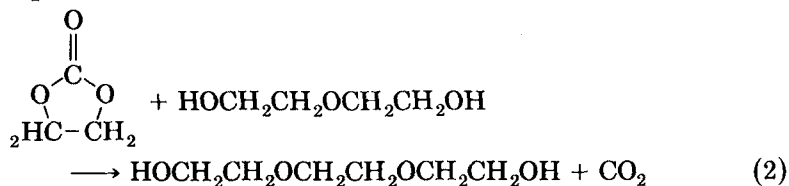
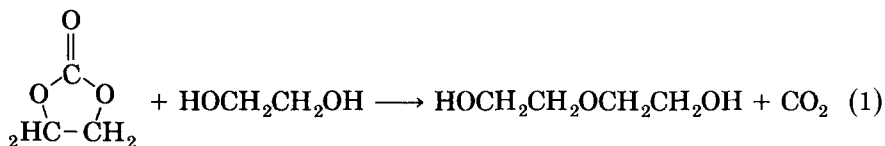


Fig. 6. Reactants consumed and DEG (×) and TriEG (○) formed vs. time; EC (*) : MEG (+) molar ratio of 1 : 1 at 150°C.

phase chromatography in order to gain insight into the reaction intermediates formed at a very early stage in the reaction. The dibutylether of diethylene glycol was added to the reactor to serve as an internal standard in order to quantify the reaction products. Samples were removed from the reactor at various times and analyzed for loss of reactants (EC and MEG) and formation of products (DEG and TriEG). Results are plotted in Figure 6.

The MEG reacts with EC to form DEG; small amounts of DEG react further with EC to form triethylene glycol (TriEG). The moles of DEG and TriEG



formed account for > 97% of the MEG consumed and > 90% of the EC consumed. Additional products were present in trace quantities only. There-

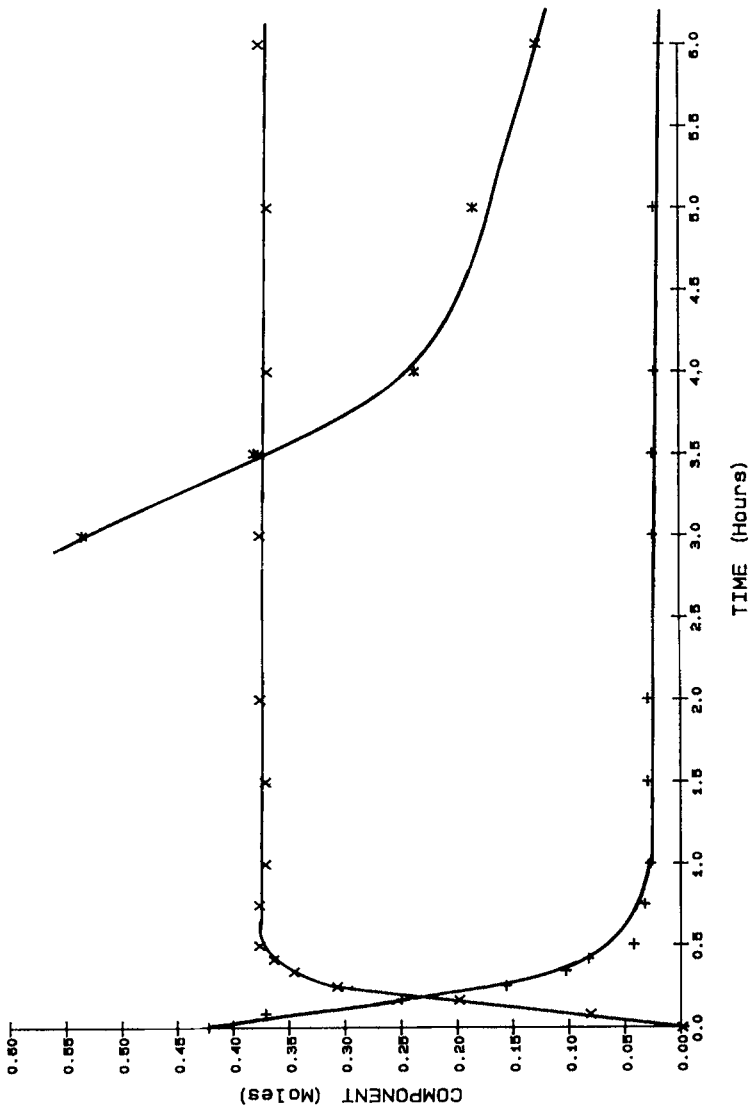


Fig. 7. Concentration of EC (+), MEG (*), and DEG (x) vs. time; EC:MEG molar ratio of 10:1 at 150°C.

fore, DEG is the initial product of the reaction of EC with MEG using sodium stannate as catalyst.

Reactions of EC with MEG Using an EC : MEG Molar Ratio of 10 : 1 at 150°C. The reactions between EC and MEG using an EC : MEG molar ratio of 10 : 1 and sodium stannate as catalyst were studied using the same technique used above to further understand the reaction sequence. Samples were removed from the reactor and analyzed by vapor-phase chromatography. The reaction was followed for 7 h (97% EC conversion). Results are plotted in Figure 7.

The MEG is rapidly consumed (90% MEG conversion) with concurrent DEG formation at a very early stage in the reaction (25% EC conversion), but MEG remains present at these low levels throughout the reaction. DEG is formed rapidly as a reaction intermediate and remains at a steady-state concentration (approximately the initial MEG concentration) throughout the rest of the reaction. This indicates that the rate of formation of DEG and the rate of reaction of DEG to form further products are in balance under the conditions of this experiment. Free DEG is present in the product.

Various other higher molecular weight products are formed during the course of the reaction. The lower molecular weight products can be detected in the vapor-phase chromatography trace. However, the majority of the products are not volatile under the conditions used. The molecular weight build as a function of time and EC conversion is plotted in Figure 8 using

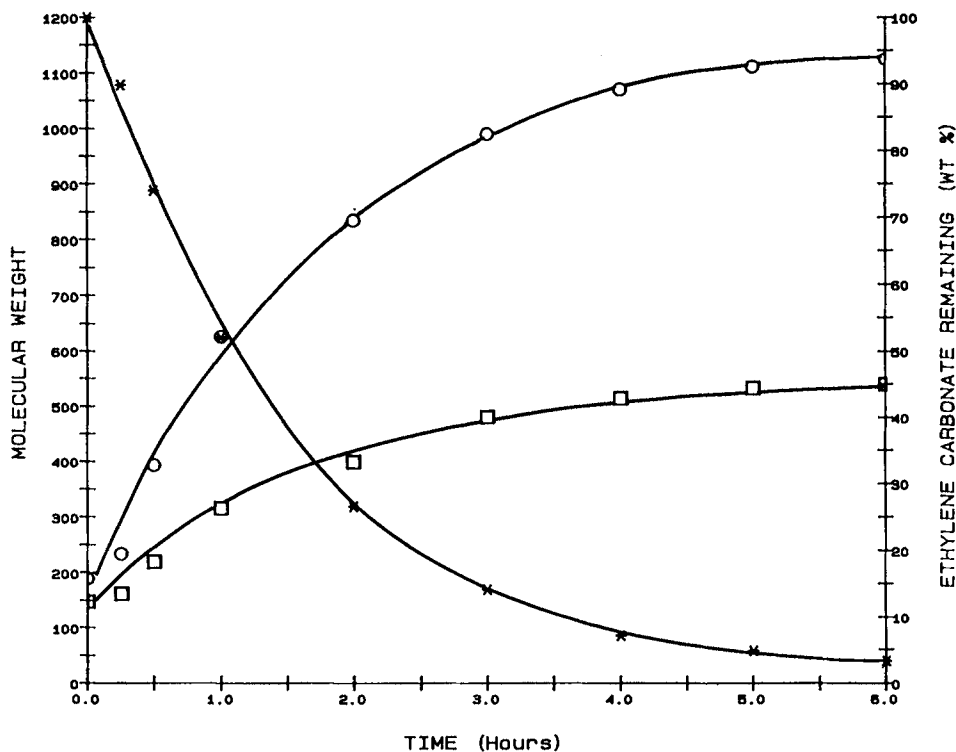


Fig. 8. Effect of time and EC conversion on molecular weight build (\circ , \bar{M}_w); EC : MEG molar ratio of 10 : 1 at 150°C. (\square) \bar{M}_n ; (+) EC remaining.

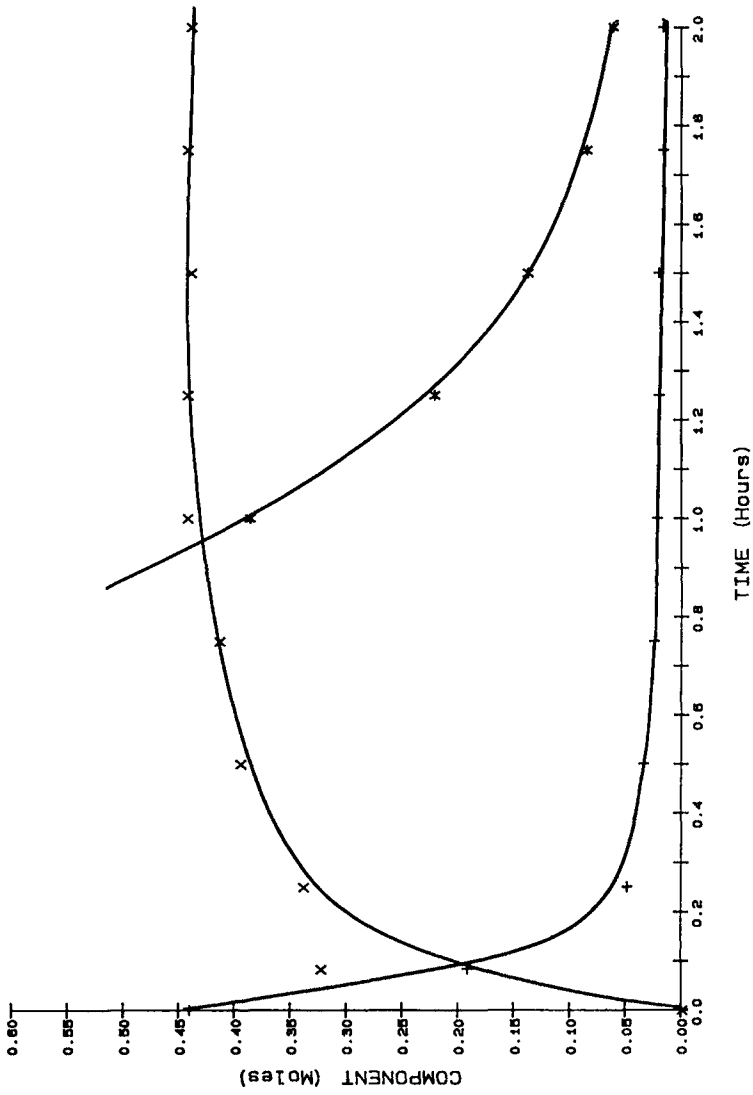


Fig. 9. Concentration of EC (*), MEG (+), and DEG (x) vs. time; EC:MEG molar ratio of 10:1 at 175°C.

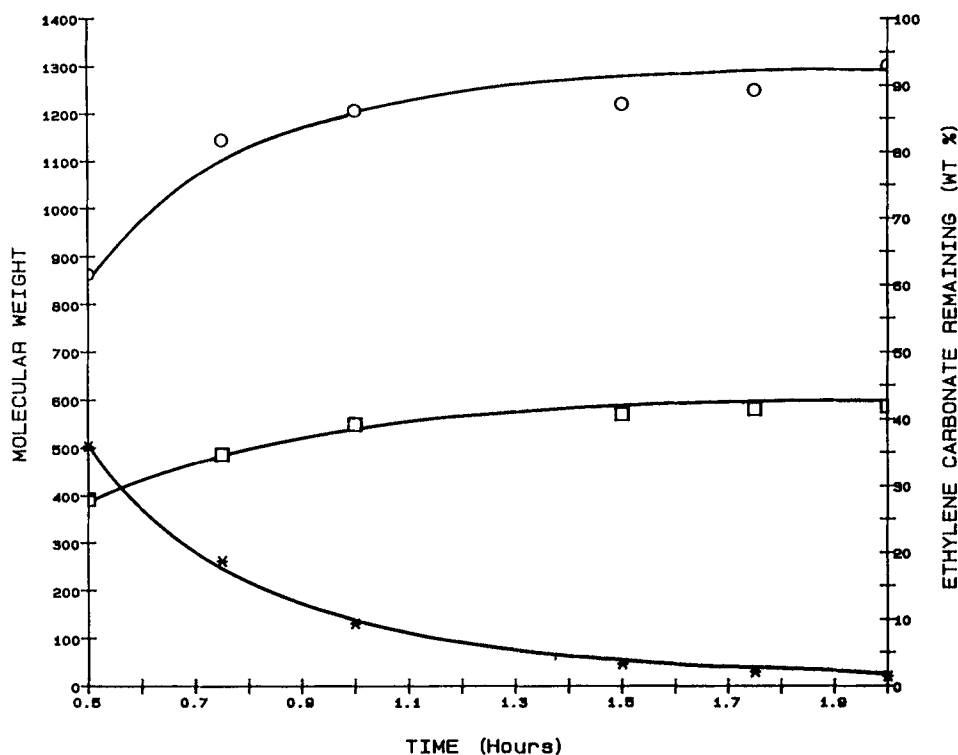


Fig. 10. Effect of time and EC conversion on molecular weight build (\circ , \bar{M}_w); EC:MEG molar ratio of 10:1 at 175°C. (\square) Mn; ($*$) EC remaining.

size-exclusion chromatography (SEC) relative to standard poly(ethylene glycols). Molecular weight increases smoothly with EC conversion with a polydispersity index of about 2.1.

At 175°C. The above reaction sequence was repeated at 175°C to determine the effects of higher temperature; no other conditions were changed. Samples were removed from the reactor and analyzed by vapor-phase chromatography. The reaction was followed through 2 h (98.5% EC conversion). Results are plotted in Figure 9. The MEG is rapidly consumed (90% MEG conversion in 15 min), but remains present at low levels throughout the reaction. DEG is formed rapidly and remains at a steady-state concentration (approximately the initial MEG concentration) throughout the rest of the reaction. TriEG is also formed in low levels as the reactions proceed. Reaction time is reduced from about 7 h to 2 h by increasing the temperature from 150°C to 175°C. The molecular weight by SEC as a function of time and EC conversion is plotted in Figure 10. Molecular weight of the 175°C product is slightly higher than that of the 150°C product.

Reaction of EC with DEG Using an EC : DEG Molar Ratio of 50 : 1 at 175°C

The reactions between EC and DEG using an EC : DEG molar ratio of 50 : 1 and sodium stannate as catalyst at 175°C were studied using the same

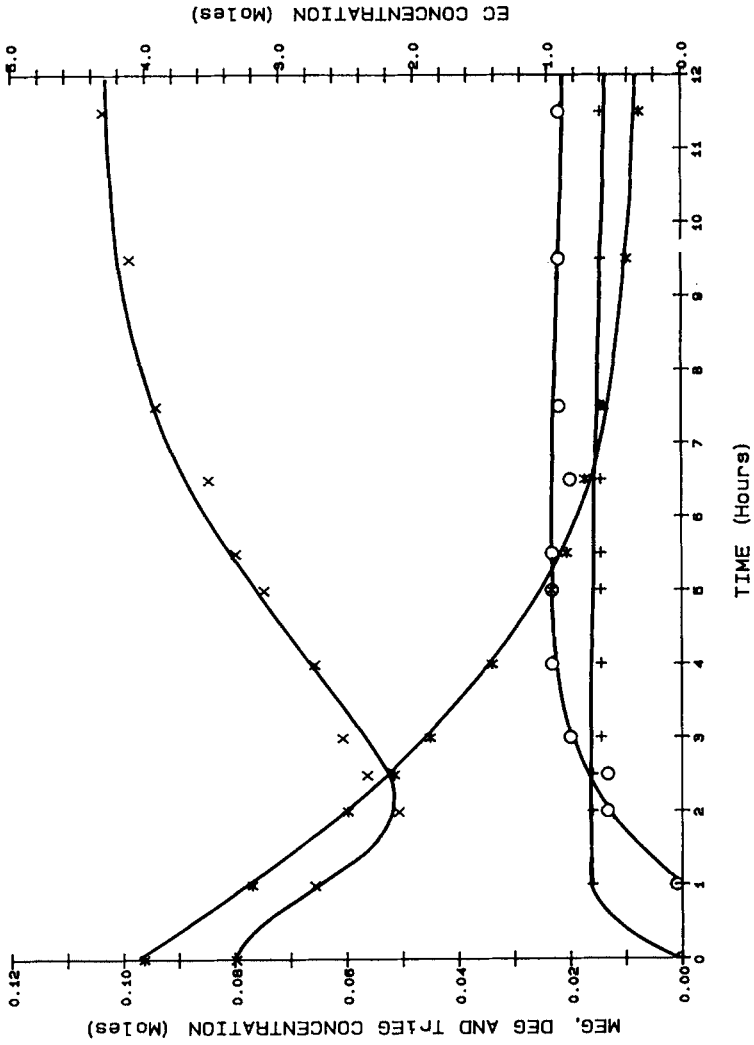


Fig. 11. Concentration of EC (*), MEG (+), DEG (X), and TriEG (O) vs. time; EC:DEG molar ratio of 50:1 at 175°C.

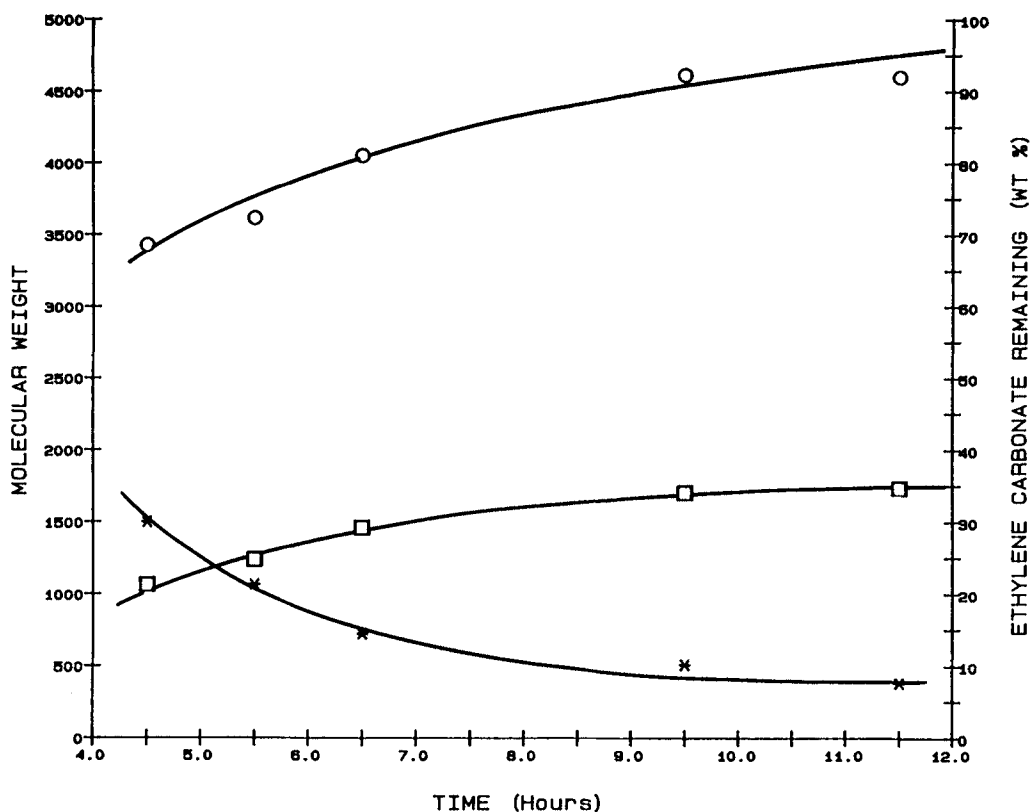


Fig. 12. Effect of time and EC conversion on molecular weight build (\circ , \bar{M}_w); EC : DEG molar ratio of 50 : 1 at 175°C. (\square) \bar{M}_n ; (*) EC remaining.

technique used above to follow the course of the reactions while making a much higher molecular weight product. Samples were removed from the reactor and analyzed by vapor-phase chromatography.

The reaction was followed for 11.5 h (92% EC conversion). Results are plotted in Figure 11. The DEG initiator concentration decreases somewhat through the first 2 h, but then increases smoothly throughout the remainder of the reaction. This indicates that the DEG is not only a reactant, but that it is also being formed during the course of the reaction. Its rate of formation is somewhat faster than its rate of reaction. MEG is formed early in the reaction and is present at a low concentration throughout the reaction. TriEG is also formed as the reactions proceed.

The molecular weight build by SEC as a function of time and EC conversion is plotted in Figure 12. Much higher molecular weights are produced using this higher EC : DEG ratio. However, the polydispersity index is also higher (about 2.7) indicating a broader distribution of molecular weights.

Reaction of EC with TriEG Using an EC : TriEG Molar Ratio of 10 : 1 at 150°C

The reactions between EC and TriEG using an EC : TriEG molar ratio of 10 : 1 and sodium stannate as catalyst at 150°C were studied using the same

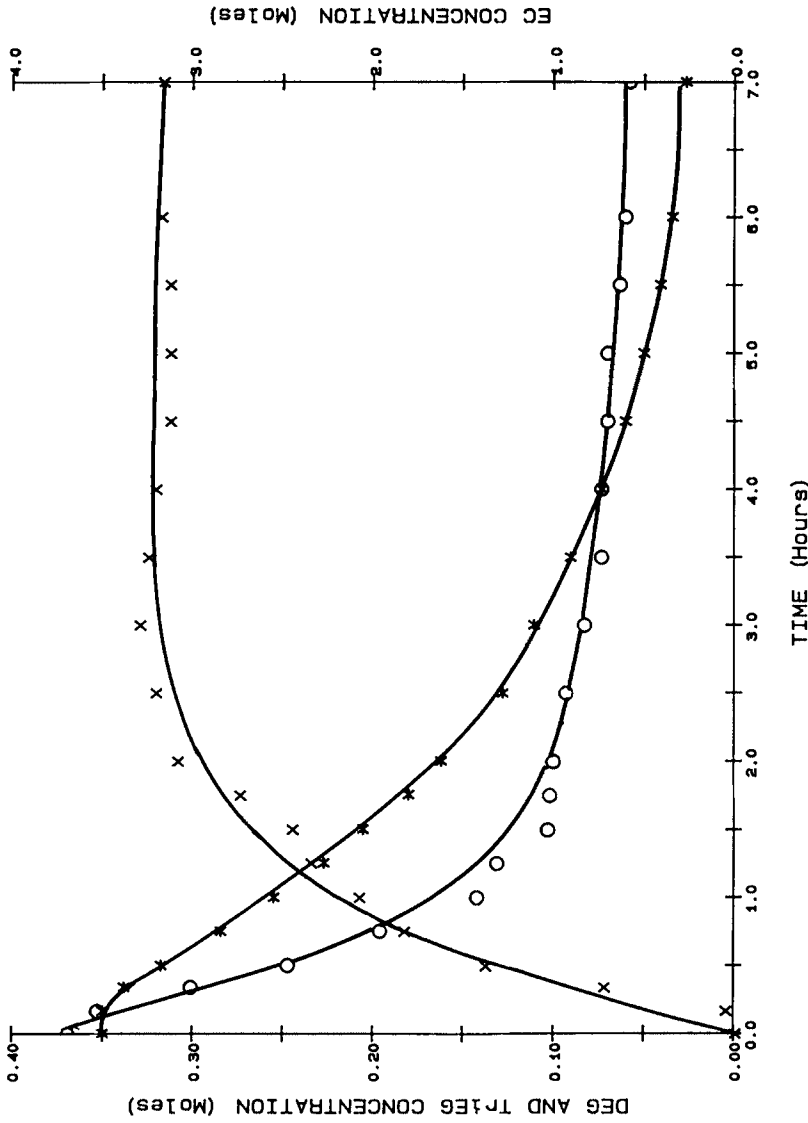


Fig. 13. Concentration of EC (●), TriEG (○), and DEG (×) vs. time; EC:TriEG molar ratio of 10:1 at 150°C.

technique used above to study the effect of using a higher molecular weight initiator on the reaction intermediates. Samples were removed from the reactor and analyzed by vapor-phase chromatography.

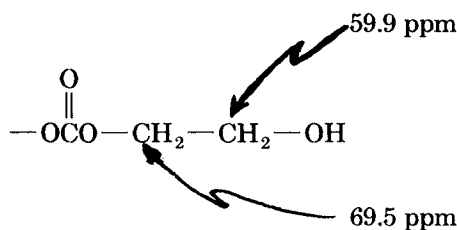
The reactions were followed through 7 h (94% EC conversion). Results are plotted in Figure 13. The TriEG concentration is reduced by 60% during the first hour of reaction and is reduced slowly during the remainder of the reaction (80% TriEG conversion after 7 h). DEG is formed slowly during the initial stages of the reaction and reaches a steady-state concentration in about 2 h, indicating that DEG is a key reaction intermediate even when the higher glycol, TriEG, is used as the initiator. The steady-state DEG concentration is very similar to the initial TriEG initiator concentration. MEG is formed early in the reaction and is present at a low concentration throughout the reaction. Very low concentrations of tetraethylene glycol (TetraEG) are also formed.

The molecular weight build by SEC as a function of time and EC conversion is plotted in Figure 14. The molecular weight of this product is slightly higher than the molecular weight of the product obtained using MEG as initiator under the same reaction conditions.

**¹³C NMR Study of the Reactions of EC with MEG Using an
EC : MEG Molar Ratio of 10 : 1 at 135°C Using Sodium Stannate
as Catalyst**

When samples are taken during the course of the reactions of EC with MEG and studied by ¹³C NMR, much more detail about the reaction pathway is ascertained. By studying the carbonyl region, the ring opening of the cyclic carbonate (156.3 ppm) to the open-chain carbonate (154.6 ppm) is clearly evident. The open-chain carbonate spectra give rise to a series of very close lines at low EC conversion, representing slightly different environments around the carbonyl due to various oligomers. These intermediates have not yet been fully characterized. At higher EC conversion, the carbonyl carbon is essentially a single line.

Much more detail is obtained by studying the methylene carbon region of the ¹³C NMR spectra as a function of EC conversion. A 10 : 1 molar ratio of EC : MEG was heated to 135°C and its ¹³C spectrum obtained (Fig. 15). The dominant lines are at 63.4 ppm (MEG) and 65.4 ppm (EC). Low levels of DEG are also present (61.1 and 72.1 ppm). Two additional lines are present (59.9 and 69.5 ppm) which have tentatively been assigned to the following structure:



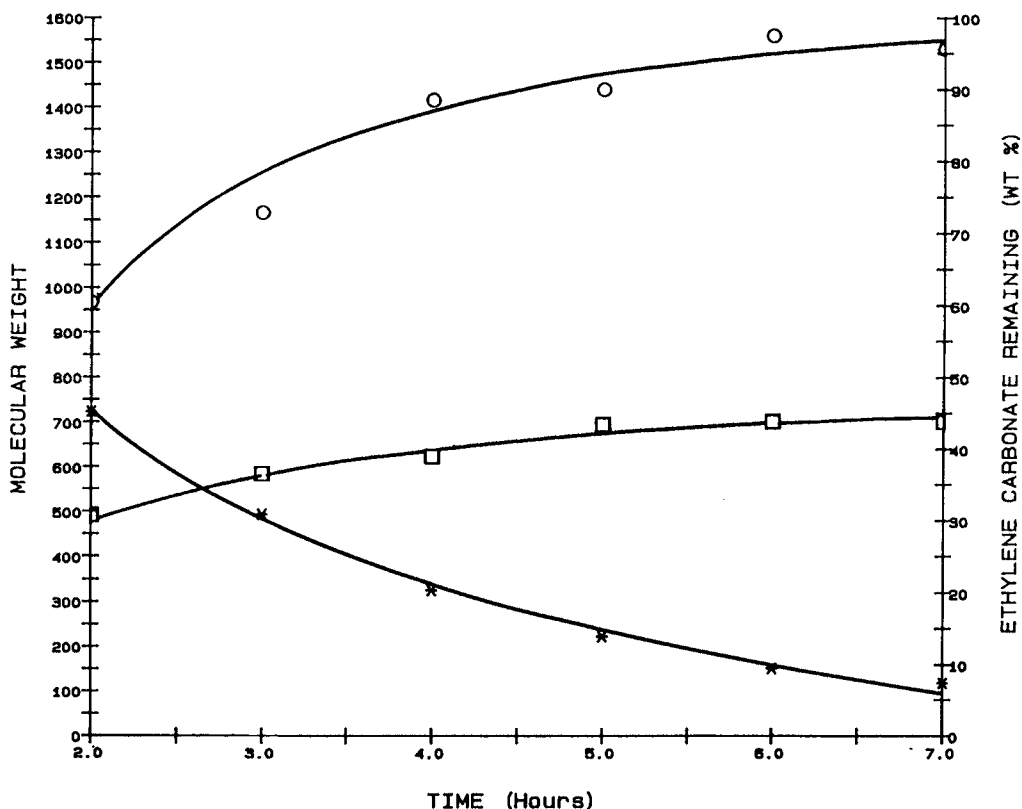
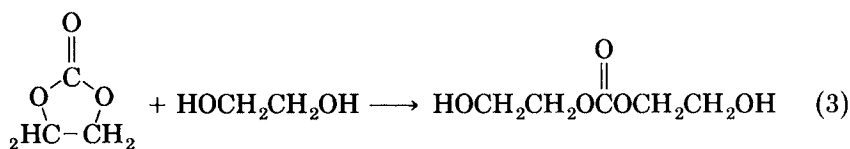


Fig. 14. Effect of time and EC conversion on molecular weight build (\circ , \bar{M}_w); EC:TriEG molar ratio of 10:1 at 150°C. (\square) \bar{M}_n ; ($*$) EC remaining.

This structure can be formed as a reactive intermediate as follows:



After heating for 2 h at 135°C, a sample has the ^{13}C NMR spectrum given in Figure 16. The MEG (63.4 ppm) has been reduced to a low level. The formation of DEG as a reaction intermediate is clearly indicated by the lines at 61.1 and 72.2 ppm. The carbons α to carbonate oxygen and β to ether oxygen are present at 67.0 and 67.2 ppm. The carbons β to carbonate oxygen and α to ether oxygen are present at 68.5 ppm. The carbons α to carbonate and β to hydroxy are present at 69.5 ppm and the carbons β to carbonate oxygen and α to hydroxy are present at 59.9 ppm.

A simpler spectrum is obtained from the sample after heating 24 h at 135°C (Fig. 17). The MEG is not detectable and the EC (65.4 ppm) is reduced to a low level. The backbone structure is composed mainly of carbons α to carbonate oxygen and β to ether oxygen (67.4 and 67.6 ppm) and carbons β to carbonate oxygen and α to ether oxygen (68.5 ppm). A much smaller portion

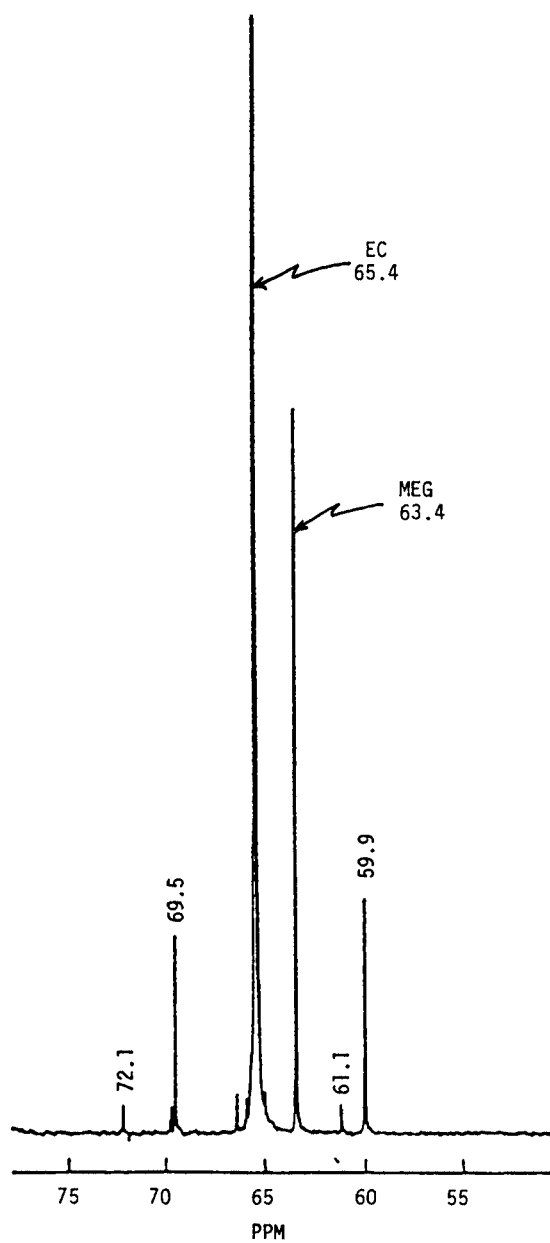


Fig. 15. ^{13}C NMR: EC : MEG molar ratio = 10 : 1; heated to 135°C.

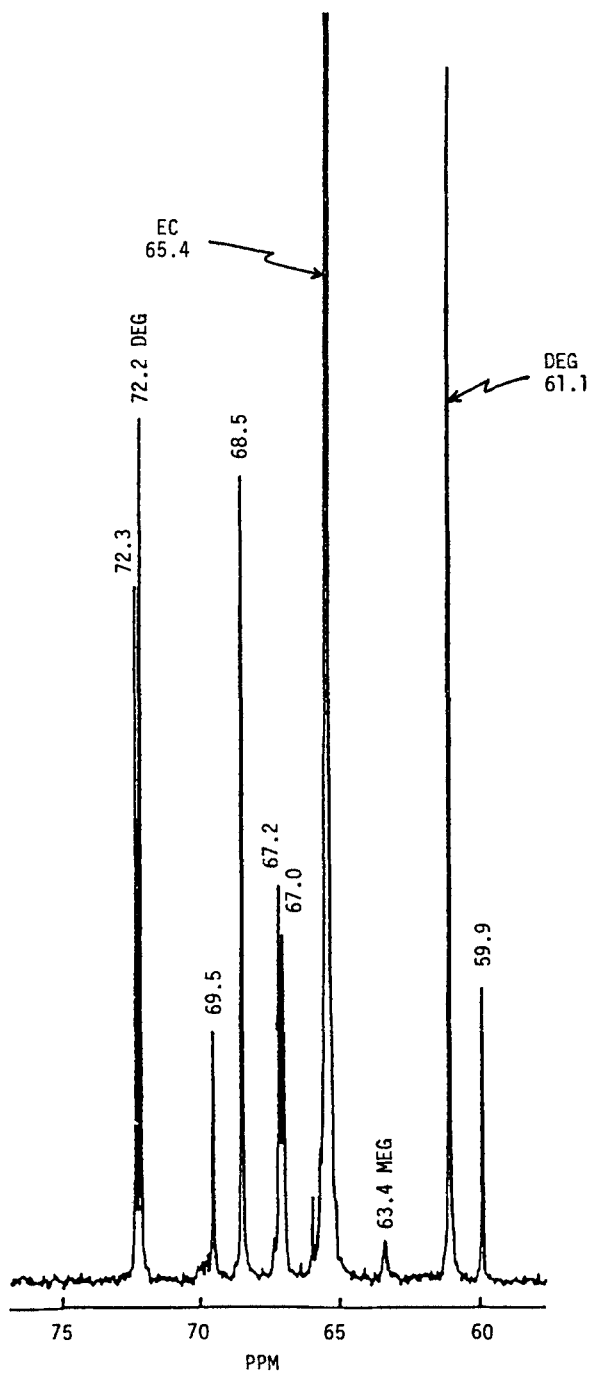


Fig. 16. ^{13}C NMR: EC : MEG molar ratio = 10 : 1; 2 h at 135°C.

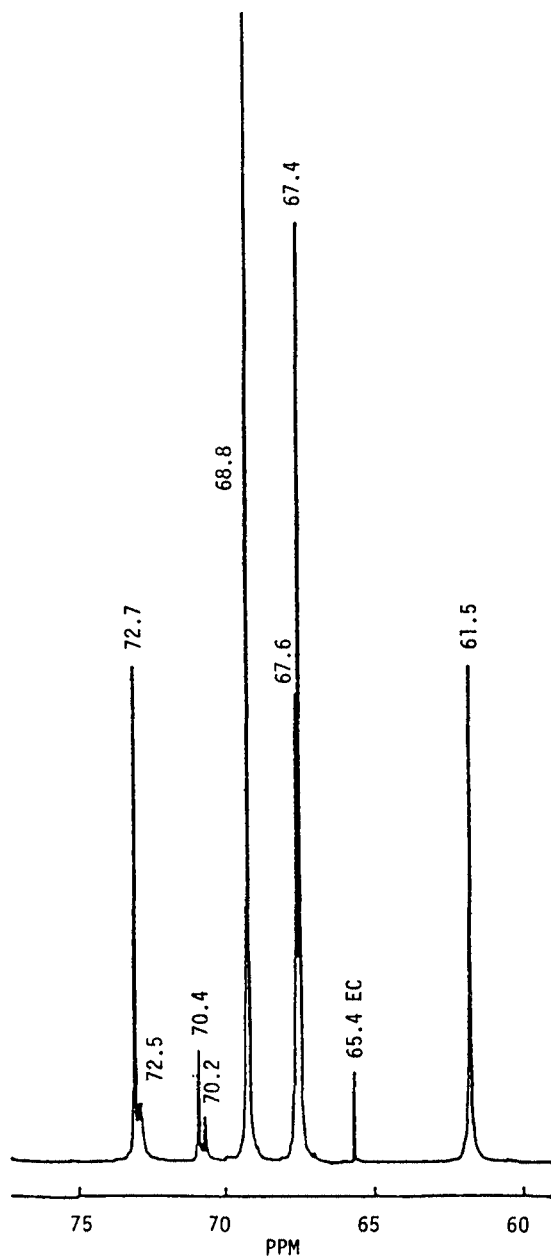


Fig. 17. ^{13}C NMR: EC:MEG molar ratio = 10:1; 24 h at 135°C.

of the backbone is composed of carbons α to ether oxygen and β to ether oxygen (70.4 ppm). The lines at 59.9 and 69.5 ppm are gone; all end groups are of the 2-hydroxyether ether type (lines are 61.5 and 72.7 ppm).

CONCLUSIONS

Capillary vapor-phase chromatography and ^{13}C NMR have been used to elucidate the structure of poly(ethylene ether carbonate) diols and certain initial intermediates produced during their formation. These diols were produced by the oligomerization of ethylene carbonate using MEG or DEG as initiator and catalyzed by sodium stannate trihydrate. Additional reaction intermediates and reaction mechanisms are the subject of current investigations.

The backbone and end-group structure of these diols have been defined by comparison of their ^{13}C NMR spectra to the spectra of model compounds. These diols are alternating copolymers of carbon dioxide and DEG which also contain smaller amounts of higher ethylene glycols in their backbone. These higher ethylene glycols are detected by a line at 70.3 ppm in their ^{13}C NMR spectrum which represents carbon atoms which are in both an α and β arrangement relative to ether oxygen.

Diethylene glycol is an important reaction intermediate regardless of whether the initiator is MEG, DEG, or TriEG. When equal molar quantities of EC and MEG are allowed to react under the experimental conditions used in this report, DEG is the major product, along with small quantities of TriEG, as measured by capillary vapor-phase chromatography. ^{13}C NMR also indicates that DEG is rapidly formed by the oligomerization of EC using MEG as initiator and that the MEG is rapidly reduced to a low concentration. The DEG reaches a steady-state concentration early in the reaction as the rate of formation of this reactive intermediate is in balance with its rate of reaction. The amount of DEG present at steady state is approximately the same number of moles as the MEG initially charged.

^{13}C NMR evidence suggests that the end groups at an intermediate stage of the reaction are both 2-hydroxyethyl carbonate and 2-hydroxyethyl ether moieties. However, the final product (high EC conversion) contains only 2-hydroxyethyl ether end groups.

The product molecular weight builds as a smooth function of conversion and time. The polydispersity index is above 2.

References

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