

# Effect of Catalyst on the Molecular Weight Advancement of Poly(Ethylene Ether Carbonate) Polyols

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## Synopsis

Sodium stannate is a preferred catalyst for the preparation of poly(ethylene ether carbonate) polyols. It can be removed from the polyol by treatment with acetone to precipitate most of the catalyst followed by adsorption of the soluble catalyst on Florisil and filtration. Sodium metaborate and potassium carbonate catalysts are not precipitated to any extent by acetone but can be reduced to lower levels by adsorption on Florisil and filtration. The molecular weight of the poly(ethylene ether carbonate) polyol and the water content of the system have a strong influence on the effectiveness of this purification technique. Catalysts are more easily removed from higher molecular weight polyols with low water content. The effect of sodium stannate catalyst level on the molecular weight advancement of poly(ethylene ether carbonate) polyols has been studied. The rate of advancement to a 3000 molecular weight product is increased with good CO<sub>2</sub> retention (95%) when the tin level is 100–500 ppm. At higher catalyst levels, product decomposition to 1,4-dioxane becomes increasingly important. Complete mass balances and distillate analyses are presented to show the effects of catalyst levels. The product composition is dominated by the CO<sub>2</sub> content of the reactant and the advancement conditions.

## INTRODUCTION

Poly(ethylene ether carbonate) polyols have been formed by the reactions of ethylene carbonate (EC), dialkyl carbonates, diphenyl carbonate, ethylene oxide and carbon dioxide, or phosgene with polyether polyol initiators in the presence of appropriate catalysts. These poly(ethylene ether carbonate) polyols are polymers which contain alternating blocks of carbon dioxide units and poly(ethylene glycol) units in their backbones when diol initiators are employed. When sodium stannate trihydrate is used as the catalyst, backbone hydrolysis studies<sup>1</sup> and carbon-13 NMR studies<sup>2</sup> have shown that these polyols contain predominantly carbon dioxide units and diethylene glycol (DEG) units with small quantities of triethylene glycol (TriEG) units and have —OC(O)OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH end groups.

When these polyols are heated to elevated temperatures (> 180°C) at reduced pressures, volatile impurities are removed, followed by molecular weight advancement and formation of DEG.<sup>3–5</sup> As DEG 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 advanced polyols form rapidly with high CO<sub>2</sub> retention, relatively low polydispersity, and high purity.

This work examines the effect of residual catalysts and added catalysts on the molecular weight advancement of poly(ethylene ether carbonate) polyols using this process. It also discusses a technique for catalyst removal and the effect of several important variables associated with this technique.

## EXPERIMENTAL

Ethylene carbonate (EC), sodium stannate trihydrate, sodium metaborate, potassium carbonate, Florisil (anhydrous magnesium silicate; 100–200 mesh), 1,6-hexanediol, and 1,4-dioxane were obtained from Aldrich Chemical Co. Monoethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TetraEG), and ethylene oxide were manufactured by the Dow Chemical Co. Acetone (high purity grade; water < 0.1 wt %) was obtained from Burdick & Jackson Laboratories, Inc. Capillary gas chromatograms were obtained on a Hewlett-Packard 5840A unit with a J&W Scientific Company DB-1 fused silica capillary column. 1,6-Hexanediol was used as internal standard. Size exclusion chromatography (SEC) was done on Waters Ultrastyrigel 1000- and 10,000-Å columns, calibrated with standard poly(ethylene glycol)s and using a refractive index detector. Carbon-13 NMR spectra were obtained on a Bruker WM 360 MHz (90.5 MHz for carbon-13) instrument. The CO<sub>2</sub> content of the poly(ethylene ether carbonate) polyols was measured by quantitative proton NMR using dimethylsulfoxide as the internal standard. Water analysis was done by Karl Fischer titration. Potentiometric titrations were done using a Brinkmann 636 Titroprocessor equipped with an E-635 Dosimat.

### Poly(Ethylene Ether Carbonate) Polyol Synthesis

Poly(ethylene ether carbonate) polyols were prepared from EC and MEG or DEG using sodium stannate trihydrate (0.5 wt %), sodium metaborate (0.5 wt %), or potassium carbonate (1.0 wt %) as catalyst.\* A polyol was also prepared from ethylene oxide, CO<sub>2</sub>, and MEG.<sup>6</sup> The catalyst was removed from many samples by dissolving the polyol in acetone, stirring with Florisil, filtering, and acetone stripping.<sup>7</sup>

### Molecular Weight Advancement Procedure

A given polyol and boiling stones were placed in a boiling flask equipped with a thermometer, heating mantle, and down draft water chilled condenser attached to a dry ice-isopropanol trap (−78°C) and a vacuum source. The polyol was heated to 60–80°C to reduce viscosity and outgassed at about 50 mm Hg. The vacuum was then adjusted to the desired pressure and heating increased to effect fractionation. The distillate was weighed and analyzed. In experiments where molecular weight data was collected at various pot temperatures, the reaction set up was modified to include a syringe port where pot samples could be removed without disturbing the system vacuum.

\* Detailed procedures are given in Refs. 1–5 and references cited therein.

## RESULTS AND DISCUSSION

**Effects of a High Level of Sodium Stannate on the Thermal Stability of Poly(Ethylene Ether Carbonate) Polyols**

When a 10 : 1 molar ratio of EC : DEG is heated at 175°C and atmospheric pressure using 0.5 wt % sodium stannate trihydrate as catalyst, EC conversion is complete (> 99%) in 2.5 h and the number average molecular weight builds to about 600. However, if heating is continued between 180 and 185°C, the molecular weight is degraded with time (Fig. 1) and volatiles are distilled from the reactor. Analysis of the distillate (IR and retention time) indicates 1,4-dioxane (99.8 wt %) and traces of MEG (0.2 wt %). After 17 h reaction time, the 1,4-dioxane accounts for 53% of the equivalents of ethylene oxide units in the EC and DEG reactants (Fig. 1).

The contents of the reactor were analyzed for EC and free glycols as a function of time by capillary vapor phase chromatography through (1) the molecular weight building sequence (0–2.5 h) and (2) the molecular weight decomposition sequence (2.5–17 h) (Fig. 2). DEG is formed quickly in the reactor and is present at high concentrations throughout most of the molecular weight building reaction sequence.<sup>2</sup> Its concentration drops off considerably as more DEG is incorporated into the oligomer backbone in the later stages of the molecular weight building sequence. However, free DEG increases again during much of the decomposition sequence as CO<sub>2</sub> is lost from the polymer. DEG concentrations drop off in the later stages of the decomposition sequence as it is partially converted to higher polyglycols. TriEG is formed in the later stages of the molecular weight building reaction sequence and increases in concentration throughout the decomposition sequence. TetraEG is absent in the molecular weight building reaction sequence but becomes increasingly important in the later stages of the decomposition sequence. When the experiment was terminated, there was nearly twice as much TriEG present as DEG. The changes in

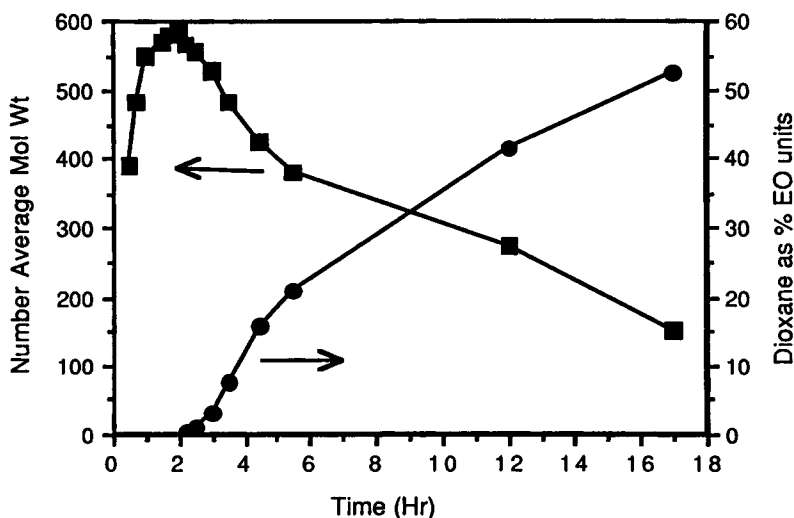


Fig. 1. Effect of reaction time on number average molecular weight and 1,4-dioxane formation.

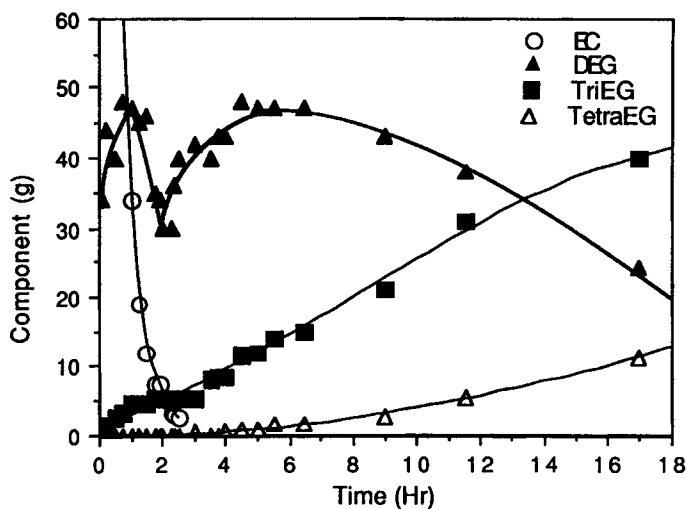


Fig. 2. Effect of time on free glycols and EC in the reactor.

concentration of these materials as a function of time are shown in Figure 2. After 17 h reaction time, the glycols account for 35% of the equivalents of ethylene oxide units in the EC and DEG reactants. The analyses of the products (volatile to vapor phase chromatography conditions) present at the end of the molecular weight building reaction sequence and at the end of the decomposition sequence are given in Table I. At least 79 wt % of the product did not contain carbonate units when the experiment was terminated.

A proposed reaction sequence for the sodium stannate catalyzed decomposition of poly(ethylene ether carbonate) polyols is given in Figure 3. This sequence involves reaction between a hydroxyl end group and a carbonate moiety in close proximity (probably through coordination with tin) to form a cyclic intermediate which can lose 1,4-dioxane and form a monoalkyl carbonic acid

TABLE I  
Concentration of Components Present in Volatiles after Molecular Weight Building Reaction Sequence and after Decomposition Sequence

Component	Present after molecular weight building sequence (wt %)	Present after decomposition sequence (wt %)
1,4-Dioxane	3.1	8.5
EC	1.0	0.0
MEG	0.3	0.3
DEG	27.0	18.4
TriEG	4.0	36.8
TetraEG	0.8	11.1
PentaEG	0.0	3.5
HexaEG	0.0	0.4
Totals	36.2	79.0

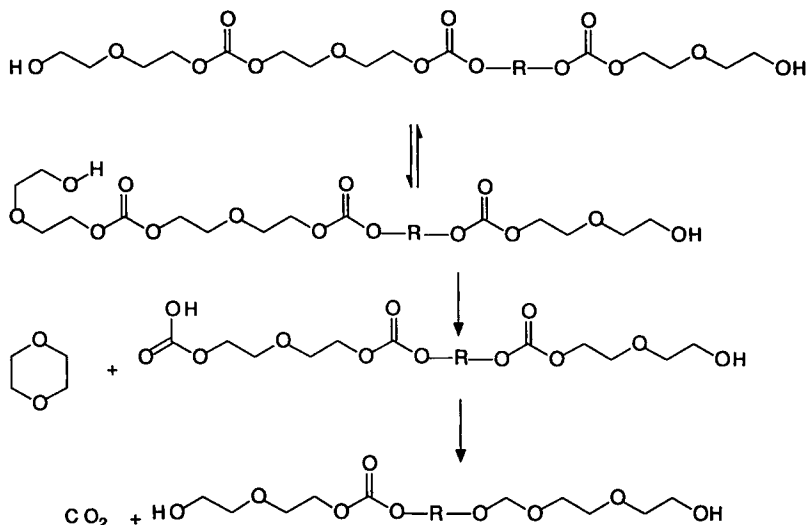


Fig. 3. Proposed reaction sequence for the sodium stannate catalyzed thermal decomposition of poly(ethylene ether carbonate) polyols.

derivative. This carbonic acid derivative will rapidly lose  $\text{CO}_2$  under the reaction conditions to give a poly(ethylene ether carbonate) polyol with one less DEG unit in its backbone. This sequence can be repeated to yield additional quantities of these decomposition products.

### Catalyst Removal from Poly(Ethylene Ether Carbonate) Polyols

When poly(ethylene ether carbonate) polyols are heated at elevated temperatures and reduced pressures with distillate removal, molecular weight advancement occurs.<sup>3-5</sup> The catalyst was removed prior to advancement in these studies by treatment with acetone and Florosil.<sup>7</sup> It is important that the catalyst be reduced to a low level for the subsequent use of these polyols in polyurethane applications.

The residual alkalinity after any treatment was followed by dilute (0.01 *N*) HCl titration using the controlled polymerization rate (CPR) technique.<sup>8</sup> A given CPR value is defined as 10 times the number of milliliters of 0.01 *N* HCl required to titrate a 30 g polyol sample. One mole of sodium stannate is titrated with 2 mol of HCl at the end point. The bulk of the sodium stannate catalyst was removed by the acetone treatment alone. The sodium stannate was precipitated by the addition of acetone and was removed by filtration.

Table II shows the effect of added acetone level on the CPR values of a filtered poly(ethylene ether carbonate) diol sample. CPR values were very high (1360) in the absence of the acetone treatment. However, when an equal weight of acetone was added to the poly(ethylene ether carbonate) diol, followed by filtration of the precipitated sodium stannate, the CPR value was reduced by more than an order of magnitude (25.9). Larger amounts of acetone produce even lower CPR values, but a large solvent handling problem was experienced.

TABLE II  
Effect of Poly(Ethylene Ether Carbonate) Polyol : Acetone Ratio on Polyol CPR,  
Sodium Stannate as Catalyst (0.5 wt %), No Florisil

Polyol <sup>a</sup> : acetone ratio (wt/wt)	CPR
100/0	1360
50/50	25.9
35/65	8.4
25/75	5.8
17/83	3.2

<sup>a</sup>  $\bar{M}_n = 744$ .

A 25/75 (wt/wt) ratio of poly(ethylene ether carbonate) diol to acetone was chosen as a good balance between effective catalyst removal and excess solvent handling. The remaining catalyst was removed by treatment with Florisil.

Table III shows the effect of solvent type on catalyst removal. The same poly(ethylene ether carbonate) diol sample was treated with various solvents using a 25/75 (wt/wt) ratio of poly(ethylene ether carbonate) diol ( $\bar{M}_n = 744$ ) to solvent, followed by overnight digestion with 10 wt % Florisil (100–200 mesh) based on poly(ethylene ether carbonate) diol and filtration. Acetone was the most effective solvent studied.

The effectiveness of this catalyst removal treatment was strongly dependent on the molecular weight of the poly(ethylene ether carbonate) diol and on the particular catalyst to be removed. Lower molecular weight materials contain much higher levels of free DEG<sup>2</sup> which interfere with sodium stannate precipitation. Table IV presents data on the removal of sodium stannate, sodium metaborate, and potassium carbonate from poly(ethylene ether carbonate) diols of different molecular weights. The effect of the amount of Florisil used is also apparent. At a number average molecular weight of 302, the acetone treatment was rather ineffective at sodium stannate removal and the Florisil does the major portion of the job. However, Sn levels were still very high even with 20 wt % Florisil loading. As the  $\bar{M}_n$  was increased to 468, the acetone became very effective at sodium stannate precipitation (CPR decreases from 640 to 15.6).

TABLE III  
Effect of Purification Solvent on CPR of a Poly(Ethylene Ether Carbonate) Polyol  
Made Using Sodium Stannate (0.5 wt %) as Catalyst

Solvent	CPR <sup>a</sup>
Acetone	0
Methyl ethyl ketone	2.6
Ethyl acetate	1.2
Methylene dichloride	10.9
Methanol	Partially insoluble
Toluene	Insoluble

<sup>a</sup> Using a 25/75 wt ratio of polyol ( $\bar{M}_n = 744$ ) to solvent and 10 wt % Florisil based on polyol.

TABLE IV  
 Effect of Catalyst Type and Molecular Weight on CPR

Catalyst	EC : DEG molar ratio	Molecular weight data				CPR after treatment, <sup>a</sup> Florisol based on polyol (wt %)		
		Peak	$\bar{M}_n$	$\bar{M}_w$	PDI	0	10	20
Sodium stannate	2	273	302	375	1.24	640	230	82
Sodium stannate	5	401	468	732	1.56	15.6	7.7	0.2
Sodium stannate	10	800	615	1000	1.63	10.0	4.7	0
Sodium stannate	10	1046	694	1166	1.68	6.0	0	0
Sodium stannate	10	1113	744	1261	1.70	5.8	0	0
Sodium metaborate	5	334	343	480	1.40	v	1033	480
Sodium metaborate	10	641	480	757	1.58	v	205	103
Sodium metaborate	10	667	499	791	1.59	v	100	33
Sodium metaborate	50	1284	754	1445	1.91	v	5.1	0.2
Potassium carbonate	10	678	448	751	1.68	v	296	285
Potassium carbonate	10	709	480	784	1.63	v	339	307
Potassium carbonate	50	2086	1191	2526	2.12	v	9.7	0.8

<sup>a</sup> v = very little catalyst precipitates; polyol : acetone = 1 : 3 (by wt), 100–200 mesh Florisol; PDI =  $\bar{M}_w/\bar{M}_n$ .

As the  $\bar{M}_n$  was further increased to 744, the catalyst was systematically further reduced. At these higher molecular weights, the Florisol treatment (10 wt %) reduced the residual catalyst to very low levels.

When either sodium metaborate or potassium carbonate was used as catalyst, very little catalyst was precipitated by the acetone treatment (Table IV). With these catalysts the acetone served as a solvent during the Florisol treatment. The treatment was most effective with the higher molecular weight poly(ethylene ether carbonate) diols. Larger amounts of Florisol were required to remove these catalysts. Based on a poly(ethylene ether carbonate) diol with an  $\bar{M}_n$  of about 500, the CPR values after treatment with Florisol (20 wt %) were 0.2, 33, and 307 for sodium stannate, sodium metaborate, and potassium carbonate, respectively.

The water content of the poly(ethylene ether carbonate) diols and of the acetone used was an important variable since sodium stannate is soluble in water. Less sodium stannate was precipitated as the total water level was increased. Table V shows the effect of various water levels in the poly(ethylene ether carbonate) diol on CPR values for five different diols prepared under similar conditions. CPR values ranged from 21.6 to 0 as the wt % water in the diol varied from 0.82 to 0.08 wt %. The water level in the acetone was constant at < 0.1 wt % in all of these studies.

### Effects of Catalyst Level on the Molecular Weight Advancement of Poly(Ethylene Ether Carbonate) Polyols

The effect of the amount of sodium stannate catalyst remaining in the polyol prior to advancement conditions was studied in order to define the required degree of purification. A large batch of poly(ethylene ether carbonate) diol was prepared. One portion was filtered at ambient temperature to remove insoluble

TABLE V  
Effect of Water Content of Polyol on CPR Using Sodium Stannate (0.5 wt %) as Catalyst

EC : DEG molar ratio	Molecular weight data				CPR <sup>a</sup>	Water in polyol (wt %)
	Peak	$\bar{M}_n$	$\bar{M}_w$	PDI		
10	950	603	1080	1.79	21.6	0.82
10	1060	638	1169	1.83	20.4	0.80
10	1050	655	1154	1.76	13.2	0.44
10	1115	664	1230	1.85	11.6	0.45
10	1046	694	1166	1.68	0	0.08

<sup>a</sup> Polyol : acetone = 1 : 3 (by wt), 100–200 mesh Florosil (10% based on polyol).

catalyst (Sample I, 2310 ppm Sn by atomic emission; CPR = 1360). A second portion of the diol was treated with acetone (25 wt % diol : 75 wt % acetone) and then filtered at ambient temperature (Sample II, 10 ppm Sn; CPR = 18.4). The majority of the sodium stannate catalyst was precipitated by this acetone treatment. A third portion of the diol was treated with acetone as above, followed by overnight digestion with Florosil (10 wt % based on diol) and filtration (Sample III, 2 ppm Sn; CPR = 6.8). A large portion of the catalyst which was not precipitated by acetone was adsorbed to the Florosil and removed by filtration. These purification results are summarized in Table VI.

Each of these purified diols was subjected to molecular weight advancement conditions (Tables VII–IX). Figure 4 shows the effect of residual catalyst level on molecular weight build. The rate of molecular weight build increased with increasing catalyst level. For example, the  $\bar{M}_n$  at a pot temperature of 220°C was about 1495, 1592, and 2200 for Sn levels of 2, 10, and 2310 ppm, respectively. Even at a pot temperature of about 240°C, the  $\bar{M}_n$  was about 2220, 2600, and 3100 for the same tin levels. However, at the highest tin level, the molecular weight decomposition sequence dominated at higher temperatures (> 240°C). As indicated above, 1,4-dioxane became a major component in the distillate as decomposition occurred (Fig. 5). The amount of 1,4-dioxane in the distillate increased with increasing tin concentration and with increasing temperature.

TABLE VI  
Effect of Purification Procedure on Residual Tin and CPR Values

Sample no.	Purification procedure used on starting polyol	After treatment	
		CPR	Tin (ppm) <sup>a</sup>
I	Filtered only	1360	2310
II	Treated with acetone and filtered; polyol : acetone = 25 : 75 (wt/wt)	18.4	10
III	Treated with acetone (polyol : acetone = 25 : 75 (wt/wt); Florosil (10 wt % based on polyol) and filtered	6.8	2

<sup>a</sup> Atomic emission.



TABLE VII

Advancement Data on a Poly(Ethylene Ether Carbonate) Polyol Made from Ethylene Carbonate and Diethylene Glycol Using Sodium Stannate as Catalyst (0.5 wt %), 2 ppm Sn

Pot temp (°C)	Distillate (wt %)	Molecular weight data <sup>a</sup>				Distillate assay data (wt %)					
		Peak	$\bar{M}_n$	$\bar{M}_w$	PDI	MEG	Dioxane	EC	DEG	TriEG	TetraEG
162	1.4	nd	nd	nd	nd	2.14	0.60	34.5	59.6	2.25	—
166	2.6	nd	nd	nd	nd	1.62	0.60	26.8	69.0	2.52	—
171	4.0	nd	nd	nd	nd	1.05	0.60	20.1	76.0	2.25	—
177	5.6	1554	819	1575	1.92	0.71	0.77	12.1	83.4	3.00	—
183	7.3	1714	955	1872	1.96	0.45	1.12	4.34	90.7	3.00	—
189	9.0	1892	994	1972	1.98	0.39	1.14	1.19	92.0	3.78	—
199	11.2	2087	1083	2081	1.92	0.37	1.38	—	92.9	4.44	—
209	13.0	2786	1193	2625	2.20	0.34	1.98	—	91.4	4.64	—
220	14.4	3408	1495	3355	2.24	0.20	3.26	—	90.2	3.73	—
230	15.6	4139	1828	4147	2.27	0.28	5.52	0.45	85.7	3.34	0.34
240	16.8	5525	2220	5311	2.39	0.33	5.85	0.49	80.6	5.42	0.87
250	18.2	8063	2696	7017	2.60	0.39	9.81	0.67	69.1	5.14	1.76
260	19.7	9704	3116	8590	2.75	0.34	14.29	0.75	55.3	5.19	3.13

<sup>a</sup> nd = not determined.

For example, the 1,4-dioxane at a pot temperature of 220°C was about 3.3, 4.5, and 46 wt % for Sn levels of 2, 10, and 2310 ppm, respectively. Some 1,4-dioxane was carried through the distillate trap and was collected in the -78°C trap due to high CO<sub>2</sub> evolution from the poly(ethylene ether carbonate) diol under conditions of rapid decomposition.

The amount of total distillate present at a given pot temperature was higher with higher tin concentrations (Fig. 6). However, this was largely an increase in rate. When the  $\bar{M}_n$  was plotted vs. wt % distillate, all the data points fell essentially on the same curve (Fig. 7). Some scatter at higher temperatures with the polyol containing 2310 ppm Sn reflects product decomposition.

TABLE VIII

Advancement Data on a Poly(Ethylene Ether Carbonate) Polyol Made from Ethylene Carbonate and Diethylene Glycol Using Sodium Stannate as Catalyst (0.5 wt %), 10 ppm Sn

Pot temp (°C)	Distillate (wt %)	Molecular weight data <sup>a</sup>				Distillate assay data (wt %)					
		Peak	$\bar{M}_n$	$\bar{M}_w$	PDI	MEG	Dioxane	EC	DEG	TriEG	TetraEG
163	1.2	nd	nd	nd	nd	2.30	1.28	32.6	60.6	2.09	—
166	2.3	nd	nd	nd	nd	1.59	0.88	27.3	68.1	2.14	—
171	3.4	nd	nd	nd	nd	1.23	1.04	21.3	73.6	2.44	—
179	5.5	nd	nd	nd	nd	0.77	1.48	11.7	83.1	2.97	—
187	8.0	1724	914	1792	1.96	0.48	1.65	2.73	91.7	3.47	—
198	10.8	2299	1109	2218	2.00	0.36	2.44	0.37	92.0	3.83	—
210	12.8	2786	1305	2728	2.09	—	3.03	—	91.0	4.38	—
220	14.6	3712	1592	3501	2.20	—	4.53	—	87.6	4.80	—
231	16.6	4490	1718	4194	2.44	0.58	8.17	—	80.9	4.51	—
245	19.0	8650	2930	8334	2.84	0.40	15.1	—	65.0	4.22	1.53
255	21.3	9483	3197	9099	2.85	0.43	23.6	—	38.8	3.49	3.24

<sup>a</sup> nd = not determined.

TABLE IX

Advancement Data on a Poly(Ethylene Ether Carbonate) Polyol Made from Ethylene Carbonate and Diethylene Glycol Using Sodium Stannate as Catalyst (0.5 wt %), 2310 ppm Sn

Pot temp (°C)	Distillate (wt %)	Molecular weight data <sup>a</sup>				Distillate assay data (wt %)					
		Peak	$\bar{M}_n$	$\bar{M}_w$	PDI	MEG	Dioxane	EC	DEG	TriEG	TetraEG
164	1.2	nd	nd	nd	nd	2.73	2.64	28.3	63.4	2.14	—
170	3.1	nd	nd	nd	nd	1.11	2.36	13.9	78.5	3.67	—
175	5.0	nd	nd	nd	nd	0.59	2.40	5.5	86.4	4.80	—
181	7.6	1566	807	1603	1.98	0.38	2.17	1.5	89.6	5.91	—
187	9.8	1898	966	2012	2.08	0.41	2.40	0.4	89.6	6.52	—
195	11.9	2531	1141	2416	2.12	0.36	2.77	—	88.6	7.26	—
203	14.3	3374	1549	3494	2.26	0.37	3.27	—	85.7	8.54	0.50
214	16.4	4936	1982	4792	2.42	0.48	21.9	—	62.9	9.20	1.18
223	19.6	7187	2275	6504	2.86	0.47	46.8	—	34.0	8.98	2.59
238	21.2	9483	3164	9546	3.02	—	16.5 <sup>b</sup>	—	30.8	17.2	8.72
250	24.6	6546	2554	7134	2.79	—	5.4 <sup>b</sup>	—	5.5	14.8	11.3

<sup>a</sup> nd = not determined.

<sup>b</sup> Some 1,4-dioxane was carried through this trap due to high CO<sub>2</sub> evolution from the poly(ethylene ether carbonate) diol under conditions of rapid decomposition.

### Effects of Added Sodium Stannate on the Molecular Weight Advancement of Poly(Ethylene Ether Carbonate) Polyols

In the above poly(ethylene ether carbonate) polyols, the sodium stannate catalyst was removed by various modifications of the purification technique to yield materials with 2310, 10, and 2 ppm Sn. In order to study the effects of Sn at intermediate levels, a large batch of poly(ethylene ether carbonate) polyol was made and sodium stannate trihydrate was added at given levels prior to molecular weight advancement. This poly(ethylene ether carbonate) polyol was made at a lower temperature (135°C) and required somewhat higher pot

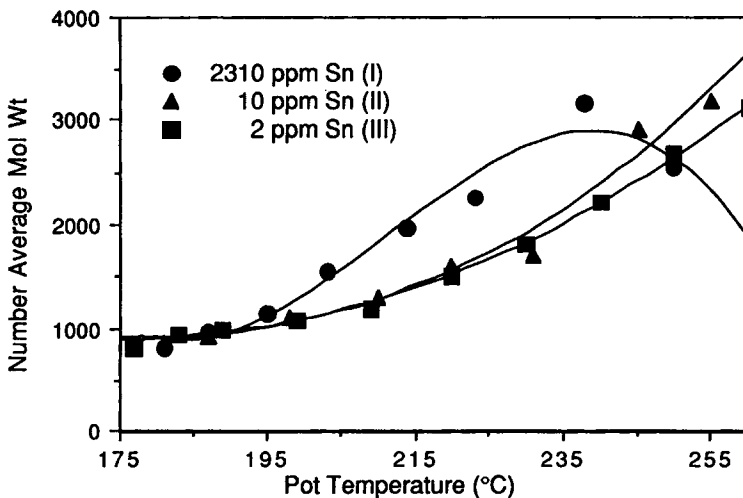


Fig. 4. Effect of residual catalyst level on molecular weight build.

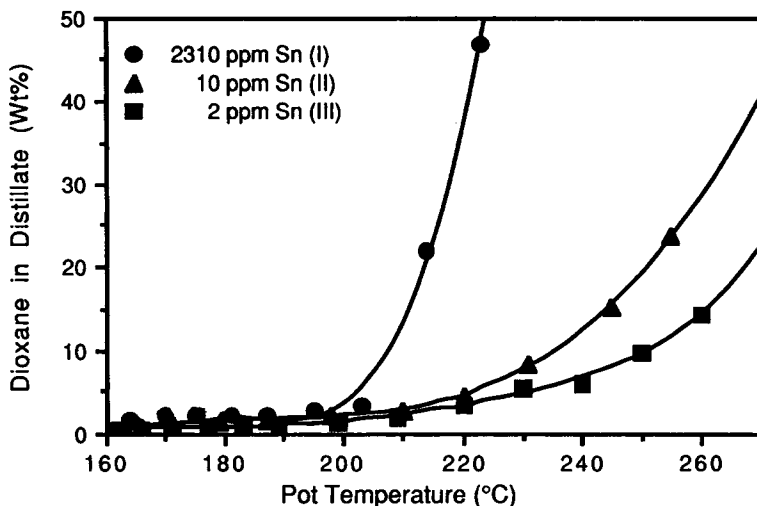


Fig. 5. Weight percent 1,4-dioxane in distillate as a function of pot temperature.

temperatures to reach the molecular weight of the advanced products of samples I–III.

Table X shows the effect of added Sn at 0, 100, 200, 500, and 1000 ppm on molecular weight build and CO<sub>2</sub> content when heated to a pot temperature of about 240°C. A filtered only sample (2310 ppm Sn) was also included in this study for comparative purposes. The  $\bar{M}_n$  was lowest for the material containing no added Sn. There was little change in  $\bar{M}_n$  between 100 and 2310 ppm Sn. No CO<sub>2</sub> was lost from sample IV (no added Sn) during advancement; the CO<sub>2</sub> content increased from 23.0 to 29.5 wt %, which is the result of concentration due to DEG removal. Carbon dioxide retention was about 95% between 100

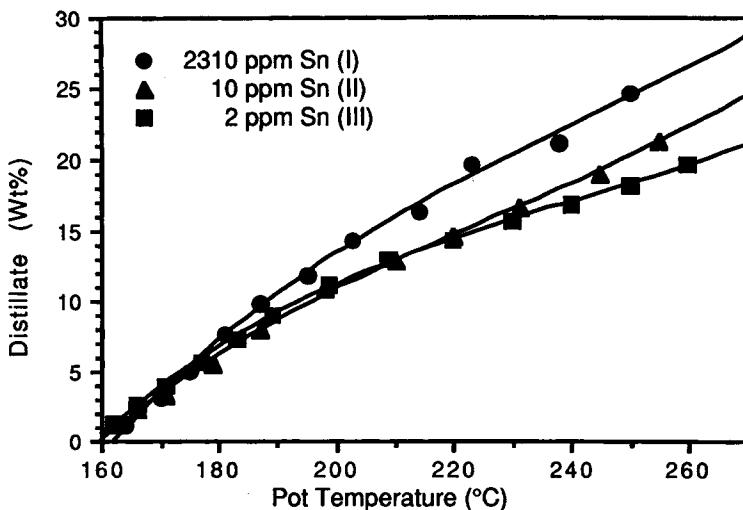


Fig. 6. Effect of pot temperature on amount of distillate formed.

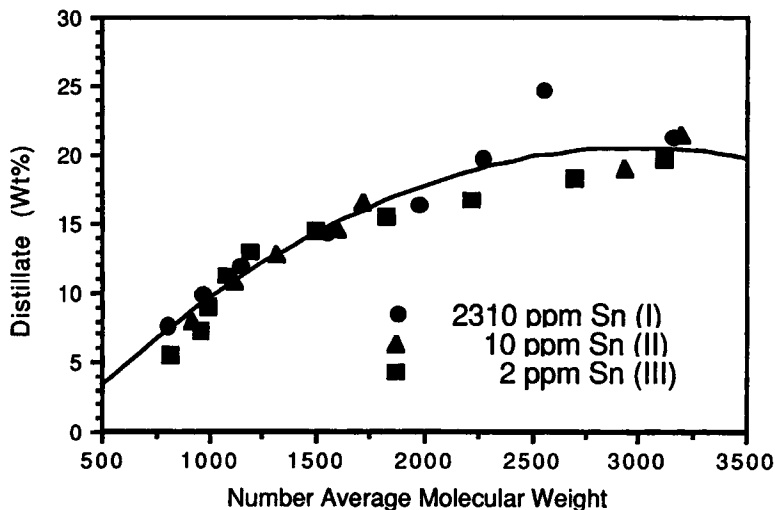


Fig. 7. Effect of wt % distillate on number average molecular weight.

and 500 ppm Sn but dropped to about 85% at 1000 ppm Sn and to about 63% at 2310 ppm Sn. Even though the  $\bar{M}_n$  was relatively constant between 100 and 2310 ppm added Sn, the polymer backbone was changing to include more higher poly(ethylene glycol) units and fewer carbonate units. This change was most pronounced above 500 ppm Sn. Table XI gives mass balance and distillate analysis data. Only small differences are indicated through 1000 ppm added Sn. About 75% of the starting mass was present as product and about 21% was present in the two distillate receivers. About 4% of the starting mass was lost from the system and represented  $\text{CO}_2$  losses. At 2310 ppm Sn, the amount of product was reduced drastically reflecting a large amount of decomposition. A large amount of 1,4-dioxane was present in the dry ice trap. Some acetone and water were also present in the dry ice trap as a consequence of the catalyst removal procedure. Reaction time was 2 h or less in all cases.

Water does not appear to be an important product of the molecular weight advancement process. If the poly(ethylene ether carbonate) diol was dried

TABLE X  
Effect of Tin Level on Molecular Weight Build of Poly(Ethylene Ether Carbonate) Polyols

Sample no.	Added sodium stannate (as ppm Sn)	Maximum pot temp ( $^{\circ}\text{C}$ )	$\text{CO}_2$ (wt %)	Molecular weight data			
				Peak	$\bar{M}_n$	$\bar{M}_w$	PDI
IV	0	240	29.5	4312	2110	4597	2.18
V	100	240	28.1	6064	2616	5875	2.25
VI	200	245	28.1	7369	2915	6686	2.29
VII	500	240	28.0	6821	2886	6659	2.31
VIII	1000	240	25.1	6433	2876	6452	2.24
IX	2310 <sup>a</sup>	240	18.6	6547	2719	6798	2.50

<sup>a</sup> No added tin, sample prepared by filtering off insoluble tin compounds and analyzing filtrate for tin by atomic emission.

TABLE XI  
Effect of Tin Level on Mass Balance and Distillate Analysis

Sample no.	Added sodium stannate (as ppm Sn)	Mass balance (wt %)				Distillate assay (wt %)				
		Product	Distillate	Dry ice trap	Unaccounted for	MEG	Dioxane	EC	DEG	TriEG
IV	0	78.0	15.4	3.8	2.8	0.70	1.38	7.97	88.5	0.85
V	100	75.0	15.8	5.4	3.8	1.31	0.96	8.93	88.0	0.81
VI	200	70.0	18.2	6.9	4.9	0.59	1.65	7.18	87.6	1.11
VII	500	75.1	17.3	4.6	3.0	1.17	1.21	7.50	84.9	2.65
VIII	1000	74.7	18.9	3.0	3.4	1.13	2.55	7.92	82.1	3.40
IX	2310 <sup>a</sup>	31.8	21.5	31.3	15.4	0.48	5.20	2.72	69.6	5.80

<sup>a</sup> No added tin, sample prepared by filtering off insoluble tin compounds and analyzing for tin by atomic emission.

prior to advancement by heating at 110°C while purging with an N<sub>2</sub> stream through the liquid, essentially no water was present (-78°C trap) after advancement.

These data indicate that a Sn content of 100–500 ppm can be useful in rapidly providing an advanced molecular weight product (3000  $\bar{M}_n$ ) with high CO<sub>2</sub> retention. However, since higher molecular weight products require higher pot temperatures, the Sn level and/or reaction time will need to be reduced accordingly to minimize CO<sub>2</sub> losses from the backbone. This Sn level must be reduced by about 2 orders of magnitude before these polyols can be reacted with polyisocyanates at controllable rates.<sup>9</sup>

### Application of Molecular Weight Advancement Technology to Poly(Ethylene Ether Carbonate) Polyols of Various CPR Levels

A series of products was made from four different poly(ethylene ether carbonate) polyols at various CPR levels. Starting poly(ethylene ether carbonate) polyols X, XI, and XIII were made from ethylene carbonate while polyol XII was made from ethylene oxide and CO<sub>2</sub>. The mass balances, CO<sub>2</sub> contents, and molecular weights are given in Table XII. The distillate assay data from both traps are given in Table XIII. The  $\bar{M}_n$ 's by end group titration and by size exclusion chromatography are very close. The hydrodynamic volume of these polyols must be very similar to the poly(ethylene glycol) standards in THF.

The product composition was dominated by the CO<sub>2</sub> content of the reactant and the advancement conditions. As the CO<sub>2</sub> content of the starting polyol was reduced, a larger proportion of higher glycol units were present in its backbone. Since sample XII has the lowest initial CO<sub>2</sub> content (higher glycol units in its backbone), it gives a somewhat lower molecular weight product at 235–237°C pot temperature than samples X and XI. Sample XIII builds molecular weight more slowly due to its lower EC conversion. Considerable EC must be removed (Table XIII) prior to effective molecular weight build. Sample XIII indicates that, although there was a systematic increase in molecular weight as pot temperature was increased, CO<sub>2</sub> retention dropped off, indicating that the backbone structure was converted to increasing higher glycol units.

TABLE XII  
Mass Balance and Molecular Weight Data of Advanced Poly(Ethylene Ether Carbonate)  
Polyols Made Using a Sodium Stannate Catalyst

Starting polyol			Mass balance						Molecular weight data			
No.	CO <sub>2</sub> (wt %)	CPR	Pot temp (°C)	Product	Distillate	Dry ice trap	Unaccounted for	CO <sub>2</sub> (wt %)				
									Titration*	$\bar{M}_n$	$\bar{M}_w$	PDI
X	25.2	21.6	235	76.0	18.1	5.1	0.8	31.4	2180	2196	5285	2.41
XI	23.7	11.6	237	77.4	16.7	4.9	1.0	29.5	2350	2372	5463	2.30
XI	23.7	11.6	237	77.6	16.7	4.9	0.8	30.0	2230	2239	5114	2.28
XII	17.8	11.1	235	67.1	31.2	0.7	1.0	20.9	1960	1973	4141	2.10
XIII	21.3	13.2	235	71.9	23.7	4.0	0.4	31.1	1941	1938	3958	2.04
XIII	21.3	13.2	249	71.1	24.1	4.1	0.7	29.8	2150	2113	4609	2.18
XIII	21.3	13.2	262	69.8	25.3	4.1	0.8	29.1	2770	ins	ins	—
XIII	21.3	13.2	275	67.7	26.0	4.3	2.0	25.4	3886	ins	ins	—

\* Determined by phthalic anhydride titration; ins = insoluble in THF, could not determine molecular weight by size exclusion chromatography.

## CONCLUSIONS

Catalysts are required for the preparation of low molecular weight poly(ethylene ether carbonate) polyols to be used as starting materials for the molecular weight advancement process. Sodium stannate can be removed by treatment with acetone to precipitate most of the catalyst followed by adsorption of the soluble catalyst on Florisil and filtration. Sodium metaborate and potassium carbonate catalysts are not precipitated to any extent by acetone but can be reduced to lower levels by adsorption on Florisil and filtration. The molecular weight of the poly(ethylene ether carbonate) polyol and the water content of the system have a strong influence on the effectiveness of this purification technique. Catalysts are more easily removed from higher molecular weight polyols with low water content. It is important that the catalyst be reduced to low levels for the subsequent use of these polyols in polyurethane applications.

The effect of sodium stannate catalyst level on the molecular weight advancement of poly(ethylene ether carbonate) polyols has been studied. The

TABLE XIII  
Analysis of Distillate and Dry Ice Trap of Advanced Poly(Ethylene Ether Carbonate) Polyols

Polyol no.	Pot temp (°C)	Distillate assay (wt %)							Dry ice trap assay (wt %)				
		MEG	Dioxane	EC	DEG	TriEG	TetraEG	Water	Total	Acetone	Dioxane	Water	Total
X	235	0.72	1.04	9.6	80.5	0.38	0.07	0.07	99.8	57.1	20.1	15.9	93.1
XI	237	0.30	1.51	10.5	76.2	0.70	0.05	0.05	99.4	60.2	25.0	8.8	94.0
XI	237	0.30	1.63	10.3	76.6	0.73	0.09	0.09	99.5	61.0	25.2	8.7	95.0
XII	235	0.44	0.90	6.7	73.7	15.2	1.29	0.02	98.2	2.4	85.7	2.6	90.7
XIII	235	1.39	0.31	44.2	47.7	1.65	—	0.05	95.3	87.6	3.54	5.4	96.5
XIII	249	0.97	0.44	43.8	49.6	1.93	—	0.05	96.7	88.7	3.84	4.3	96.8
XIII	262	0.97	0.47	41.5	49.7	1.96	—	0.03	94.6	86.1	5.19	4.0	95.3
XIII	275	0.90	0.83	41.0	52.4	2.24	—	0.02	97.4	83.2	9.07	3.6	95.8

rate of advancement to a 3000 molecular weight product is increased with good CO<sub>2</sub> retention (95%) when the tin level is 100–500 ppm. At higher catalyst levels, product decomposition becomes increasingly important. 1,4-Dioxane is the major decomposition product under these conditions. Complete mass balances and distillate analyses are presented to show the effects of catalyst levels. The product composition is dominated by the CO<sub>2</sub> content of the reactant and the advancement conditions.

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