Molecular Weight Advancement of Poly(ethylene Ether Carbonate) Polyols

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Synopsis

Poly(ethylene ether carbonate) polyols have been prepared from ethylene carbonate and monoethylene glycol (MEG) or diethylene glycol (DEG) using sodium stannate trihydrate as catalyst. When these polyols (catalyst removed) are heated to elevated temperatures ($> 180°C$) at reduced pressures, volatile impurities are removed, followed by molecular weight advancement and formation of DEG. As DEG is removed as distillate, molecular weight builds in a controllable manner. This is thought to be a transesterification process in which $-OC(O)CH_2CH_2OCH_2CH_2OH$ 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_2 retention and relatively low polydispersity. This process has been characterized by size exclusion chromatography, quantitative capillary gas chromatography of the distillates, ^{13}C-NMR of the products, and alkaline hydrolysis of the products followed by quantification of the resultant glycols. The advanced polyols are largely alternating copolymers of DEG and CO_2. They are valuable polyols for polyurethane fabrication.

INTRODUCTION

Poly(ethylene ether carbonate) polyols are the reaction products of ethylene carbonate (EC), dialkyl carbonates, diphenyl carbonate, ethylene oxide and CO_2, or phosgene with aliphatic polyols in the presence of an appropriate catalyst. These polyols are copolymers of carbon dioxide and polyglycols when diol initiators are employed. When sodium stannate trihydrate is used as the catalyst, backbone hydrolysis studies[1] and ^{13}C-NMR studies[2] have shown that these polyols are predominantly copolymers of carbon dioxide and diethylene glycol (DEG) containing small quantities of triethylene glycol (TriEG) and have $-OC(O)OCH_2CH_2OCH_2CH_2OH$ end groups.[2]

Very little prior art exists on the chemistry of poly(ethylene ether carbonate) polyols at elevated temperatures and reduced pressures. Stevens[3] topped an EC–monoethylene glycol (MEG) adduct at $160°C/2$ mm to remove unreacted EC. Hostettler and Cox[4] have removed unreacted EC from similar products by heating at about $130°C/1-5$ mm. Maximovich[5] has heated EC–DEG reaction products under reduced pressure to remove unreacted EC and DEG. Malkemus,[6] Springmann and Dietrich,[7] and Lai and Silvers[8] have studied the formation of poly(ethylene ether carbonate) diols by the reaction of glycols with EC at elevated temperatures and reduced pressures with concurrent removal of MEG.

This work examines the oligomerization of poly(ethylene ether carbonate) polyols under conditions of elevated temperatures and reduced presssures.[9]

EXPERIMENTAL

Ethylene carbonate (EC), diethyl carbonate (DEC), sodium stannate trihydrate, sodium metaborate, and 1,4-dioxane were obtained from the Aldrich Chemical Co. Monoethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TriEG), and tetraethylene glycol (TetraEG) were manufactured by the Dow Chemical Co. 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 Ultrstyragel 1000-Å and 10,000-Å columns, calibrated with standard poly(ethylene glycols) and using a refractive index detector. ^{13}C-NMR spectra were obtained on a Bruker WM 360 MHz (90.5 MHz for ^{13}C) instrument.

Poly(ethylene Ether Carbonate) Polyol Synthesis

Poly(ethylene ether carbonate) polyols were prepared from EC and MEG or DEG using sodium stannate trihydrate or sodium metaborate as catalyst. Conditions varied from 3 to 125 h at 135–175°C. A polyol was also prepared from DEC and DEG by heating the reactor slowly to 180°C with ethanol removal. The catalyst was removed from each sample by dissolving the polyol in acetone, stirring with magnesium silicate, filtering, and acetone stripping.[10]

Advancement Procedure

A given polyol and boiling stones were placed in a boiling flask equipped with a thermometer, heating mantle, and small distillation head and attached to a dry ice–isopropanol trap 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 by capillary GC. When the process was scaled up to produce 1–2 lb quantities of advanced polyol, the distillation head was removed and a down draft condenser was employed.

RESULTS AND DISCUSSION

The Effects of Reduced Pressures and Elevated Temperatures on Poly(ethylene Ether Carbonate) Diols

A series of poly(ethylene ether carbonate) diol oligomers was prepared from EC and either MEG or DEG using sodium stannate trihydrate as catalyst. The EC:DEG (or MEG) molar ratios were 5, 10, 15, 50, and 100 in order to study a broad molecular weight range (samples I–V). A product was also made from DEC and DEG to include a material with a somewhat different microstructure (sample VI). The materials prepared and the conditions of their preparation are listed in Table I.

Each material in Table I (catalyst removed) was heated under reduced pressure using a small column and volatile components were removed. Table II, showing the results of each treatment, is organized into a series of data pairs. The first line of each pair describes the properties of that poly(ethylene ether carbonate) diol before treatment, while the second line in each pair

TABLE I
Poly(ethylene Ether Carbonate) Diol Starting Materials
(Sodium Stannate Trihydrate Catalyst)

Sample	Catalyst (wt %)	Initiator	EC: Initiator mol ratio	Reaction conditions
I	0.5	DEG	5	7 h at 150°C
II	0.5	MEG	10	29 h at 135°C
III	0.5	DEG	15	8 h at 150°C
IV	0.5	MEG	50	114 h at 135°C
V	0.5	MEG	100	121 h at 140°C
VI	0.5	DEG	2	125–181°C
VII	0.2	DEG	10	2.5 h at 175°C
VIII	0.2	DEG	10	16 h at 150°C
IX	1.0[a]	DEG	50	23 h at 155°C
X	0.2	DEG	10	3 h at 175°C
XI	0.2	DEG	10	3 h at 175°C
XII	0.2	DEG	10	24 h at 135°C
XIII	0.5[b]	MEG	—	4 h at 175°C/400 psi

[a]Sodium metaborate as catalyst.
[b]Also contained 0.5 wt % potassium carbonate as catalyst.

describes the properties after treatment at the specified conditions of temperature and pressure with distillate removal. It is clear from Table II that considerable molecular weight advancement has occurred during treatment. The polydispersity of the advanced polyol is reduced considerably.

Several other points are also apparent. The T_g has increased in each case to a value approaching about $-14°C$. The low T_g's before advancement are due in part to the plasticizing effect of small molecules present and in part to the lower molecular weights. The wt % of carbon dioxide has increased in each case. This is due to the fact that the CO_2 content has been concentrated by removal of non-CO_2-containing materials. The calculated maximum CO_2 con-

TABLE II
Oligomerization of Poly(ethylene Ether Carbonate) Diols

Sample	Conditions	Adv.	Residue (wt %)	CO_2 (wt %)	T_g (°C)	Molecular weight data			
						Peak	$\overline{M}_n$	$\overline{M}_w$	PDI
I	EC : DEG = 5	No	—	23.1	−57.3	570	325	998	3.07
IA	185°C/1.0 mm	Yes	70.3	29.0	−24.6	4255	2146	3749	1.75
II	EC : MEG = 10 : 1	No	—	25.8	−47.9	1171	491	1251	2.55
IIA	194°C/1.0 mm	Yes	78.8	32.1	−19.3	6861	3077	5829	1.89
III	EC : DEG = 15 : 1	No	—	21.8	−45.1	1557	462	1627	3.52
IIIA	210°C/0.7 mm	Yes	79.3	30.8	−23.2	6219	2840	4892	1.72
IV	EC : MEG = 50 : 1	No	—	27.6	−34.3	3539	947	3185	3.36
IVA	210°C/1.3 mm	Yes	90.2	29.3	−19.4	6219	2889	4663	1.61
V	EC : MEG = 100 : 1	No	—	26.9	−29.1	5132	961	4320	4.50
VA	227°C/1.5 mm	Yes	87.3	30.0	−13.9	Ins[a]	Ins	Ins	Ins
VI	DEG : DEC = 2	No	—	27.7	−56.7	785	469	1599	3.41
VIA	215°C/2.0 mm	Yes	79.2	33.4	−16.6	5646	2614	4608	1.76

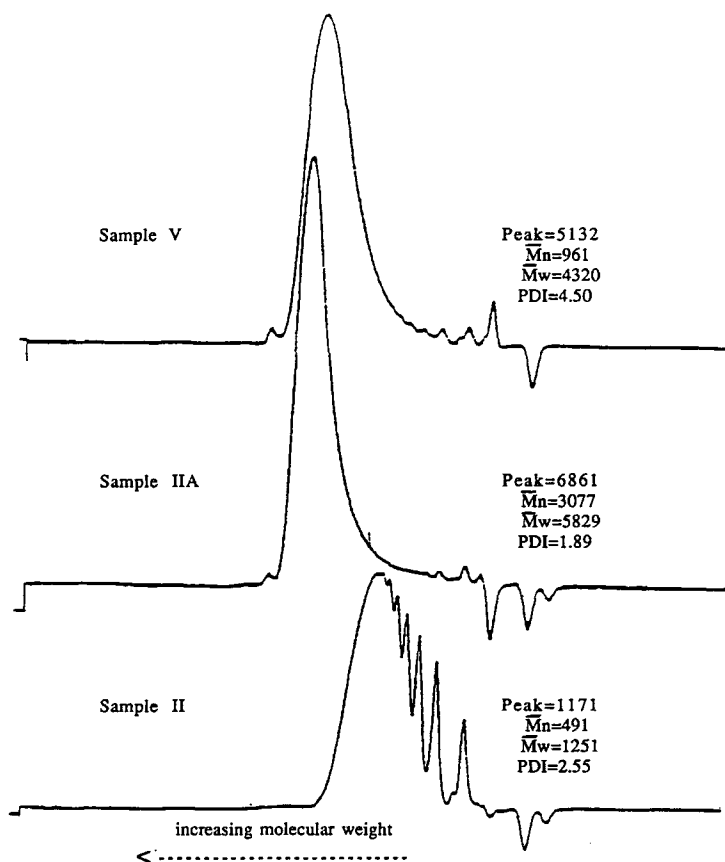[a]Ins = insoluble in THF; hydroxyl equivalent weight was 3667.

Fig. 1. Size exclusion chromatograms of selected materials.

tent of the alternating copolymer of CO_2 and DEG is 33.3 wt %. The amount of CO_2 in an advanced polyol depends on the CO_2 content of the polyol before advancement and on any losses during advancement. Therefore, this advancement process occurs with high CO_2 retention. The residue (product) after advancement is 70–90% by weight of the starting poly(ethylene ether carbonate) diol. This is dependent on the molecular weights of the starting materials and products. The molecular weight of product (VA) could not be determined by SEC since it was not soluble in the continuous phase, THF. It had an equivalent weight of 3667 by end group titration.

Figure 1 shows selected size exclusion chromatograms. The lower trace is a 10:1 molar ratio material (II) before advancement. The low molecular weight and numerous lights are readily apparent. The middle trace is sample II after advancement to a pot temperature of 194°C under a vacuum of 1.0 mm Hg (IIA). Not only has the number average molecular weight increased by a factor of about 6, but the polydispersity of the sample has been reduced. The upper trace shows a comparable molecular weight material made from an EC : MEG molar ratio of 100 : 1 (V). This advancement process offers the advantage of rapidly producing poly(ethylene ether carbonate) polyols with high CO_2 retention and with relatively low polydispersity indexes. Reaction
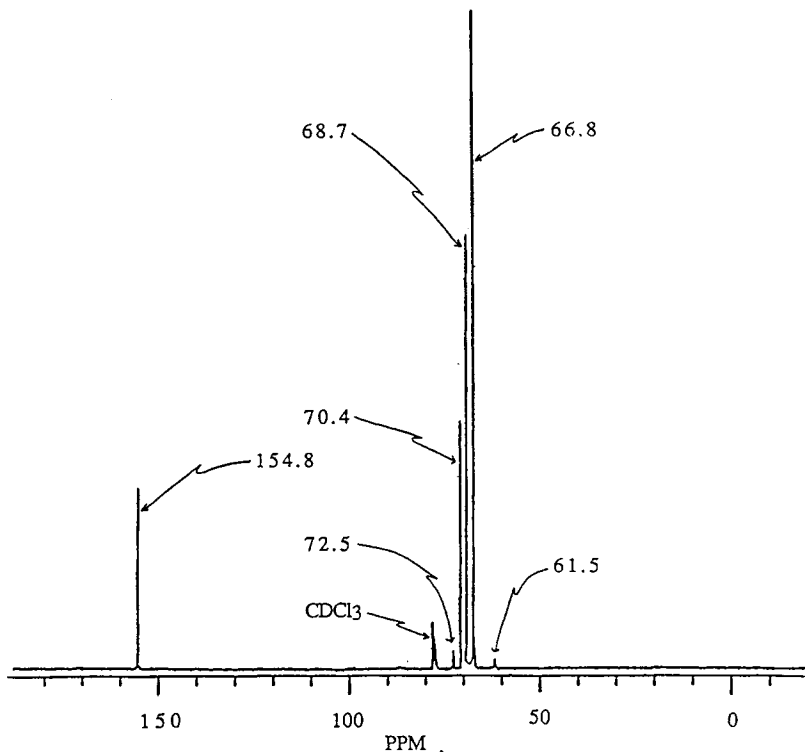
Fig. 2. ^{13}C-NMR of sample IIA.

times to produce high molecular weight poly(ethylene ether carbonate) diols from EC are of the order of 5 days (see Table II; samples IV and V). Only a few hours reaction time are required to produce low molecular weight diols from EC. Such materials are excellent feed for advancement. The molecular weight advancement process requires about 2 h.

The ^{13}C-NMR spectrum of sample IIA (Fig. 2) contains only 6 lines: carbonyl carbon (154.8 ppm), carbon atoms α and β to the carbonate units (66.8 and 68.7 ppm), carbon atoms of higher glycol units (e.g., triethylene glycol, 70.4 ppm), and carbon atoms associated with end groups (61.5 and 72.5 ppm). All assignments are consistent with previous work.[2] The polymer consists of an alternating structure of carbonate and diethylene glycol units along with small amounts of higher glycol units.

The distillates (condensed using a water chilled condenser) from each advancement reaction were analyzed by capillary gas chromatography (Table III). At low EC:diol molar ratios the major volatile component is DEG. At higher ratios, larger quantities of EC are also present, reflecting the lower EC conversions experienced when making higher molecular weight poly(ethylene ether carbonate) polyols. Some 1,4-dioxane (a decomposition product) is present at higher pot temperatures.

The volatile, free glycols and EC present in the polyols before and after advancement were determined by capillary vapor phase chromatography.[2]

TABLE III
Distillate Compositions after Oligomerization

Sample	EC : diol mol ratio	Diol	Maximum conditions	Composition of distillate (wt %)				
				Dioxane	MEG	DEG	TriEG	EC
ID	5	DEG	185°C/1.0 mm	—	0.4	92.5	0.4	6.6
IID	10	MEG	194°C/1.0 mm	—	3.0	86.1	0.9	6.0
IIID	15	DEG	210°C/0.7 mm	—	0.6	73.4	Trace	25.3
IVD	50	MEG	210°C/1.3 mm	1.75	1.5	25.3	Trace	71.5
VD	100	MEG	227°C/1.5 mm	2.49	0.6	36.9	0.5	46.3

TABLE IV
Effect of Oligomerization Conditions on Free Glycols in Product

Sample	Conditions	Assay (wt %)			
		MEG	DEG	TriEG	EC
II	EC : MEG = 10 : 1	0.72	6.70	0.56	1.84
IIA	heated to 194°C/1.0 mm	0.51	—	—	—
IV	EC : MEG = 50 : 1	0.20	0.18	—	4.64
IVA	heated to 210°C/1.3 mm	0.25	—	—	—

Selected results are given in Table IV. These results show that the advanced polyols are obtained in a high state of purity.

Selected samples of the advanced polyols were degraded to CO_2 and the corresponding diols by treatment with methanolic NaOH and analyzed by capillary vapor phase chromatography using 1,6-hexanediol as internal standard[1] (Table V). The polymer backbones consist of DEG with smaller quantities of TriEG and TetraEG. Some DEG is removed as distillate during advancement. The MEG present in the unadvanced samples is formed by hydrolysis of unreacted EC. TriEG is not present in sample VI since EC was not used; TriEG is formed by reaction of DEG with EC.[2]

TABLE V
Effect of Oligomerization on Microstructure

Sample	Conditions	Composition of hydrolyzed polymer (wt %)			
		MEG	DEG	TriEG	TetraEG
I	EC : DEG = 5 : 1	1.88	78.6	12.9	0.17
IA	heated to 185°C/1.0 mm	—	71.1	16.9	1.10
II	EC : MEG = 10 : 1	1.21	77.9	10.5	Trace
IIA	heated to 194°C/1.0 mm	—	62.8	15.5	1.92
III	EC : DEG = 15 : 1	4.23	68.5	13.2	1.49
IIIA	heated to 210°C/0.7 mm	—	69.9	15.3	1.84
VI	DEG : DEC = 2	1.74	72.9	—	1.80
VIA	heated to 215°C/2.0 mm	—	85.7	—	3.70

HOCH₂CH₂OCH₂CH₂OCO —R—OCOCH₂CH₂OCH₂CH₂OH   +   Lights

HOCH₂CH₂OCH₂CH₂OCO —R—OCOCH₂CH₂OCH₂CH₂OCO —R—OCOCH₂CH₂OCH₂CH₂OH

OCH₂CH₂OCH₂CH₂OH

HOCH₂CH₂OCH₂CH₂OCO—R—OCOCH₂CH₂OCH₂CH₂OCO—R—OCOCH₂CH₂OCH₂CH₂OH
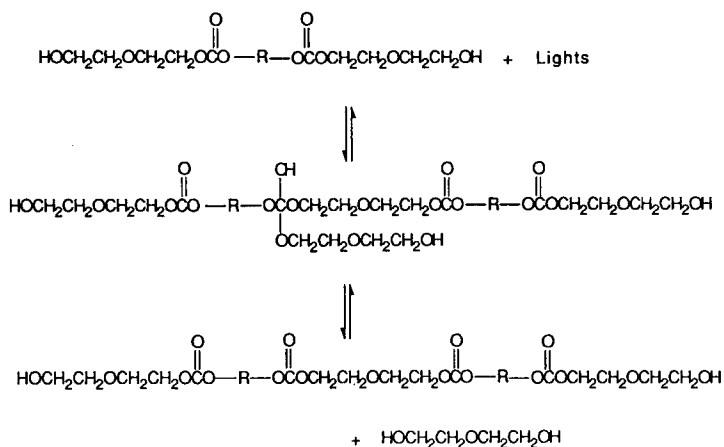
+   HOCH₂CH₂OCH₂CH₂OH

Fig. 3.   Proposed mechanism of oligomerization.

Proposed Mechanism of Advancement

Molecular weight build probably takes place by a series of transesterification reactions (Fig. 3). After the more volatile components have been removed as distillate, a hydroxyl end group on one molecule can react with a carbonate group on a second molecule to form a transient species which loses DEG as distillate under the reaction conditions. This results in the coupling of the two molecules and an increased molecular weight. Since the product of this reaction also contains hydroxyl end groups, it can continue this series of reactions to build even higher molecular weight products. As the molecular weight increases, the concentration of hydroxyl end groups decreases and higher temperatures (or reduced pressures) are required for further reaction at reasonable rates.

Larger Quantities of Advanced Polyols at 10 and 30 mm Hg

After a probing study to understand the effects of reduced pressures (~ 1 mm Hg) and elevated temperatures on poly(ethylene ether carbonate) polyols, studies were conducted at 10 and 30 mm Hg to simulate conditions possible in a manufacturing facility. The process was also scaled up to produce 1–2-lb quantities of advanced polyols. The reactor was equipped with a simple take off head attached to a down draft, water-chilled condenser (~ 15°C) connected to a vacuum source through a −78°C trap. Distillate condensing at both 15 and −78°C was collected. No fractionation column was employed. Figure 4 shows peak molecular weight by size exclusion chromatography (SEC) for a 10 : 1 EC : DEG molar ratio poly(ethylene ether carbonate) diol at 30 mm Hg with increasing pot temperatures. Molecular weight increases smoothly and the light end of the distribution is removed.

Figure 5 shows the application of this process to produce a series of products of increasing molecular weight at both 10 and 30 mm Hg reduced pressures (samples VII and VIII, respectively). A plot of number average molecular weight vs. pot temperature gives a smooth line relationship. About a 20°C higher pot temperature is required at 30 mm Hg to give the same
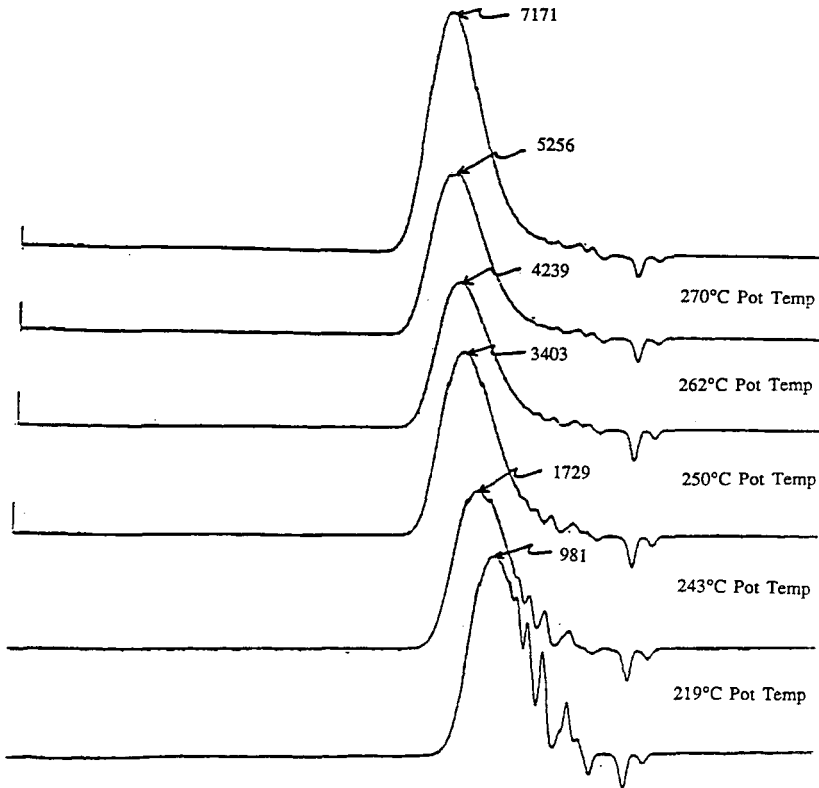
Fig. 4. Molecular weight build of sample VIII; SEC trace vs. pot temperature at 30 mm Hg vacuum.

molecular weight polyol. This illustrates commercially viable processing conditions.

The advancement of sample VII (10 mm Hg) was studied in detail to better understand the advancement process. Figure 6 shows the relationship between the wt % of distillate removed (15°C trap) and the pot temperature. A smooth line relationship exists. Figure 7 shows the relationship between the wt % of
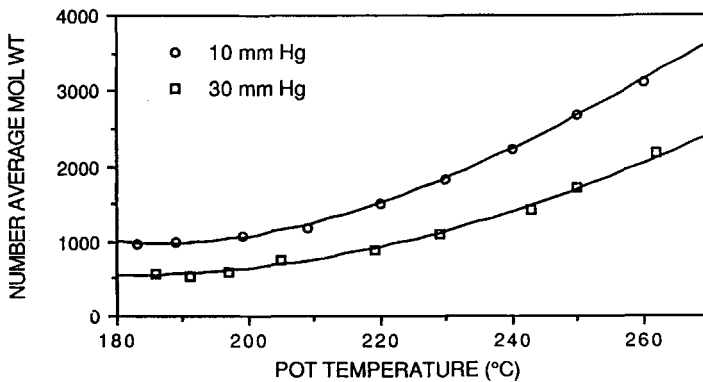

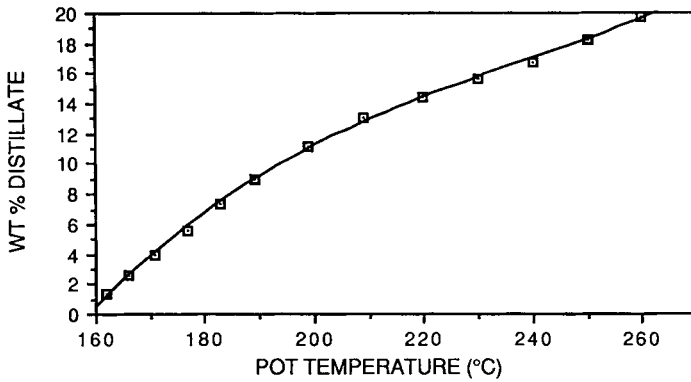Fig. 5. Number average molecular weight vs pot temperature.

Fig. 6. Effect of pot temperature on distillate formation.

distillate removed (15°C trap) and the number average molecular weight of the advanced polyol. It is clear that very little advancement occurs during initial distillate removal. This is due to the fact that volatile components in the sample are removed prior to advancement. As distillate removal is continued, polyol advancement occurs. Polyol molecular weight can be controlled by the amount of distillate removed and/or the pot temperature at a given heat input rate.

The composition of the distillate is shown in Figures 8 and 9. The major distillate components are EC and DEG. The EC is present as unreacted starting material. Since it is more volatile than DEG, EC is removed completely at an early stage in the advancement process. The DEG is the largest component of the distillate and its removal is the driving force in molecular weight build. Figure 9 shows the variations in composition of the minor components in the distillate during advancement. MEG is present at very low levels throughout most of the advancement process. TriEG is present at very low levels initially but increases in the distillate at higher pot temperatures due to increased vapor pressure as the pot temperature increases. The removal of TriEG as distillate is also responsible for molecular weight build, but to a lesser extent than DEG removal. At the higher pot temperatures, TetraEG vapor pressure increases and TetraEG is present in the distillate in small but
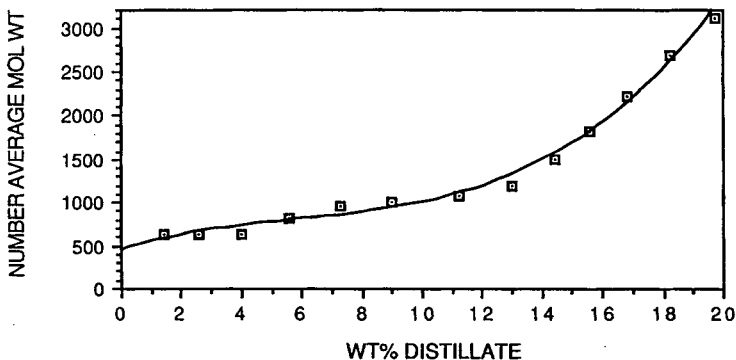

Fig. 7. Molecular weight build as a function of distillate removed.
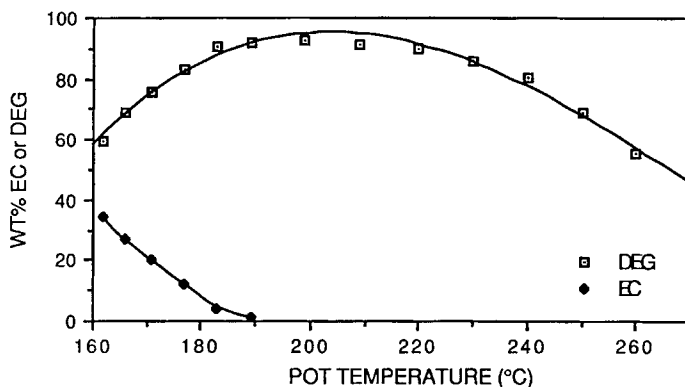
Fig. 8.   Effect of pot temperature on EC and DEG in distillate.

increasing concentrations. 1,4-Dioxane is a decomposition product which increases in the distillate at the higher pot temperature.

Effect of Poly(ethylene Ether Carbonate) Polyol Starting Composition

The composition of an advanced polyol will be in part dependent on the composition of the starting polyol. When sodium metaborate is used to catalyze EC oligomerization, the polyol microstructure contains proportionately larger quantities of TriEG and TetraEG units.[1] Figure 10 compares the molecular weight build at 10 mm Hg of a diol produced by sodium metaborate catalysis (IX) to a comparable molecular weight diol produce by sodium stannate catalysis (VII). The catalyst was removed prior to advancement in both cases. Molecular weight builds more slowly with sample IX since its microstructure contains a lower proportion of DEG units. This effect can be seen by studying the composition of the distillate removed (15°C trap) as a function of pot temperature (Fig. 11). Relatively large quantities of TriEG are present in the distillate throughout the advancement process. At higher temperatures, the distillate contains appreciable quantities of TetraEG. Low
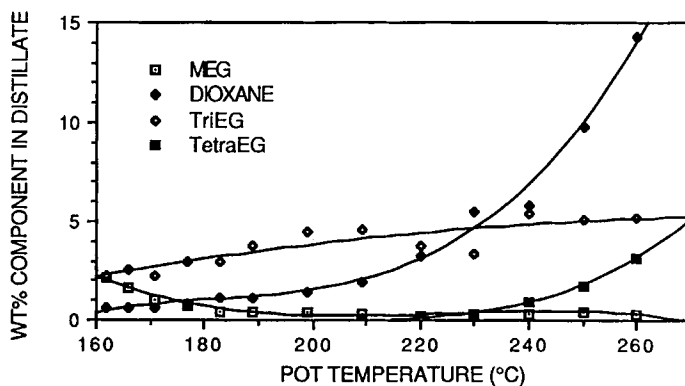

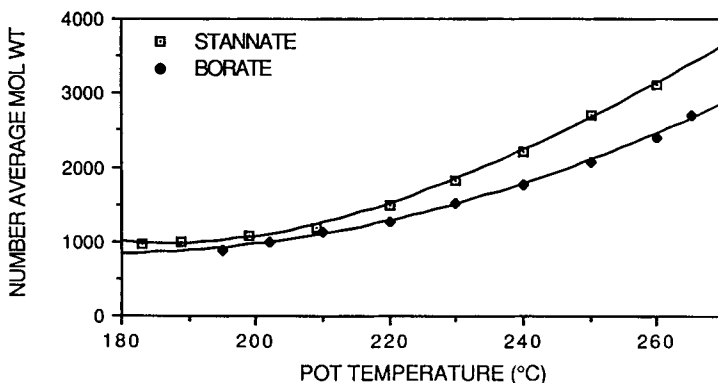Fig. 9.   Concentration of minor components in distillate.

Fig. 10. Advancement of different starting materials.

levels of PentaEG are present at the highest temperatures. Higher pot temperatures are required to build molecular weight by removal of higher molecular weight glycols.

This relationship between starting composition and molecular weight build was studied further using the following compositions:

1. Samples X and XI are oligomers prepared from EC and DEG at higher temperatures (175°C) using lower levels of sodium stannate as catalyst. The higher reaction temperature produces a polyol with a little higher TriEG content.

2. Sample XII is a polyol prepared from EC and DEG at lower temperatures (135°C) for longer reaction times. It contains considerable unreacted EC but only a very low level of TriEG units in its backbone.

3. Sample XIII is a poly(ethylene ether carbonate) diol prepared from ethylene oxide and CO_2 using a mixed sodium stannate and potassium carbonate catalyst.[11] This catalyst system produces a polyol containing considerable TriEG and TetraEG units in its backbone.

The effects of these starting polyol compositions and pot temperatures on the material balance, molecular weight, and CO_2 content are given in Table
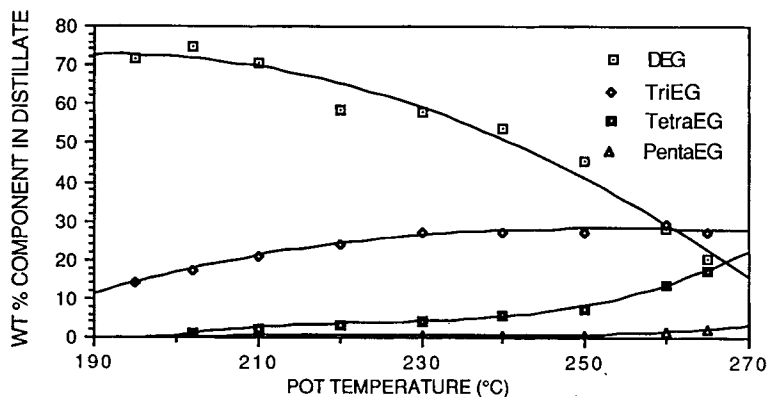

Fig. 11. Concentration of components in distillate.

TABLE VI
Effect of Maximum Pot Temperature on Material Balance

Starting material	Max pot temp (°C)	Material balance (wt %)				Mol wt[a]	CO_2 (wt %)
		Product	15°C Trap	−78°C Trap	Total		
X	235	76.0	18.1	5.1	99.2	2196	31.4
XI	237	77.4	16.7	4.9	99.0	2372	29.5
XI	237	77.6	16.7	4.9	99.2	2239	30.0
XII	235	71.9	23.7	4.0	99.6	1941	31.1
XII	249	71.1	24.1	4.1	99.3	2250	29.8
XII	262	69.8	25.3	4.1	99.2	2779	29.1
XII	275	67.7	26.0	4.3	97.0	3886	25.4
XIII	225	85.8	13.3	0.4	99.3	1795	28.4
XIII	230	84.6	14.3	0.5	99.4	1918	28.3
XIII	235	83.5	15.1	0.6	99.2	2262	27.4

[a] Number average molecular weight.

TABLE VII
Effect of Maximum Pot Temperature on Distillate Assay

Starting material	Distillate assay (wt %)						
	MEG	Dioxane	EC	DEG	TriEG	TetraEG	Water
X	0.72	1.04	9.6	80.5	7.6	0.38	0.07
XI	0.30	1.51	10.5	76.3	10.1	0.70	0.05
XI	0.30	1.63	10.3	74.6	9.9	0.73	0.09
XII	1.39	0.31	44.2	47.7	1.7	0.0	0.05
XII	0.97	0.44	43.8	49.6	1.9	0.0	0.05
XII	0.97	0.47	41.5	49.7	2.0	0.0	0.03
XII	0.90	0.83	41.0	52.4	2.2	0.0	0.02
XIII	0.0	0.85	6.3	54.0	26.6	5.35	0.03
XIII	0.0	1.07	6.9	56.1	23.3	3.74	0.03
XIII	0.0	1.25	6.9	57.5	23.6	4.25	0.03

TABLE VIII
Effect of Maximum Pot Temperature on Condensate in −78°C Trap

Starting material	Assay of condensate in −78°C trap (wt %)			
	Acetone	Dioxane	Water	Total
X	57.1	20.1	15.9	93.1
XI	60.2	25.0	8.8	94.0
XI	61.1	25.2	8.7	95.0
XII	87.6	3.5	5.4	96.5
XII	88.7	3.8	4.3	96.8
XII	86.1	5.2	4.0	95.3
XII	83.2	9.1	3.6	95.9

VI. The amount of advanced polyol produced decreases as pot temperature increases coupled with a systemmatic increase in the amount of material present in both the 15 and $-78°C$ traps. The molecular weight of the advanced polyol increases accordingly. The total material balance accountability is at least 99%, except for the highest pot temperature (275°C).

The effects of starting polyol composition and pot temperature on the distillate composition are given in Table VII. As molecular weight of the advanced polyol increases, the amount of DEG in the distillate increases. 1,4-Dioxane increases with increasing pot temperature.

The effects of starting polyol composition and pot temperature on the condensate in the $-78°C$ trap are shown in Table VIII. Acetone is present as a consequence of the catalyst removal procedure. Low levels of water were probably introduced in the acetone. 1,4-Dioxane is present in increasing quantities as the maximum pot temperature is increased due to decomposition. The total accountability is 93–97%.

CONCLUSIONS

Poly(ethylene ether carbonate) polyols have been prepared from ethylene carbonate and monoethylene glycol (MEG) or diethylene glycol (DEG) using sodium stannate trihydrate as catalyst. When these polyols (catalyst removed) are heated to elevated temperatures (> 180°C) at reduced pressures, volatile impurities are removed, followed by molecular weight advancement and formation of DEG. As DEG is removed as distillate, molecular weight builds in a controllable manner. This is thought to be a transesterification process in which $-OC(O)CH_2CH_2OCH_2CH_2OH$ 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_2 retention, high purity, and relatively low polydispersity.

Considerable insight into the process has been gained by analysis of both the products and the distillates. The product is largely an alternating copolymer of DEG and CO_2 with smaller quantities of higher glycol units. This structure has been established by ^{13}C-NMR, by CO_2 content, and by alkaline hydrolysis followed by quantification of the resultant glycols. The distillate has been quantified by capillary vapor phase chromatography. DEG is the major component in the distillate. TriEG and TetraEG are present at higher pot temperatures, particularly when the polyol starting materials have appreciable quantities of these materials in their backbone structure. 1,4-Dioxane is present in the distillate as a decomposition product. Excellent material balances were obtained.

A process has been developed at 10 mm Hg to simulate conditions possible in a manufacturing facility. Polyol molecular weight can be controlled by the amount of distillate removed and/or by the pot temperature. These polyols are valuable for polyurethane fabrication.

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