Polyglycol Modified Poly(Ethylene Ether Carbonate) Polyols by Molecular Weight Advancement

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Synopsis

Poly(ethylene ether carbonate) polyols can be modified by chemical reactions with polyglycol modifiers under conditions of elevated temperatures and reduced pressures, where diethylene glycol is removed as distillate. Molecular weight builds in a predictable manner and can be controlled by the amount of distillate removed. A reaction pathway for this transformation is proposed. It is important that the modifier be stable to reaction conditions and have a higher boiling point than diethylene glycol. The process has been characterized by following the distillate formation and composition as a function of reactor temperature and product molecular weight build. The product has been characterized by molecular weight, CO_2 content, carbon–13 NMR and viscosity/temperature relationships. Carbon–13 NMR of the carbonyl and methyl regions of the spectra are particularly useful for following the chemical changes. A new family of modified poly(ethylene ether carbonate) polyols has been prepared which was not available with prior technology. The modification procedure permits the control of properties such as modifier type and content, molecular weight, CO_2 content, viscosity, T_g, density, etc., in the resultant polyol. Since poly(ethylene ether carbonate) polyols have predominantly polyester polyol properties, modification with polyether polyols can be used to adjust properties. These polyols are useful in polyurethane applications.

INTRODUCTION

Poly(ethylene ether carbonate) polyols are polymers which contain alternating blocks of carbon dioxide units and poly(ethylene glycol) units in their backbones. When these polyols are made using sodium stannate trihydrate as the catalyst, backbone hydrolysis studies[1] and carbon-13 NMR studies[2] have shown that these poly(ethylene glycol) units are predominantly diethylene glycol (DEG) units with small quantities of triethylene glycol (TriEG) units and that the polyols have predominantly $-OC(O)OCH_2CH_2OCH_2CH_2OH$ end groups. When heated to elevated temperatures ($> 180°C$) at reduced pressures, volatile impurities are removed from the polyols, followed by molecular weight advancement and formation of DEG.[3-6] 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 molecular weight advanced polyols form rapidly with high CO_2 retention, relatively low polydispersity, and high purity.

This study extends this work to include other polyols in the reaction mixture during the molecular weight advancement process. This is an initial report of polyglycol modifiers which can become chemically incorporated into a

$$HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2CH_2OH$$

(1)

$$\left[HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{OH}{|}}{\underset{\underset{OCH_2CH_2OCH_2CH_2OH}{|}}{C}}OCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2CH_2OH \right]$$

$$HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2CH_2OH$$

(2)   + $HOCH_2CH_2OCH_2CH_2OH$

Fig. 1.   Proposed reaction pathway of molecular weight advancement process.

$$HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2CH_2OH \quad + \quad HOR'OH$$

(1)   (Modifier)

$$\left[HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{OH}{|}}{\underset{\underset{OCH_2CH_2OCH_2CH_2OH}{|}}{C}}OR'OH \right]$$

$$HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OR'OH \quad + \quad HOCH_2CH_2OCH_2CH_2OH$$

(3)

$$\left[HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OR'O\overset{\overset{OH}{|}}{\underset{\underset{OCH_2CH_2OCH_2CH_2OH}{|}}{C}}O-R-O\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2CH_2OH \right]$$

$$HOCH_2CH_2OCH_2CH_2O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OR'O\overset{\overset{O}{\|}}{C}O-R-O\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2CH_2OH$$

(4)   + $HOCH_2CH_2OCH_2CH_2OH$

Fig. 2.   Proposed reaction pathway of modification process.

TABLE I
Boiling Points of Potential Diol Modifiers[a]

Potential diol modifier	Boiling point at 10 mm Hg (°C)
Dipropylene glycol (DPG)	116
1,4–Butanediol (BDO)	120
Thiodiethanol (TDE)	128
1,6–Hexanediol (HDO)	132
Diethylene glycol (DEG)	134
Tripropylene glycol (TPG)	141
Triethylene glycol (TriEG)	158
Tetraethylene glycol (TetraEG)	197

[a] CRC Handbook of Chemistry and Physics, 60th ed.

poly(ethylene ether carbonate) polyol to yield a new class of compounds.[7,8] These polyols are useful in polyurethane applications.

EXPERIMENTAL

Materials

Ethylene carbonate (EC), sodium stannate trihydrate, 1,4-butanediol, 1,6-hexanediol, thiodiethanol, 1,4-dioxane, and a polypropylene glycol of 725 molecular weight (P-725) were obtained from Aldrich Chemical Co. Monoethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TetraEG), dipropylene glycol (DPG), tripropylene glycol (TPG), P-425 (a polypropylene glycol of 425 molecular weight), and P-1200 (a polypropylene glycol of 1200 molecular weight) were manufactured by Dow Chemical

TABLE II
Conditions Employed for Incorporation of Different Diol Modifiers

Run no.	Modifier	Modifier boiling point (°C)	Carbonate diol/ modifier diol molar ratio	Reaction conditions used		
				Column used	Vacuum (mm Hg)	Maximum pot temperature (°C)
1	DPG	116	2 : 1	Yes	10	270
2	TDE	128	3 : 1	Yes	20	240
3	HDO	132	3 : 1	No	10	241
4	HDO	132	3 : 1	No	50/20/10	240
5	TPG	141	3 : 1	No	10	242
6	TPG	141	3 : 1	No	50/10	240
7	TPG	141	3 : 1	Yes	30	220
8	TPG	141	1 : 1	Yes	30	210
9	TriEG	158	3 : 1	No	10	242

TABLE III
Effect of Different Diol Modifiers on Product Composition

Run no.	Modifier	Mass balance (wt %)			Molecular weight data				% Modifier charged in distillate	Modifier in product (wt %)
		Product	Distillate trap	Dry ice trap	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$		
Starting material[a]		—	—	—	1029	643	1179	1.84	—	—
1	DPG	43.7	48.4	3.5	9250	3200	8800	2.75	98.8	0.8
2	TDE	51.7	40.3	2.7	nd	nd	nd	nd	nd	nd
3	HDO	59.0	38.3	2.4	5420	2150	5268	2.45	98.2	0.7
4	HDO	61.1	36.3	2.4	5081	2684	6259	2.33	22.8	31.6
5	TPG	65.3	32.2	2.4	5525	2226	5590	2.51	56.9	16.4
6	TPG	63.6	33.0	2.3	5010	2054	4950	2.41	53.8	18.2
7	TPG	72.6	18.8	5.1	1250	779	1482	1.90	15.8	29.0
8	TPG	64.1	32.0	3.0	1875	1068	2217	2.08	30.4	54.2
9	TriEG	64.1	32.3	3.0	5525	2234	5360	2.40	8.6	62.0

[a] Poly(ethylene ether carbonate) diol starting material; nd = not determined.

TABLE IV
Distillate Assay Using Dipropylene Glycol as Modifier

Pot temperature (°C)	Distillate[a] (wt %)	Distillate assay (wt %)						Wt % of total DPG in distillate
		MEG	Dioxane	EC	DEG	TriEG	DPG	
116	0	0	0	0	0	0	0	0
118	12.3	0.63	0	1.71	1.91	0	95.2	35.1
159	25.1	0	0	2.66	15.7	0	81.6	66.4
177	30.0	0	0	0	33.9	0	66.1	76.2
192	37.1	0	0.87	0	44.0	0.53	54.6	87.9
229	41.9	0	4.06	0	48.1	0	47.8	94.5
270	48.4	0	21.4	0	34.6	0	20.9	98.8

[a] Weight percent of reactants charged present as distillate.

TABLE V
Distillate Assay Using Triethylene Glycol as Modifier

Pot temperature (°C)	Distillate[a] (wt %)	Distillate assay (wt %)					Wt % of total TriEG in distillate
		MEG	Dioxane	EC	DEG	TriEG	
153	0	0	0	0	0	0	0
156	4.8	2.71	0	14.9	76.0	6.4	0.7
166	12.3	0.82	0	3.1	86.3	9.8	2.4
176	18.1	0.61	0	0	88.2	11.1	3.8
191	23.2	0	1.00	0	88.9	10.1	5.0
220	29.0	0	1.46	0	75.9	18.4	7.4
242	32.0	0	4.71	0	62.6	15.8	8.6

[a] Weight percent of reactants charged present as distillate.

TABLE VI
Distillate Assay Using 1,6–Hexanediol as Modifier; 10 mm Hg Vacuum

Pot temperature (°C)	Distillate[a] (wt %)	Distillate assay (wt %)						Wt % of total 1,6–HDO in distillate
		MEG	Dioxane	EC	DEG	TriEG	1,6–HDO	
140	0	0	0	0	0	0	0	0
142	1.8	1.53	0	10.50	10.0	0	76.8	5.6
145	7.3	0.36	0	3.51	8.3	0	87.3	24.6
148	11.2	0	0	1.97	7.2	0.34	89.9	38.9
151	16.8	0	0	0.89	6.0	0.51	92.1	59.5
160	22.6	0	0	0.35	5.3	0.75	93.1	81.0
174	27.2	0	0	0	13.5	1.65	83.9	96.7
191	32.4	0	0.77	0	89.0	4.29	5.9	98.1
215	35.6	0	1.44	0	91.1	4.55	1.6	98.1
241	38.3	0	4.42	0	85.1	3.87	1.4	98.2

[a] Weight percent of reactants charged present as distillate.

Co. Poly(ethylene ether carbonate) diol starting materials were prepared from EC and DEG using sodium stannate trihydrate (0.5 wt %) as catalyst.*

Polyol Modification/Molecular Weight Advancement Procedure

A given amount of poly(ethylene ether carbonate) diol, modifier diol, and boiling stones were placed in a boiling flask equipped with a thermometer and heating mantle and attached to a water–chilled condenser trap, dry ice-isopropanol trap ($-78°C$) and a vacuum source. In some cases a short path distillation head was used. In other cases only a simple take off head was used (no column). In scale up runs only a down draft, water-chilled condenser was used. The system 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

* Detailed procedures are given in Refs. 1–6 and references cited therein.

TABLE VII
Distillate Assay Using 1,6–Hexanediol as Modifier; Staged Pressure Reduction

Pot temperature (°C)	Vacuum (mm Hg)	Distillate[a] (wt %)	Distillate assay (wt %)						Wt % of total HDO in distillate
			MEG	Dioxane	EC	DEG	TriEG	1,6-HDO	
184	50	0	0	0	0	0	0	0	0
185	50	0.9	3.85	2.65	7.85	58.0	2.55	22.7	0.8
189	50	4.9	2.38	0.64	5.86	75.5	2.93	12.7	2.9
198	50	13.7	0.75	0.82	1.83	78.3	3.94	14.3	7.9
198	10	31.1	0	0.58	0	73.3	9.55	16.6	19.5
220	10	34.9	0	0.62	0	73.3	9.12	15.8	21.9
240	10	36.3	0	1.59	0	70.0	7.61	15.2	22.8

[a] Weight percent of reactants charged present as distillate.

TABLE VIII
Distillate Assay Using Tripropylene Glycol as Modifier; Fractionation
Column Used; 30 mm Hg Vacuum

Pot temperature (°C)	Distillate[a] (wt %)	Distillate assay (wt %)						Wt % of total TPG in distillate
		MEG	Dioxane	EC	DEG	TriEG	TPG	
143	0	0	0	0	0	0	0	0
156	4.9	1.24	0	8.59	17.7	0	69.0	13.6
163	9.4	0.73	0	6.14	49.6	1.97	41.6	21.1
170	14.8	0.44	0	1.87	58.4	2.65	36.6	28.9
180	20.1	0	0	0.54	56.9	3.17	39.4	37.3
196	25.1	0	0	0	55.2	3.52	41.3	45.6
221	29.3	0	0	0	52.2	3.91	40.5	52.5
242	32.3	0	1.28	0	45.7	3.67	37.0	56.9

[a] Weight percent of reactants charged present as distillate.

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.

Distillate Analysis

Capillary gas chromatograms were obtained on a Hewlett-Packard 5840A unit with a J&W Scientific Co. DB-1 fused silica capillary column. 1,6-Hexanediol was used as internal standard. Water analysis was done by Karl Fischer titration.

Polyol Characterization

Size exclusion chromatography (SEC) was done on Waters Ultrastyragel 500, 1000, and 10,000 Å columns and, using a refractive index detector, calibrated with standard poly(ethylene glycols). NMR spectra were obtained on a Varian Gemini 300 NMR instrument (300 MHz for proton and 75 MHz for carbon) using DMSO-d_6 as solvent. The CO_2 content of the poly(ethylene ether car-

TABLE IX
Distillate Assay Using Tripropylene Glycol as Modifier; No Fractionation
Column Used; 10 mm Hg Vacuum

Pot temperature (°C)	Distillate[a] (wt %)	Distillate assay (wt %)						Wt % of total TPG in distillate
		MEG	Dioxane	EC	DEG	TriEG	TPG	
182	0	0	0	0	0	0	0	0
186	2.6	9.83	1.93	25.2	44.5	0	7.05	0.7
192	7.4	0.38	0.63	0	72.0	0	24.1	5.4
202	12.6	0.53	1.24	0	72.3	0	24.9	10.6
220	18.8	0.28	1.56	0	71.5	0	20.8	15.8

[a] Weight percent of reactants charged present as distillate.

TABLE X
Molecular Weight and Distillate Data for a P-725 Modified
Poly(Ethylene Ether Carbonate) Diol

Pot temp (°C)	Distillate (wt %)	Distillate assay (wt %)						Molecular weight data			
		MEG	Dioxane	EC	DEG	TriEG	TetraEG	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
25	0	0	0	0	0	0	0	1060	638	1169	1.83
165	1.7	1.46	0	24.2	62.9	0.92	0	969	808	1506	1.86
176	4.3	0	0	5.2	82.1	3.04	0	1050	940	1895	2.21
188	7.2	0	0	0.7	89.3	4.25	0	2224	1183	2490	2.10
205	10.1	0	0.57	0	87.3	4.48	0	3212	1545	3606	2.33
220	11.7	0	1.03	0	85.2	3.95	0	3781	2012	4720	2.35
235	12.8	0	1.92	0	80.9	4.64	0.63	4101	2362	5692	2.41
250	14.1	0	3.36	0	74.4	5.44	1.04	5903	2742	7186	2.62
260	15.3	0	3.72	0	65.2	6.32	1.77	6908	2935	7541	2.57

bonate) polyols was measured by quantitative proton NMR in $CDCl_3$ using dimethylsulfoxide as the internal standard. Viscosity/temperature profiles were obtained on a Brookfield Synchro-Lectric digital viscometer with a Brookfield Thermosel heater using a HBTD #21 spindle. Temperature was controlled with a Model 84 Brookfield programmable temperature controller.

RESULTS AND DISCUSSION

Proposed Reaction Pathway for Modification of Poly(Ethylene Ether Carbonate) Polyols

When poly(ethylene ether carbonate) polyols are heated to elevated temperatures (> 180°C) at reduced pressures, a transesterification process occurs 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 to build molecular
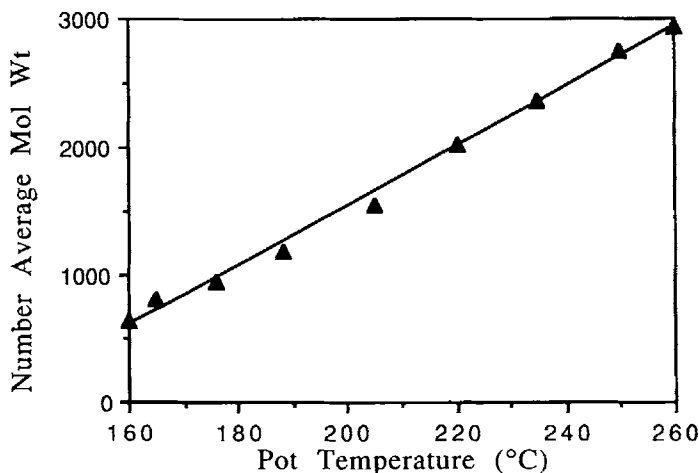
Fig. 3. Effect of pot temperature on molecular weight.
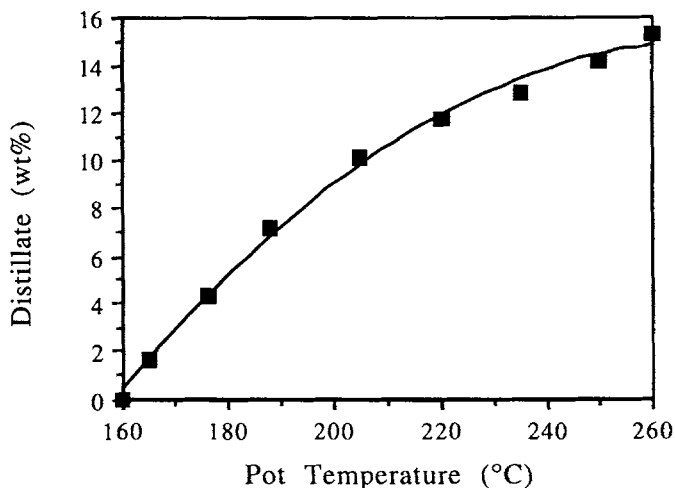
Fig. 4.   Effect of pot temperature on distillate removed.

weight in a controllable manner.[3-6] Figure 1 shows this proposed reaction pathway when a poly(ethylene ether carbonate) diol (1) is used to form a molecular weight advanced poly(ethylene ether carbonate) diol (2); R represents the poly(ethylene ether carbonate) backbone. These advanced polyols form rapidly with high CO_2 retention and high purity.

If a second polyol is included in the reaction mixture, it should be incorporated into the backbone during the molecular weight advancement process to produce a molecular weight advanced modified poly(ethylene ether carbonate) polyol. This proposed reaction pathway is illustrated in Figure 2, where both the poly(ethylene ether carbonate) polyol (1) and the modifier (HOR'OH) are diols. A similar process is applicable for higher functional materials.

In the first step, a hydroxyl end group on the modifier molecule reacts with a carbonyl moiety on the poly(ethylene ether carbonate) diol. This is an equi-
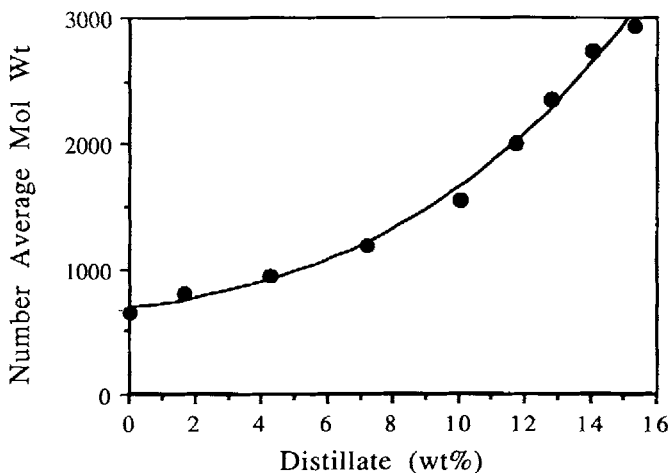
Fig. 5.   Effects of distillate removal on molecular weight.
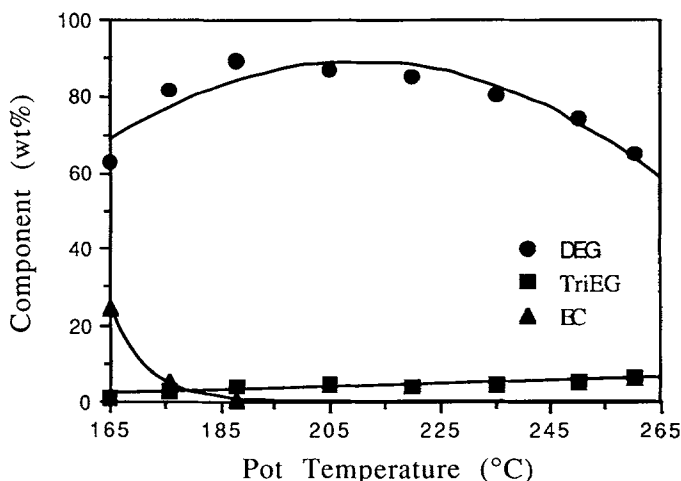
Fig. 6. Effect of pot temperature on components in distillate.

librium reaction in which the transient intermediate can either release the modifier molecule to reform the reactants or release DEG to form a modified poly(ethylene ether carbonate) diol (3) in which the modifier becomes chemically bonded to the poly(ethylene ether carbonate) diol and is present as an end group unit.

In the second step, the hydroxyl end group on the modified poly(ethylene ether carbonate) diol (3) reacts with a carbonyl moiety on the poly(ethylene ether carbonate) diol (1). This second transient intermediate can either release large poly(ethylene ether carbonate) diol molecules or release DEG to form a modified poly(ethylene ether carbonate) diol (4) in which the modifier becomes chemically bonded into the molecular weight advanced poly(ethylene ether carbonate) diol backbone. These equilibria reactions are controlled by using reaction conditions of elevated temperatures and reduced pressures where the DEG is removed as distillate as it forms. The relative amounts of (3) and (4) formed will be dependent on the ratio of the reactants and the relative reactivities of their hydroxyl end groups. Since the modified poly(ethylene ether carbonate) diol (4) contains hydroxyl end groups and carbonyl backbone moieties, 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.

Of course, a process similar to that given in Figure 1 can occur simultaneously with the process given in Figure 2. Also, a hydroxyl end group moiety can attack any carbonyl moiety in the backbone. This leads to a series of equilibria reactions in which only reactions at carbonyl moieties near the end of a molecule lead to molecular weight advancement by loss of DEG.

Effect of Modifier Boiling Point

In order for this process (Fig. 2) to work, DEG must be distilled from the reaction system preferentially over the modifier. Table I gives the boiling points

TABLE XI
Product Molecular Weight Using Poly(Propylene Glycol) Modifiers

Polyol no.	Modifier	Modifier (wt %)	Max pot temp (°C)	Molecular weight data					CO_2 (wt %)	Tg (°C)	Density (g/cc)
				Titration[a]	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$			
I	None	0	237	2330	4880	2239	5114	2.28	30.0	−26	1.27
II	P-1200	26.0	225	nd	5420	2208	5746	2.60	nd	nd	nd
III	P-1200	48.9	215	nd	5400	2326	5644	2.43	14.4	nd	nd
IV	P-1200	72.3	202	nd	3850	1712	4006	2.34	9.5	nd	nd
V	P-725	23.7	225	1977	4356	1921	4555	2.37	23.7	−34	1.21
VI	P-725	49.1	225	2447	3768	2413	5225	2.22	14.7	−45	1.14
VII	P-725	72.1	216	1907	3742	1904	4665	2.45	7.7	−57	1.09
VIII	P-425	25.2	235	2466	4356	2317	5481	2.37	23.2	−34	1.21
IX	P-425	51.2	235	2625	4760	2545	5667	2.23	13.4	−41	1.14
X	TPG	12.3	230	2050	4235	2096	4628	2.21	25.0	−35	1.25
XI	TPG	27.0	235	2596	5820	2674	5924	2.22	20.4	−37	1.20

[a] By end group titration with phthalic anhydride in pyridine; nd = not determined.

TABLE XII
Mass Balance Data Using Poly(Propylene Glycol) Modifiers

Polyol no.	Modifier	Modifier (wt %)	Mass balance (wt %)			
			Product	Distillate trap	Dry ice trap	Unaccounted for
I	None	0	77.6	16.7	4.9	0.8
II	P-1200	26.0	80.7	14.9	4.0	0.4
III	P-1200	48.9	84.7	12.1	2.7	0.5
IV	P-1200	72.3	86.6	11.5	1.6	0.3
V	P-725	23.7	80.0	15.5	4.1	0.4
VI	P-725	49.1	83.5	15.7	0.7	0.1
VII	P-725	72.1	86.3	11.7	1.7	0.3
VIII	P-425	25.2	75.7	19.5	4.2	0.6
IX	P-425	51.2	76.1	22.5	1.0	0.4
X	TPG	12.3	88.2	10.8	0.4	0.6
XI	TPG	27.0	73.0	26.0	0.7	0.3

(at 10 mm Hg) of several potential diol modifiers of interest. Since DEG has a boiling point of 134°C at 10 mm Hg, it would be expected that a material like dipropylene glycol (boiling point of 116°C/10 mm Hg) could not be incorporated into the backbone of poly(ethylene ether carbonate) polyols by this process. On the other hand, a material like triethylene glycol (boiling point of 158°C/10 mm Hg) should readily be incorporated into the backbone of poly(ethylene ether carbonate) polyols. Materials which have boiling points very close to DEG, such as 1,6-hexanediol (boiling point of 132°C/10 mm Hg) and tripropylene glycol (boiling point of 141°C/10 mm Hg), might be expected to be incorporated into the backbone of poly(ethylene ether carbonate) polyols to a limited extent.

TABLE XIII
Distillate Data Using Poly(Propylene Glycol) Modifiers

Polyol no.	Modifier	Modifier (wt %)	Distillate assay[a] (wt %)						
			MEG	Dioxane	EC	DEG	TriEG	TetraEG	H_2O
I	None	0	0.72	1.04	9.6	80.5	7.60	0.38	0.07
II	P-1200	26.0	0.39	0.83	9.72	81.1	6.66	0.26	0.07
III	P-1200	48.9	0.38	1.45	11.11	73.6	6.52	0.52	0.02
IV	P-1200	72.3	0.34	0.74	8.42	60.2	6.98	0.54	0.04
V	P-725	23.7	0.72	0.76	9.19	79.8	6.51	0	0.08
VI	P-725	49.1	0	0.47	3.47	86.4	9.69	0.27	0.11
VII	P-725	72.1	0.28	0.60	7.17	75.2	8.87	0.40	0.04
VIII	P-425	25.2	0.35	0.66	7.93	79.8	7.67	0.35	0.06
IX	P-425	51.2	0	0.67	2.48	78.0	10.3	0.35	0.03
X	TPG[b]	12.3	0	1.46	0	45.7	3.67	0.30	0.08
XI	TPG[c]	27.0	0	0.52	1.47	44.5	3.90	0.36	0.12

[a] Weight of material in the trap attached to the water chilled condenser; [b] also contains 45.8% TPG; [c] also contains 44.9% TPG.
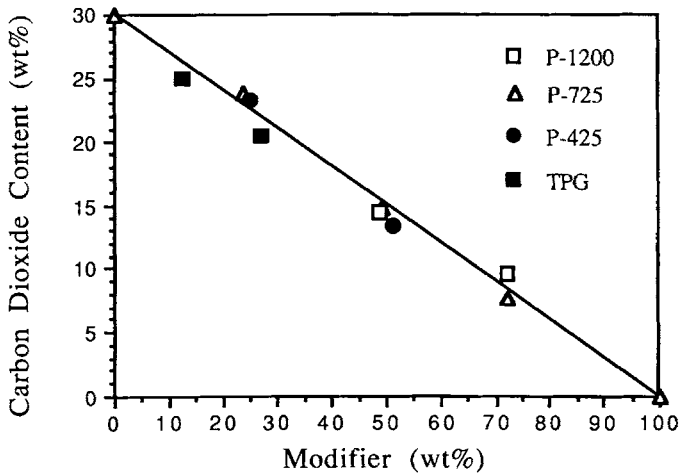
Fig. 7. Effect of modifier on CO_2 content of modified diol.

Dipropylene Glycol as a Modifier

A poly(ethylene ether carbonate) diol and dipropylene glycol (2 : 1 wt ratio) were combined (immiscible at ambient temperature) and subjected to molecular weight advancement conditions (Table II; run 1). A small fractionating column was used to partially equilibrate the vapors being removed as distillate. The mass balance and product molecular weight are given in Table III; the distillate composition is given in Table IV. The distillate assay indicated that 98.8% of the dipropylene glycol charged was removed with the distillate and therefore that essentially none was incorporated into the product backbone. The product molecular weight indicates that the poly(ethylene ether carbonate) diol starting material reacted with itself (reaction scheme in Fig. 1) to produce a molecular weight advanced product.
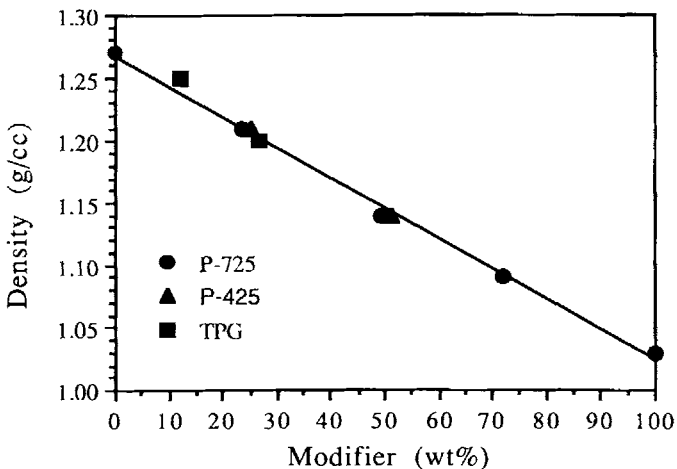
Fig. 8. Effect of modifier on density of modified diol.
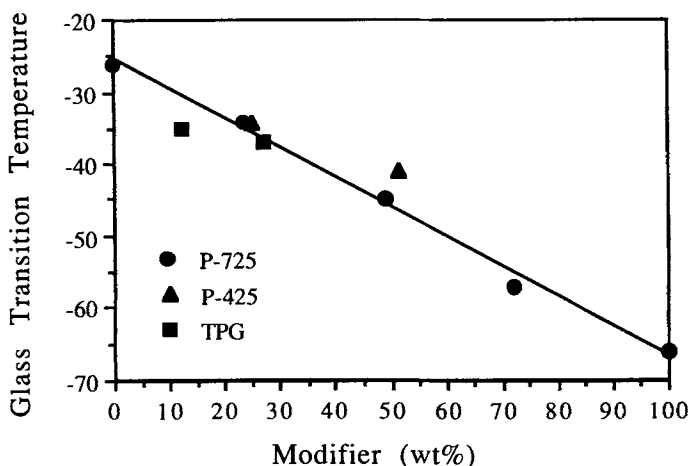
Fig. 9.   Effect of modifier on glass transition temperature of modified diol.

Triethylene Glycol as a Modifier

A poly(ethylene ether carbonate) diol and triethylene glycol (3 : 1 wt ratio) were combined and subjected to molecular weight advancement conditions (Table II; run 9). No fractionating column was used. The mass balance and product molecular weight are given in Table III; the distillate composition is given in Table V. The distillate assay indicates that only 8.6% of the triethylene glycol 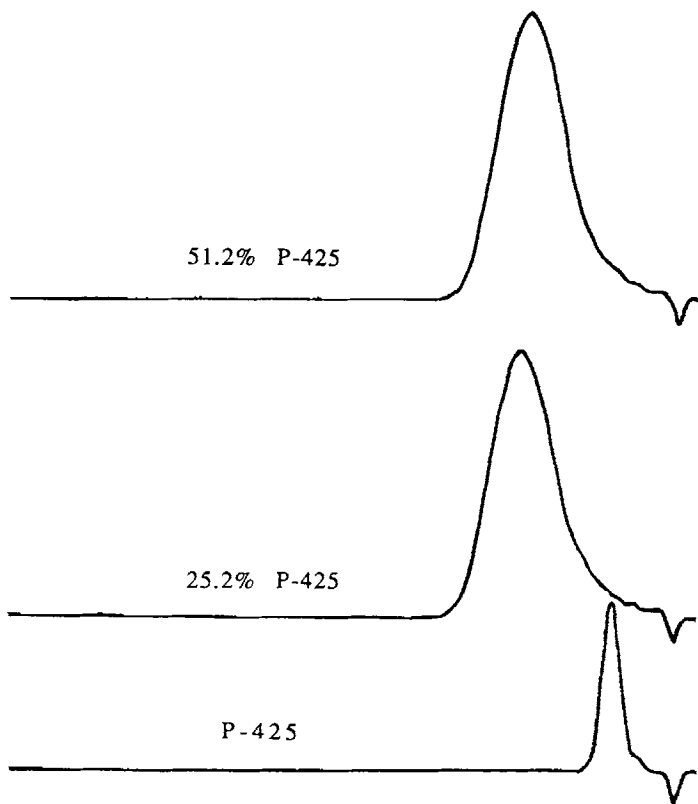charged was removed with the distillate and therefore that 91.4% was incorporated into the product backbone. This gives a molecular weight advanced modified poly(ethylene ether carbonate) diol containing 62.0 wt % triethylene glycol as modifier.

Thiodiethanol as a Modifier

A poly(ethylene ether carbonate) diol and thiodiethanol (3 : 1 wt ratio) were combined and subjected to molecular weight advancement conditions (Table II). A fractionating column was used. The mass balance is given in Table III. The thiodiethanol dissociated under the experimental conditions; therefore no further work was done with this potential modifier.

1,6-Hexanediol as a Modifier

A poly(ethylene ether carbonate) diol and 1,6-hexanediol (3 : 1 wt ratio) were combined and subjected to molecular weight advancement conditions (Table II; run 3). No fractionating column was used. The mass balance and product molecular weight are given in Table III; the distillate composition is given in Table VI. The distillate assay shows that 98.2% of the 1,6-hexanediol charged was removed with the distillate, indicating that essentially none was incorporated into the product backbone. The distillate assay data and product molecular weight indicate that the 1,6-hexanediol distilled from the reactor prior to reaction ($\sim$ 97% distilled at a pot temperature < 175°C). The poly(ethylene ether carbonate) diol starting material then reacted with itself

(reaction scheme in Fig. 1) at the normal reaction temperature (pot temperature > 185°C) to produce a molecular weight advanced product.

The above experiment was repeated using a staged pressure reduction from 50 mm Hg to 10 mm Hg to keep the 1,6-hexanediol in the reactor at the pot temperatures required for reaction and allow for efficient removal of DEG and molecular weight build (Table II; run 4). No fractionating column was used. The mass balance and product molecular weight are given in Table III; the distillate composition is given in Table VII. The distillate assay indicates that only 22.8% of the 1,6-hexanediol charged was removed with the distillate and therefore that 77.2% was incorporated into the product backbone. This gives a molecular weight advanced modified poly(ethylene ether carbonate) diol containing 31.6 wt % 1,6-hexanediol as modifier.

Tripropylene Glycol as a Modifier

A poly(ethylene ether carbonate) diol and tripropylene glycol (3:1 wt ratio) were combined and subjected to molecular weight advancement conditions (Table II; run 5). No fractionating column was used. The mass balance and product molecular weight are given in Table III; the distillate composition is given in Table VIII. The distillate assay indicates that 56.9% of the tripropylene glycol charged was removed with the distillate; and therefore that less than

Fig. 10.   SEC traces for P–425 modified poly(ethylene ether carbonate) diols.

23.7% P-725

49.1% P-725

72.1% P-725
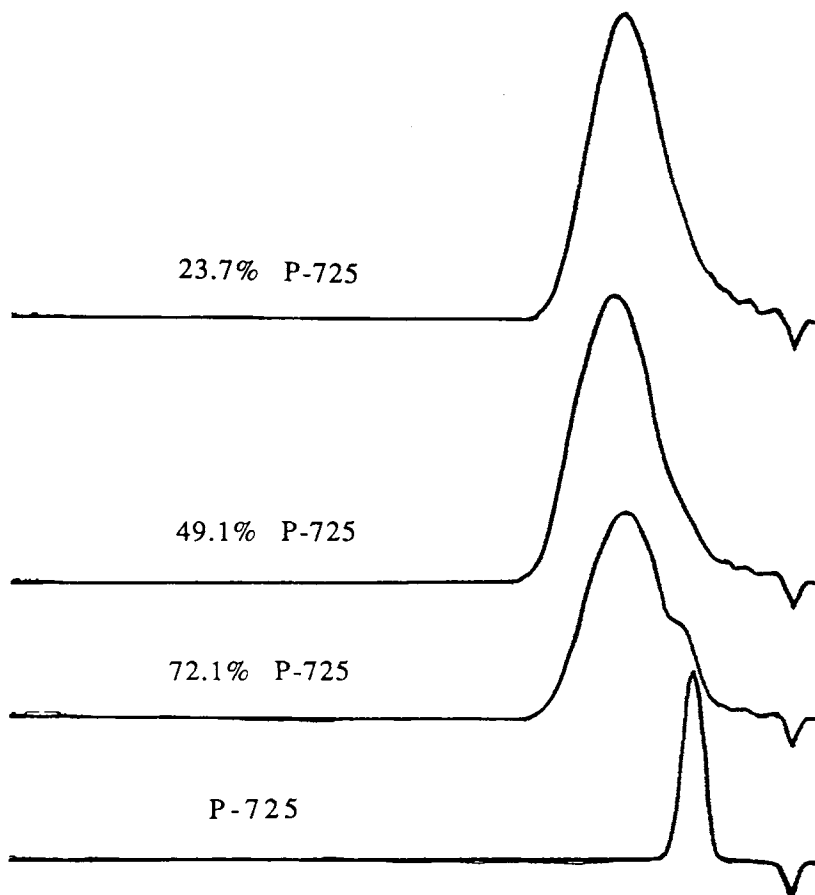
P-725

Fig. 11.   SEC traces for P-725 modified poly(ethylene ether carbonate) diols.

half was incorporated into the product backbone. When the above experiment was repeated, except that a staged pressure reduction from 50 to 10 mm Hg was used, 53.8% of the tripropylene glycol charged was still removed with the distillate (Table III; run 6).

The above experiments were repeated, except that a small fractionating column was used to partially equilibrate the vapors being removed as distillate. The mass balance and product molecular weight are given in Table III (run 7); the distillate composition is given in Table IX. The distillate assay indicates that only 15.8% of the tripropylene glycol charged was removed with the distillate and therefore that 84.2% was incorporated into the product backbone. This gives a molecular weight advanced modified poly(ethylene ether carbonate) diol containing 29.0 wt % tripropylene glycol as modifier. When the experiment was repeated using a smaller poly(ethylene ether carbonate) diol and tripropylene glycol ratio (1 : 1 wt ratio), a molecular weight advanced modified poly(ethylene ether carbonate) diol containing 54.2 wt % tripropylene glycol as modifier was produced.

TABLE XIV
Effect of Temperature and Modifier on Brookfield Viscosity (cps)

Temp (°C)	Polyol I (0% modifier)	Polyol V (23.7% P725)	Polyol VI (49.1% P-725)	Polyol VII (72.1% P-725)	Polyol VIII (25.2% P-425)	Polyol IX (51.2% P-425)
30	136,000	23,160	8660	1444	40,400	5808
40	40,640	8400	4336	784	14,080	2680
50	15,640	3744	2260	440	5400	1360
60	6880	1920	1280		2760	760
70	3520	1100	768		1548	460
80	2008	680	488		952	
90	1560				616	
100	932					
110	584					

P-725 as a Modifier

A poly(ethylene ether carbonate) diol and P-725 (2 : 3 wt ratio) were combined and heated at 10 mm Hg vacuum. No fractionating column was used. The distillate was removed, weighed, and analyzed at various pot temperatures. In addition, samples of the product were removed for molecular weight measurement. The results are listed in Table X.

There is a linear relationship between the pot temperature and the number average molecular weight in the temperature region studied at the vacuum and heat input employed (Fig. 3). This relationship is represented by

$$\bar{M}_n = 23.273 \text{ (pot temperature)} - 3122.1$$

$$\text{correlation coefficient} = 0.995$$
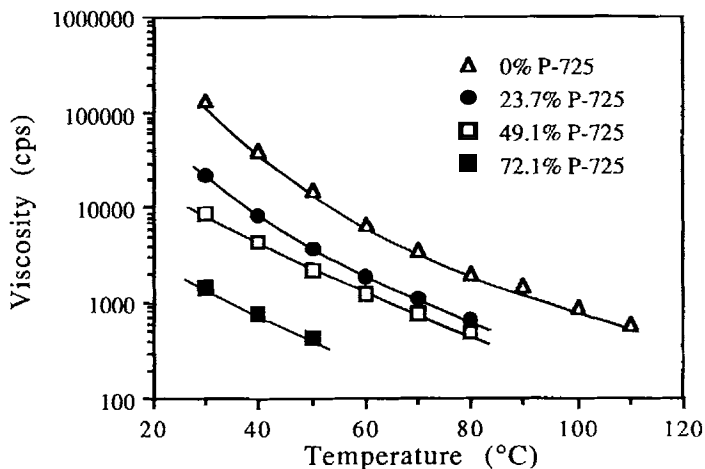
Fig. 12. Effects of temperature on the viscosity of P-725 modified diols.
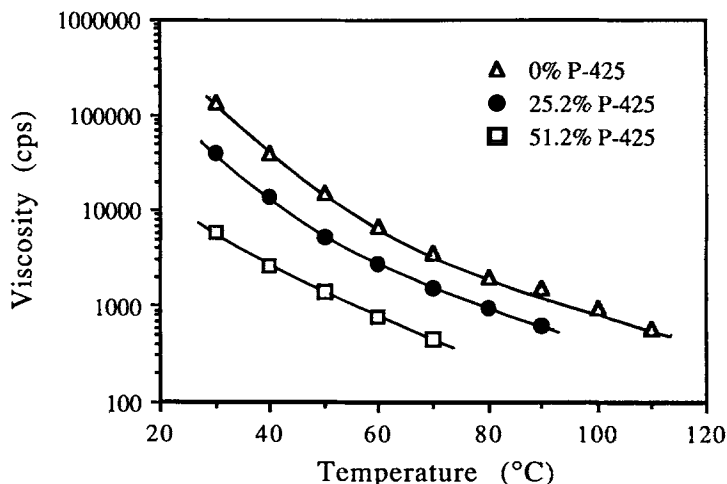
Fig. 13. Effects of temperature on the viscosity of P-425 modified diols.

The effect of pot temperature on the amount of distillate removed is shown in Figure 4. Figure 5 shows how the amount of distillate removed controls the molecular weight build. This relationship is represented by

$$\bar{M}_n = 34.578 \, (\text{distillate}) + 3.1347 \, (\text{distillate})^2 + 0.3038 \, (\text{distillate})^3 + 681.2$$

$$\text{correlation coefficient} = 0.992$$

The distillate composition as a function of pot temperature is given in Figure 6. Ethylene carbonate is removed from the reaction quickly. Diethylene glycol is the major component of the distillate. Triethylene glycol is a minor component which increases slowly with increasing pot temperatures.
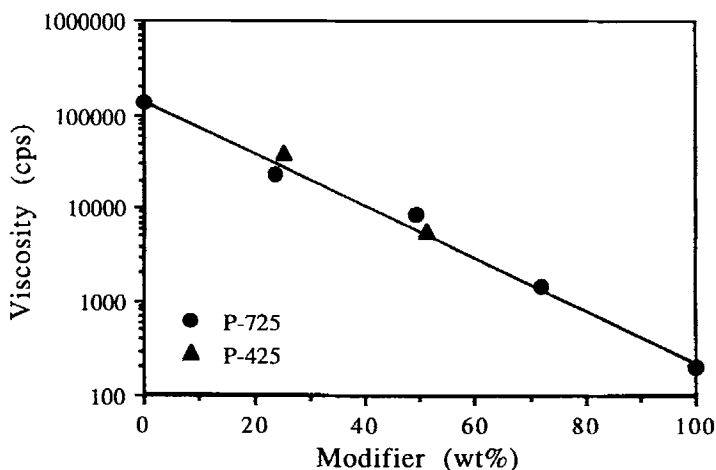
Fig. 14. Effects of modifier level on Brookfield viscosity at 30°C.

16.2

17.0/17.1

19.9/20.0

60.4

66.8/66.9

69.9

68.2/68.3

72.6/72.7

74.8/74.9

154.7

155.1
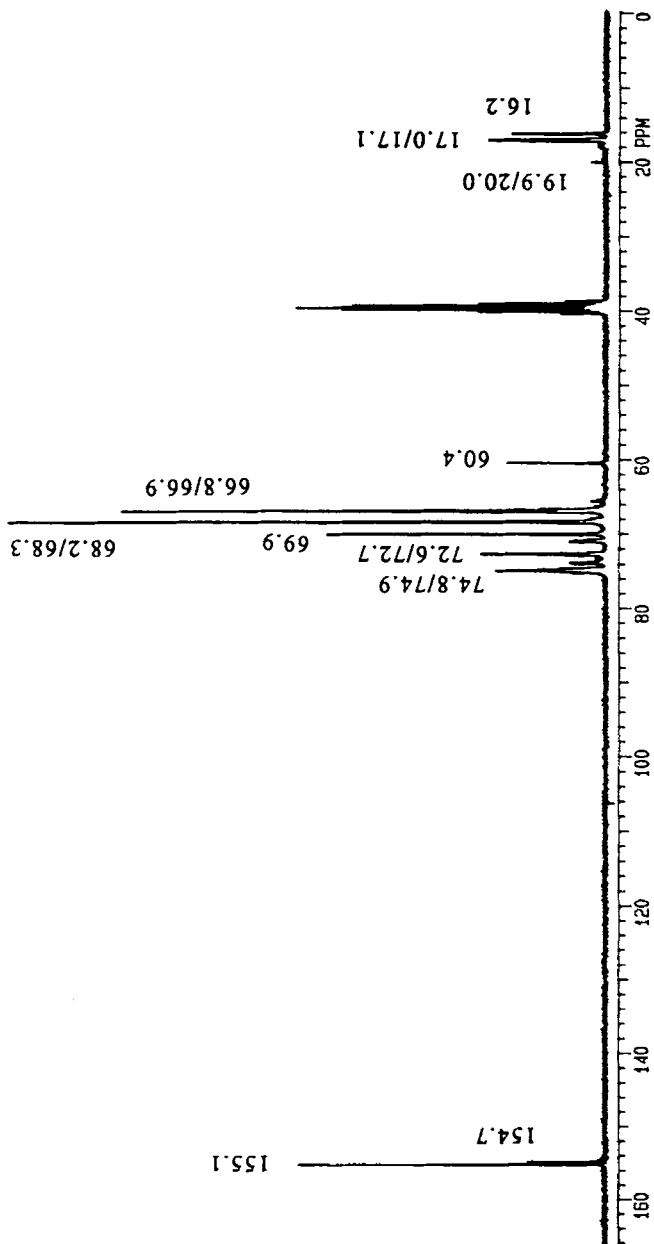
Fig. 15.   Carbon-13 NMR spectrum of poly(ethylene ether carbonate) diol modified with 25.2 wt % P-425.

TABLE XV
Carbon–13 NMR Structural Assignments of Poly(Propylene Glycol) Modified
Poly(Ethylene Ether Carbonate) Diols

Chemical shift[a]	Structural assignment
155.1 ppm	$CH_2OC(O)OCH_2$
154.7 ppm	$CH_2OC(O)OCH(CH_3)CH_2$
154.4 ppm	$CH_2CH(CH_3)OC(O)OCH(CH_3)CH_2$
74.8/74.9 ppm	$OCH_2CH(CH_3)OCH_2$
74.4/74.5 ppm	$OCH_2CH(CH_3)OCH_2$
72.6/72.7 ppm	$OCH_2CH(CH_3)OH$
72.5 ppm	OCH_2CH_2OH
69.9 ppm	$CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2$
68.2/68.3 ppm	$CH_2OC(O)OCH_2CH_2OCH_2$
66.8/66.9 ppm	$CH_2OC(O)OCH_2CH_2OCH_2$
65.4/65.6 ppm	$OCH_2CH(CH_3)OH$
60.4 ppm	OCH_2CH_2OH
19.9/20.0 ppm	$OCH_2CH(CH_3)OH$
17.0/17.1 ppm	$OCH_2CH(CH_3)OCH_2$
16.2 ppm	$CH_2OC(O)OCH(CH_3)CH_2O$

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6.

Scale Up Using Poly (Propylene Glycol) Modifiers

Once the scope of the molecular weight advancement reaction conditions were ascertained and the distillate removal and molecular weight build were studied, this process (Figure 2) was used to prepare larger quantities (1–2 lb)
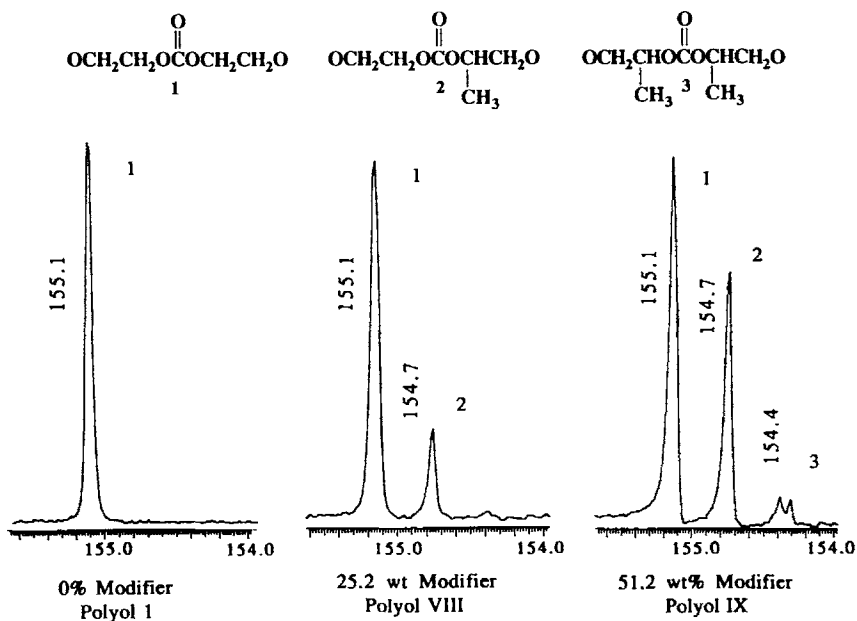

Fig. 16. Structural assignments of carbonyl carbon atoms in Carbon–13 NMR spectra.

TABLE XVI

Carbon-13 NMR Relative Intensities for Carbonyl Carbon and Methyl Carbon Lines

Polyol number	Modifier	Modifier (wt %)	Relative intensities of carbonyl moieties			Relative intensities of methyl moieties		
			155.1 ppm	154.7 ppm	154.4 ppm	19.9 ppm	17.0 ppm	16.2 ppm
I	None	0	100	—	—	—	—	—
V	P-725	23.7	89	11	—	3	81	16
VI	P-725	49.1	72	28	—	4	85	11
VII	P-725	72.1	45	50	5	7	82	11
VIII	P-425	25.2	80	20	—	7	52	41
IX	P-425	51.2	56	40	4	11	50	39
X	TPG	12.3	80	20	—	10	32	58

of a series of poly(propylene glycol) modified poly(ethylene ether carbonate) diols. All reactions were carried out at 10 mm Hg using a down-draft condenser (no column). The properties of these materials are listed in Table XI. The mass balances and distillate assay from each preparation are given in Tables XII and XIII, respectively.

Since the molecular weight advancement process (as applied above) essentially replaces poly(ethylene glycol) units (mostly DEG units) by a given poly(propylene glycol) modifier, many of the properties have a linear dependance on the amount of modifier used. Figure 7 shows such an effect when considering the CO_2 content of a modified diol. Since the molecular weight ad-
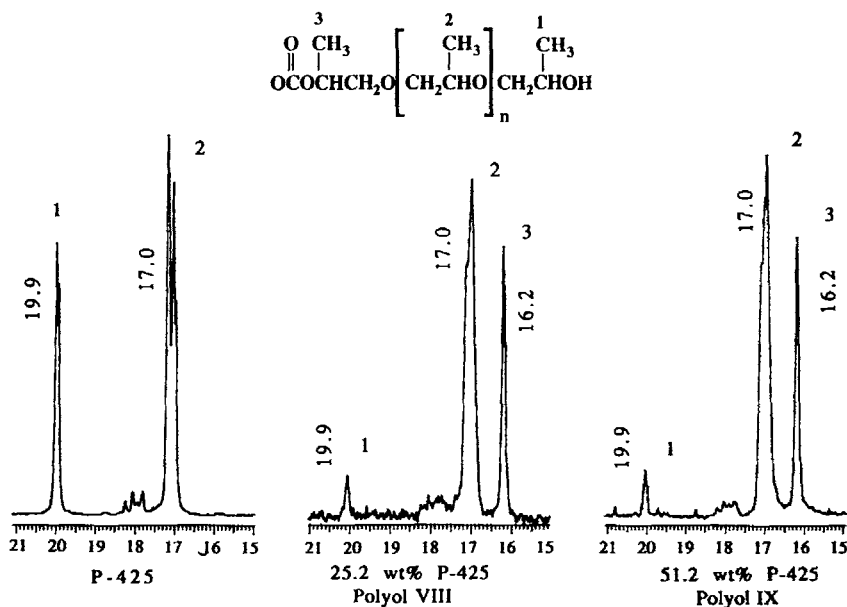

Fig. 17. Structural assignments of methyl carbon atoms in Carbon-13 NMR spectra.
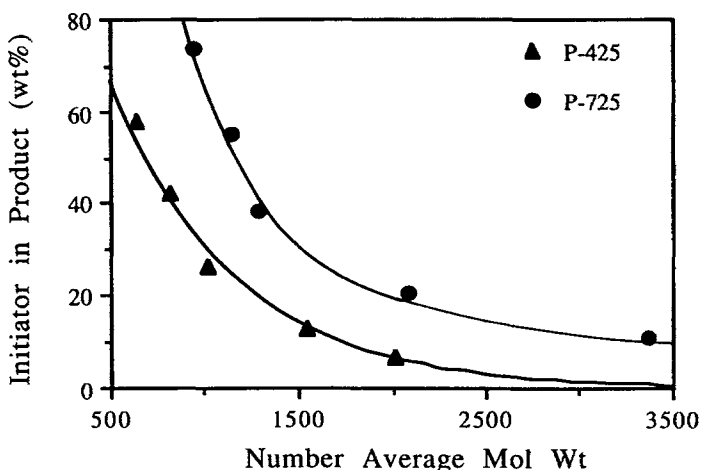
Fig. 18.   Effect of initiator level on modifier content in modified poly(ethylene ether carbonate) diols.

vancement process proceeds with high CO_2 retention, a plot of CO_2 content *vs.* weight percent modifier is a straight line, regardless of which poly(propylene glycol) modifier is used. The same effect exists when the densities or the glass transition temperatures (T_g) of the poly(propylene glycol) modified poly(ethylene ether carbonate) diols are plotted *vs.* weight percent modifier (Figs. 8 and 9, respectively). All modifiers fall on the same line in each case. Therefore, the modification process can be used to modify polyol properties such as CO_2 content (polyester character) and T_g.

Representative size exclusion chromatography (SEC) traces for the P–425 and P–725 modified molecular weight advanced poly(ethylene ether carbonate) diols are given in Figures 10 and 11. All advanced polyols have a $\bar{M}_n$ of about 2000. Well-shaped curves were obtained in all cases. Only in the case of the 72.1 wt % P-725 does there appear to be a low molecular weight shoulder. Although P-425 and P-725 are immiscible in poly(ethylene ether carbonate) polyols at ambient temperatures, they are chemically bonded into the modified molecular weight advanced poly(ethylene ether carbonate) diols to give a homogeneous product, as clearly shown by the SEC traces.

All unmodified poly(ethylene ether carbonate) diols studied were highly viscous liquids. However, viscosity can be dramatically reduced by increased temperature and/or increased amounts of poly(propylene glycol) modifiers (Table XIV). The temperature dependence on viscosity (at low shear) is illustrated for P-725 and P-425 modifiers at constant levels in Figures 12 and 13. Since viscosity in these systems is largely due to intermolecular hydrogen bonding, increased temperature has a pronounced lowering effect. The effect of modifier level on viscosity at constant temperature (30°) is illustrated in Figure 14. As the modifier level is increased, the weight percent CO_2 (see Fig. 7) is decreased, leading to reduced polyester character and reduced viscosity.

Structural Assignments by Carbon-13 NMR

The poly(propylene glycol)-modified poly(ethylene ether carbonate) diols were studied by carbon-13 NMR to ascertain their structures and to gain ad-

ditional insight into the modification process. A typical spectrum (25.2 wt %
P-425 modification) is given in Figure 15. A listing of all the line assignments
is given in Table XV.

The poly(ethylene ether carbonate) diol starting material has only one kind
of carbonyl carbon atom (155.1 ppm). However, since poly(propylene glycols)
have secondary hydroxyl end groups, their reactions with carbonyl moieties
during advancement conditions produce a different kind of carbonyl moiety—
a carbonate connected to both methylene and methyne carbon atoms (154.7
ppm). Under conditions of high modifier level, a third kind of carbonyl species
is formed—a carbonate connected to two methyne carbon atoms (154.4 ppm).
Figure 16 illustrates these structures and gives the associated line spectra. The
carbon-13 NMR was not run under quantitative conditions, but, since the car-
bonyl carbon atoms should have comparable relaxation times, line intensities
were measured (Table XVI). Although the modifier weights are different, the
number of moles of modifier are nearly the same for Polyols VI, VIII, and X,
because of molecular weight differences. Product carbonyl ratios are very similar
for these three modified polyols.

There are no methyl moieties in the poly(ethylene ether carbonate) diol
starting material. Poly(propylene glycol) modifiers have two methyl moieties:
the methyl groups attached to the polyether backbone (17.0 ppm), and the
methyl groups associated with the end group moieties (19.9 ppm). The mod-
ification reaction produces an additional kind of methyl group—methyl groups
on the methyne carbon atoms attached to carbonyl moieties (16.2 ppm). Figure
17 illustrates these structures and gives the associated line spectra. Line in-
tensities indicate that some secondary hydroxyl end groups are present in all
modified polyol samples. Larger proportions of methyl groups on the methyne
carbon atoms attached to carbonyl moieties (16.2 ppm) are produced at lower
poly(propylene glycol) block size and lower modifier levels.

New Materials

Previously to this work, poly(ethylene ether carbonate) polyols have been
modified, for example, by the particular initiator used in the oligomerization
of cyclic alkylene carbonates or by reaction with alkylene oxides and CO_2. A
relationship exists between the amount of initiator used and the molecular
weight of a given product. For example, as larger quantities of ethylene carbonate
are added to a given amount of an initiator to produce higher molecular weight
products, the initiator concentration is reduced (diluted). This relationship is
illustrated in Figure 18 by a series of reaction products formed using P-425 and
P-725 as initiators in the oligomerization of ethylene carbonate.[9] A smooth
curve is obtained in each case.

Initiators and modifiers can be similar materials, but are added by different
processes. The major advantage in using the modifier approach, as described
in this paper, is that not only can the compositions on the line (Fig. 18) be
made, but any composition to the right of the line can also be made. This is
accomplished because molecular weight and modifier content have effectively
been decoupled. At a given modifier level, a large series of molecular weight
products are possible. This paper demonstrates the preparation of a wide variety
of modifier types and amounts in modified polyols of about 2000 molecular
weight.

CONCLUSIONS

Poly(ethylene ether carbonate) polyols can be modified by chemical reactions with polyglycol modifiers under conditions of elevated temperatures and reduced pressures, where diethylene glycol is removed as distillate. Molecular weight builds in a predictable manner and can be controlled by the amount of distillate removed. A reaction pathway for this transformation, consisting of a series of transesterification equilibria reactions, is proposed. It is important that the modifier be stable to the reaction conditions and have a higher boiling point than that of diethylene glycol. A fractionating column can be used effectively when boiling points are close. Many modifiers are incompatible with the poly(ethylene ether carbonate) polyol starting material, but are compatibilized by reaction.

The process has been characterized by following the distillate formation and composition as a function of reactor temperature and product molecular weight build. The product has been characterized by molecular weight, CO_2 content, carbon-13 NMR, and viscosity/temperature relationships. Carbon-13 NMR of the carbonyl and methyl regions of the spectra are particularly useful for following the chemical changes occurring during the molecular weight advancement process.

A new family of modified poly(ethylene ether carbonate) polyols has been prepared which was not available with prior technology. The modification procedure permits the control of properties such as modifier type and content, molecular weight, CO_2 content, viscosity, T_g, density, etc., in the resultant polyol. Since poly(ethylene ether carbonate) polyols have predominantly polyester polyol properties, modification with polyether polyols can be used to adjust properties between those of polyether and polyester polyols. Hydrophilic/hydrophobic balances can be controlled. These polyols are useful in polyurethane applications.

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