

Polyester-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 polyester polyols, poly(carboxylic acids), poly(carboxylic acid) esters, or poly(carboxylic acid) cyclic anhydrides under conditions of elevated temperatures and reduced pressures to give ester-modified poly(ethylene ether carbonate) polyols. Polyester polyols and poly(carboxylic acid) ester are incorporated into the polymer backbone by transesterification/advancement reactions. Poly(carboxylic acids) and poly(carboxylic acid) cyclic anhydrides first undergo esterification and then transesterification/advancement reactions. Molecular weight builds in a predictable manner and can be controlled by the amount of distillate removed. The processes have been characterized by following the distillate formation and composition as a function of reactor temperature and product molecular weight build. The products have been characterized by molecular weight and carbon-13 NMR spectroscopy. A new family of ester-modified poly(ethylene ether carbonate) polyols has been prepared, most of which were not available with prior technology. These polyols are useful in polyurethane applications, where the degree and type of polyol modification can be used to adjust polyurethane properties. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene ether carbonate) polyols are polymers that contain alternating blocks of carbon dioxide units and poly(ethylene glycol) units in their backbones.^{1,2} When these polyols are heated to elevated temperatures ($> 180^{\circ}\text{C}$) at reduced pressures, volatile impurities are removed, followed by formation of diethylene glycol (DEG).³⁻⁶ As DEG is removed as distillate, molecular weight builds in a controllable manner. This is a transesterification process in which $-\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ 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_2 retention, relatively low polydispersity, and high purity.

Poly(ethylene ether carbonate) diols (2025 mol wt) made by the molecular weight advancement of lower molecular weight oligomers have been fabri-

cated into polyurethane elastomers by reaction with 4,4'-methylenediphenyl diisocyanate (MDI) and 1,4-butanediol using the prepolymer method.⁷⁻⁹ Poly(ethylene ether carbonate) diols gave polymers with a partially phase-mixed morphology, a higher ambient temperature modulus, and a lower ΔH_m than those of the other polyester polyols studied. Resistance to organic solvents was their most outstanding property. Diisocyanates have been used to modify poly(ethylene ether carbonate) polyols and their urethane polymers studied.¹⁰⁻¹¹

Recently, this technology was extended to include other polyols in the reaction mixture during the molecular weight advancement process.¹² These polyol modifiers become chemically incorporated into the poly(ethylene ether carbonate) polyol backbone to yield a new class of compounds.^{13,14} The preparation and characterization of polyurethanes prepared from poly(propylene glycol)-modified poly(ethylene ether carbonate) polyols was recently published.¹⁵⁻¹⁷ This paper extends this work to the use of polyester modifiers.^{18,19}

EXPERIMENTAL

Starting Materials

The hydroxy-functional polyester polyol of adipic acid and DEG (Formrez™ 11-225; molecular weight = 500) was obtained from Witco Chemical Co. Polycaprolactone diol (molecular weight = 530), adipic acid, dimethyl adipate, dimethyl terephthalate, and succinic anhydride were obtained from Aldrich Chemical Co. The poly(ethylene ether carbonate) diol starting materials were prepared by the monoethylene glycol-initiated oligomerization of ethylene oxide and carbon dioxide,²⁰ followed by removal of the residual catalyst.^{6,21}

Polyol Modification/Molecular Weight Advancement Procedure

A given amount of poly(ethylene ether carbonate) diol, polyester modifier, and boiling stones were placed in a boiling flask equipped with a thermometer, heating mantle, and water-chilled condenser attached to a dry-ice/isopropanol trap and a vacuum source. When noted, a small fractionating column was used between the flask and the condenser. The polyol was heated to 60–80°C to reduce viscosity and outgassed at about 50 mmHg. The vacuum was then adjusted to 10 mmHg. Heating was increased to effect fractionation and continued until the desired pot temperature was reached. The residue and distillate were weighed and analyzed.

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 the internal standard. Water analysis was done by Karl Fischer titration.

Polyol Analytical Procedures

Molecular weights of the polyols (0.5 wt % in tetrahydrofuran [THF]) were determined by size-exclusion chromatography (SEC) on Waters Ultrastaygel™ 10³ and 10⁴ Å columns in series at 25°C using THF as the continuous phase (1.5 mL/min), calibrated with standard poly(ethylene glycols) and using a refractive index detector. NMR spectra (5 wt % in DMSO-*d*₆) were obtained on a Varian Gemini 300 instrument (75 MHz for carbon). Viscosity/temperature profiles were obtained on a Brookfield Synchro-Lectric digital viscometer

with a Brookfield thermosel heater using an HBTD #21 spindle. Temperature was controlled with a Model 84 Brookfield programmable temperature controller.

RESULTS AND DISCUSSION

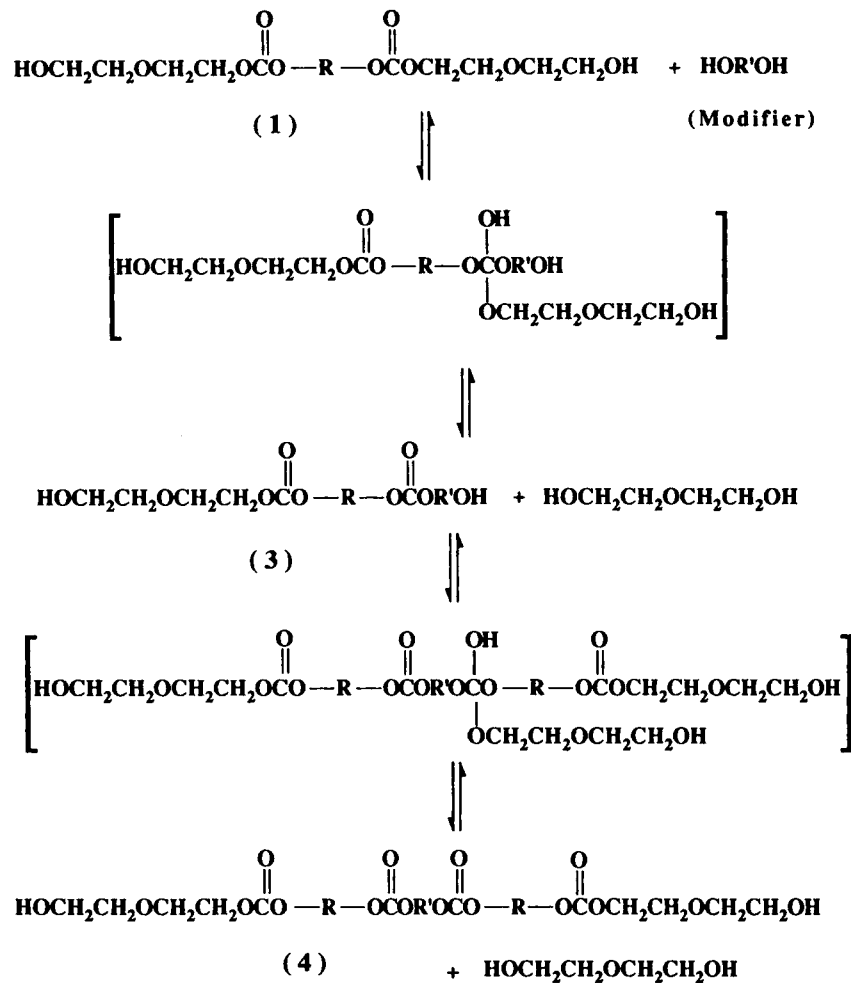
Reaction Pathway for Modification of Poly(Ethylene Ether Carbonate) Polyols by Transesterification/Advancement

When poly(ethylene ether carbonate) polyols are heated to elevated temperatures (> 180°C) at reduced pressures, a transesterification process occurs in which —OC(O)CH₂CH₂OCH₂CH₂OH end groups on one molecule react with carbonate moieties on a second molecule with a loss of DEG to build molecular weight in a controllable manner.^{3–6} If a second polyol is included in the reaction mixture, it is incorporated into the backbone during the molecular weight advancement process to produce a molecular weight advanced, modified poly(ethylene ether carbonate) polyol. This reaction pathway is illustrated in Figure 1, 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.

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.

Poly(Diethylene Glycol Adipate) Diol as a Modifier

A poly(ethylene ether carbonate) diol (553.6 g) and a poly(diethylene glycol adipate) diol (380.2 g) were combined and heated at 10 mmHg. No fractionating column was used. Distillate was removed until the pot temperature reached 235°C. The mass balance and product molecular weight data are given in Table I; the distillate composition is given in Table II. The



where R = poly(ethylene ether carbonate) backbone.

Figure 1 Reaction pathway of modification process using a polyol modifier.

Table I Products Formed by Reactions of Polyester Diols with Poly(Ethylene Ether Carbonate) Diols under Molecular Weight Advancement Conditions

Polyol No.	Modifier ^a (Wt %)	Max Pot Temp (°C)	Mass Balance (Wt %)			Molecular Weight Data					Polyol Density (g/cc)
			Product	Distillate Trap	-78°C Trap	Titration ^b	Peak	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	
I	None	230	83.7	14.9	0.6	ND	3749	2021	4362	2.16	1.24
II	21.8 A	228	87.5	12.2	0.2	1455	2847	1590	3189	2.09	1.22
III	48.9 A	235	83.3	16.5	0.1	1765	3700	2007	4203	2.19	1.22
IV	13.0 B	235	81.7	17.1	0.5	2446	5181	2569	5584	2.17	1.22
V	25.6 B	235	82.1	16.9	0.4	2118	4790	2355	5089	2.16	1.20
VI^d	53.1 B	235	75.4	23.4	0.8	2658	3695	2765	6226	2.25	1.18

^a A = 500 molecular weight poly(diethylene glycol) diol; B = 530 molecular weight polycaprolactone diol.

^b By end-group titration with phthalic anhydride in pyridine; ND = not determined.

^d Different poly(ethylene ether carbonate) diol starting material.

Table II Distillate Formed by Reactions of Polyester Diols with Poly(Ethylene Ether Carbonate) Diols under Molecular Weight Advancement Conditions

Polyol No.	Modifier (Wt %) ^a	Distillate Assay ^b (Wt %)								Distillate Density (g/cc)
		MEG	Dioxane	EC	DEG	TriEG	TetraEG	Water	ϵ -Caprolactone	
II	21.8 A	0.1	0.3	7.4	62.5	23.6	6.0	0.08	—	1.13
III	48.9 A	0.1	0.1	4.8	56.2	22.3	8.1	0.09	—	1.13
IV	13.0 B	0.1	0.7	5.4	47.9	24.4	5.6	0.08	3.4	1.13
V	25.6 B	0.1	0.9	4.8	51.9	26.0	6.8	0.07	5.7	1.13
VI ^c	53.1 B	0.2	0.3	9.9	67.7	12.8	1.1	0.13	6.6	1.14

^a A = 500 molecular weight poly(diethylene glycol) diol; B = 350 molecular weight polycaprolactone diol.

^b Weight of material trapped by water chilled condenser.

^c Different poly(ethylene ether carbonate) diol starting material.

product (III) accounted for 83.3 wt % of the reactants charged, contained 48.9 wt % DEG adipate blocks, and had a number-average molecular weight of 2007 by SEC. The distillate was predominately DEG and triethylene glycol (TriEG). By way of comparison, the same poly(ethylene ether carbonate) diol was heated in the absence of a modifier. The product (I) accounted for 83.7 wt % of the reactants charged and had a number-average molecular weight of 2021 by SEC.

The ¹³C-NMR spectrum of III is given in Figure 2. Structural assignments are given in Table III and compared to the two reactants.^{5,7,12} The most im-

portant chemical shifts in the reactants from a structural assignment point of view are given below:

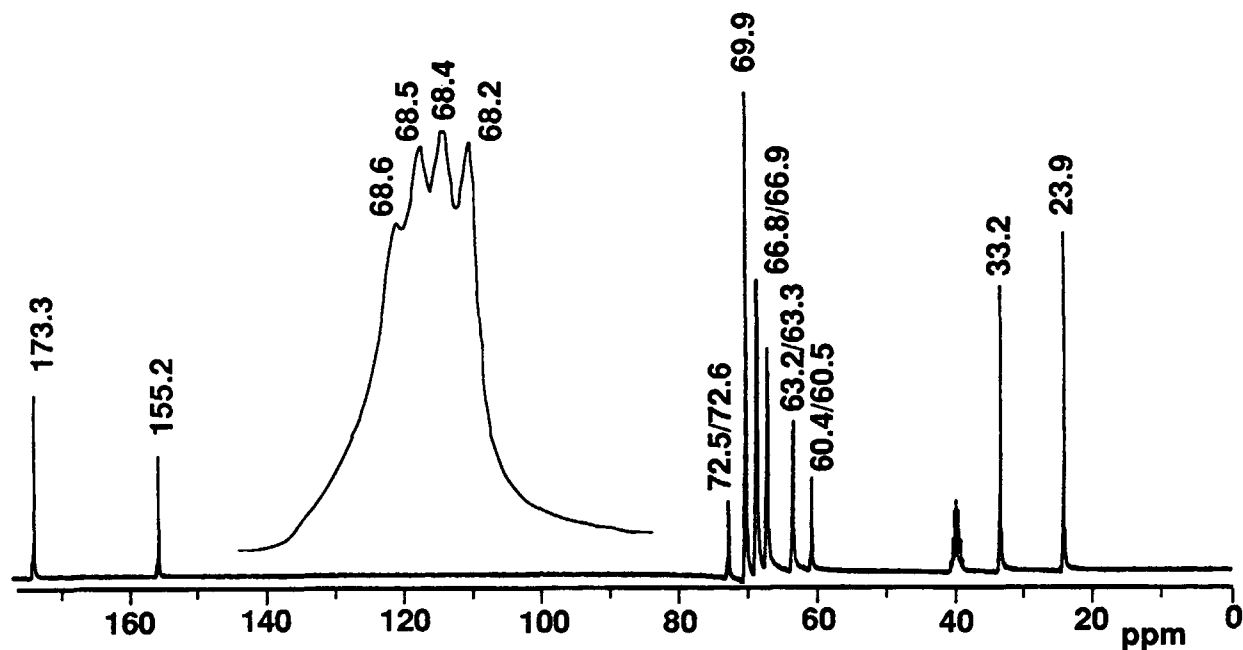
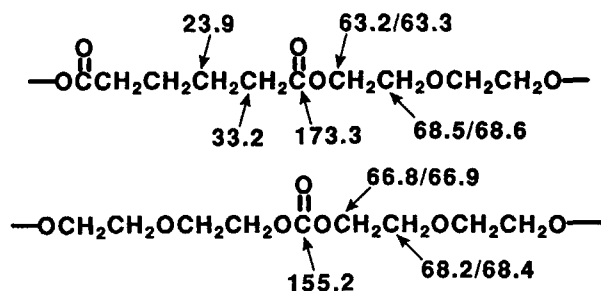


Figure 2 ¹³C-NMR spectrum of 48.9% poly(ethylene glycol adipate) diol-modified poly(ethylene ether carbonate) diol (III).

Table III ^{13}C -NMR Structural Assignments of Poly(Diethylene Glycol Adipate) Diol Modified Poly(Ethylene Ether Carbonate) Diol

Chemical Shift ^a (ppm)			
Poly(Ethylene Ether Carbonate) Diol	Poly(Diethylene Glycol Adipate) Diol	Modified Diol III	Structural Assignments
—	173.3	173.3	—OCH ₂ CH ₂ OC(O)CH ₂ CH ₂ —
155.2	—	155.2	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ O—
72.5/72.6	72.6	72.5/72.6	—CH ₂ OCH ₂ CH ₂ OH
69.9	—	69.9	—CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ —
—	68.5/68.6	68.5/68.6	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
68.2/68.4	—	68.2/68.4	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
66.8/66.9	—	66.8/66.9	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
—	63.2/63.3	63.2/63.3	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
60.4/60.5	60.4/60.5	60.4/60.5	—CH ₂ OCH ₂ CH ₂ OH
—	33.2	33.2	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
—	23.9	23.9	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —

^a ppm from tetramethylsilane (TMS = 0); DMSO-*d*₆.

Since the product is essentially a transesterification product of two diacids (adipic and carbonic) and two diols (DEG and TriEG), only the chemical shifts present in these reactants are present in the products. Detailed examination of the ^{13}C -NMR spectrum indicates that DEG units attached to adipate carbonyls are clearly distinguishable from DEG units attached to carbonate carbonyls by the chemical shifts of the α -carbon atoms (63.2/63.3 vs. 66.8/66.9 ppm for the α -carbon atoms attached to adipate and carbonate, respectively). A very small chemical shift difference was also detected in the corresponding β -carbon atoms (see Fig. 2; 68.5/68.6 vs. 68.2/68.4 ppm for the β -carbon atoms attached to adipate and carbonate, respectively). The carbonyl carbon atoms are well resolved (173.3 vs. 155.2 ppm for the adipate and carbonate, respectively). A 21.8 wt % DEG adipate-modified poly(ethylene ether carbonate) diol (II) was prepared by a similar procedure (see Tables I and II).

Polycaprolactone Diol as a Modifier

A poly(ethylene ether carbonate) diol (854.8 g) and polycaprolactone diol (102.1 g) were combined and heated at 10 mmHg. No fractionating column was used. Distillate was removed until the pot temperature reached 235°C. The mass balance and product molecular weight data are given in Table I; the distillate composition is given in Table II. The product (IV) accounted for 81.7 wt % of the reactants charged, contained 13.0 wt % polycaprolactone

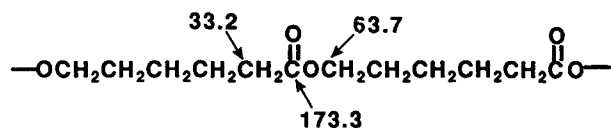
blocks, and had a number-average molecular weight of 2569 by SEC.

A 25.6 wt % polycaprolactone-modified poly(ethylene ether carbonate) diol (V) and a 53.1 wt % polycaprolactone-modified poly(ethylene ether carbonate) diol (VI) were prepared by similar procedures (see Tables I and II).

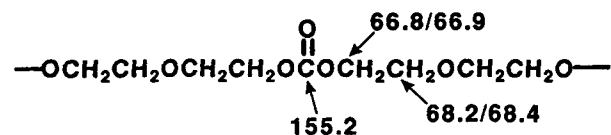
^{13}C -NMR structural assignments are given in Table IV and compared to the two reactants. The most important chemical shifts in the reactants are those around the carbonyl moieties.

Reactants

A. Carboxylic acid ester of 6-hydroxyhexanoic acid:



B. Carbonic acid ester of poly(ethylene glycols):



Three transesterification products are possible in this case. The first (C) is the carboxylic acid ester of poly(ethylene glycols). This would be expected to have very similar ^{13}C -NMR chemical shifts to the

Table IV ^{13}C -NMR Structural Assignments of Polycaprolactone Diol-modified Poly(Ethylene Ether Carbonate) Diol

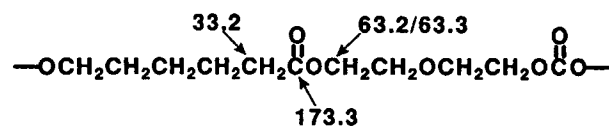
Chemical Shift ^a (ppm)			
Poly(Ethylene Ether Carbonate) Diol	Polycaprolactone Diol	Modified Diol VI	Structural Assignments
—	173.3	173.3	—OCH ₂ CH ₂ OC(O)CH ₂ CH ₂ CH ₂ —
155.2	—	155.2	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ O—
72.5/72.6	—	72.5/72.6	—CH ₂ OCH ₂ CH ₂ OH
69.9	—	69.9	—CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ —
—	—	68.5/68.6	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
68.2/68.4	—	68.2/68.4	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
—	—	67.3/67.5	—OCH ₂ CH ₂ OC(O)CH ₂ CH ₂ CH ₂ CH ₂ —
66.8/66.9	—	66.8/66.9	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
—	63.7	63.7	—CH ₂ CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ CH ₂ CH ₂ —
—	—	63.2/63.3	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
60.4/60.5	60.8	60.8	—CH ₂ OC(O)CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH
—	—	60.4/60.5	—CH ₂ OCH ₂ CH ₂ OH
—	33.4	33.2	—CH ₂ OC(O)CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OC(O)—
—	32.3	32.3	—CH ₂ OC(O)CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH
—	28.0	27.9	—CH ₂ OC(O)CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OC(O)—
—	25.0	24.7/24.9	—CH ₂ OC(O)CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OC(O)—
—	24.1	24.1	—CH ₂ OC(O)CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OC(O)—

^a ppm from tetramethylsilane (TMS = 0); DMSO-*d*₆.

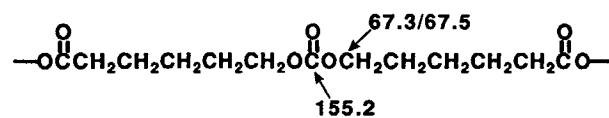
adipic acid ester of poly(ethylene glycols) indicated above. The second transesterification product (**D**) would be the carbonic acid ester of 6-hydroxyhexanoic acid, whereas the third transesterification product (**E**) would be the carbonic acid ester of 6-hydroxyhexanoic acid and poly(ethylene glycols). These three product structures are given below with the relevant ^{13}C -NMR chemical shifts.

Products

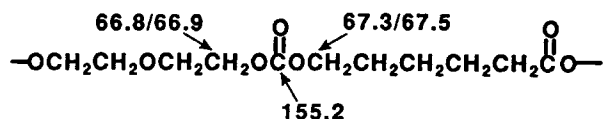
C. Carboxylic acid ester of poly(ethylene glycols):



D. Carbonic acid ester of 6-hydroxyhexanoic acid:



E. Carbonic acid ester of 6-hydroxyhexanoic acid and poly(ethylene glycols):



Detailed examination indicates that the ^{13}C -NMR chemical shifts are consistent with the presence of all five structures. Carboxylic acid esters of poly(ethylene glycols) are indicated by the chemical shift of the α -carbon atoms of the poly(ethylene glycols) at the point of attachment (63.2/63.3 ppm). Carbonic acid esters of 6-hydroxyhexanoic acid are indicated by the chemical shift of the α -carbon atoms of the 6-hydroxyhexanoic acid at the point of attachment (67.3/67.5 ppm).

^{13}C -NMR chemical shifts for polycaprolactone diols have been reported.²² Several of the ^{13}C -NMR chemical shift assignments in the product can be made on the basis of the systematic increase in the polycaprolactone diol modifier content in the series 0, 13.0, 25.6, 53.1, and 100% polycaprolactone. Some of these trends are clearly indicated in Figure 3, where the ^{13}C -NMR spectra are given for the 13.0 and 53.1% polycaprolactone modification between 60 and 70 ppm. Structures **A** (63.7 ppm), **C** (63.2/63.3 ppm), and **E** (67.3/67.5 ppm) increase systematically with increasing polycaprolactone content.

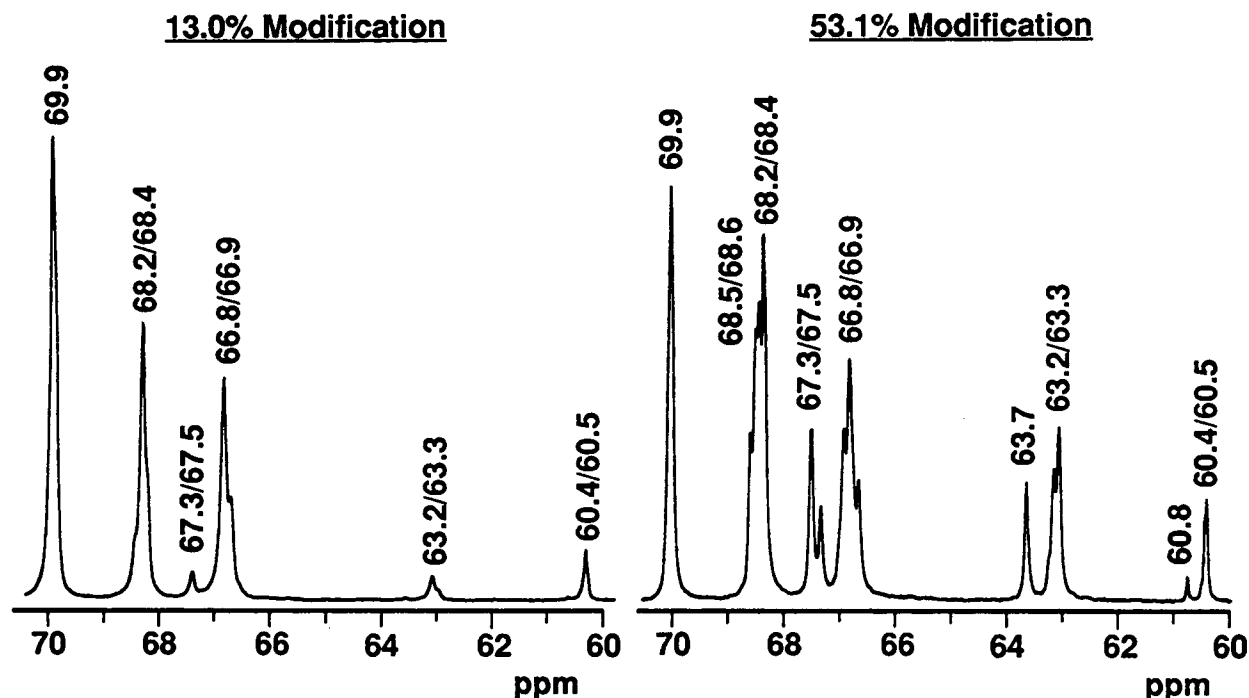
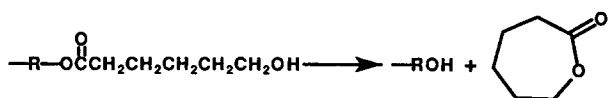


Figure 3 ^{13}C -NMR chemical shift changes with increasing polycaprolactone diol modification.

In addition, some of the hydroxyl end groups from 6-hydroxyhexanoic esters are also present (60.8 ppm for methylene carbon α to hydroxyl).²²

Distillate analyses (Table II) indicate that small amounts of ϵ -caprolactone are present in the distillate and increase with increasing polycaprolactone diol modification. This is probably a consequence of end-group depolymerization under the molecular weight advancement conditions:



Since ϵ -caprolactone has a boiling point of 96°C at 10 mmHg, it would flash from the reactor as formed. Losses to this reaction are minor.

Viscosities of Polyester-modified Diols

All polyester-modified poly(ethylene ether carbonate) diols studied were highly viscous liquids. Viscosities increased with increasing ester modification but are dramatically reduced by increasing temperature (Table V and Fig. 4).

Adipic Acid as a Modifier

Previous modification reactions studied were transesterification reactions where hydroxyl-functional

modifiers could react with ester moieties. Molecular weight advancement was controlled by the amount of volatile hydroxyl compounds (DEG, TriEG, etc.) removed as distillate. The use of a carboxylic acid-functional modifier like adipic acid would involve direct esterification in addition to transesterification around carbonate and adipate ester moieties.

A poly(ethylene ether carbonate) diol (71.7 g, 0.315 eq OH) and adipic acid (10.0 g, 0.137 eq CO_2H) were combined and heated to 262°C at 10 mmHg. 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 VI.

Representative SEC traces for the adipic acid-modified, molecular weight-advanced poly(ethylene ether carbonate) diol (VII) are given in Figure 5. There is a systematic increase in molecular weight with increasing pot temperature and a corresponding decrease in the adipic acid peak. Titration of the product indicates 0.121 meq/g acid, which represents 5.4% of the acid charged. Therefore, 94.6% of the acid charged was converted to ester. The number-average molecular weight is plotted vs. pot temperature in Figure 6. The amount of distillate removed controls the molecular weight build (Fig. 7). The rate of molecular weight build with adipic acid

Table V Viscosity of Polyester-modified Diols as a Function of Temperature

Temperature (°C)	Viscosity (cps) vs. Polyol No.				
	21.8% A II	48.9% A III	13.0% B IV	25.6% B V	53.1% B VI
30	5,664	7,688	10,020	16,740	23,760
40	2,656	3,704	5,100	8,600	11,480
50	1,376	1,960	2,728	4,400	6,000
60	796	1,116	1,588	2,444	3,440
70	480	700	992	1,488	2,112
80		468	712	972	1,388
90			468	676	960
100					688

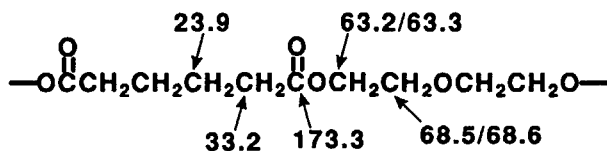
A = 500 molecular weight poly(diethylene glycol) diol; B = 530 molecular weight polycaprolactone diol.

as the modifier is significantly reduced relative to the corresponding molecular weight build in the absence of adipic acid.

In the second experiment, the same starting materials were heated as above, but to a pot temperature of only 240°C. The number-average molecular weight of the product (VIII) was significantly lower (848 vs. 1183).

The mass balance and final product molecular weight data for each experiment are given in Table VII; the distillate composition and the composition of the material in the dry-ice trap are given in Table VIII. The product (VII) accounted for 74.3 wt % of the reactants charged and contained 16.5 wt % adipic acid modification. The distillate was predominately DEG and TriEG. Water formed by esterification was present in the dry-ice trap.

¹³C-NMR structural assignments are given in Table IX; all expected features are present. Esterification of the adipic acid with poly(ethylene glycols) is indicated by the following structure (in addition to the consumption of adipic acid and the formation of water):



Residual adipic acid is indicated by small chemical shifts at 175.1, 33.4, and 24.1 ppm, corresponding to the carbonyl carbon, the methylene carbon α to the carbonyl carbon, and the methylene carbon β to the carbonyl carbon, respectively.

Dimethyl Adipate as a Modifier

A poly(ethylene ether carbonate) diol (72.7 g) and dimethyl adipate (14.0 g) were combined in a reactor equipped with a small fractionating column. After heating for 2 h at 10 mmHg and total reflux (120°C pot temperature), no reaction had occurred. The vacuum was adjusted to 30 mmHg and the reactor was heated at total reflux (144°C pot temperature). Little, if any, reaction had occurred after 2 additional h (by SEC). The vacuum was adjusted to 55 mmHg and the reactor was heated at total reflux (166°C pot temperature). A useful reaction rate was obtained. Under conditions of total reflux, dimethyl adipate is returned to the reactor, while byproduct methanol flashes through the water chilled condenser and is caught in the dry-ice trap (-78°C). When the initial transesterification reaction is complete [methanol displaced by poly(ethylene

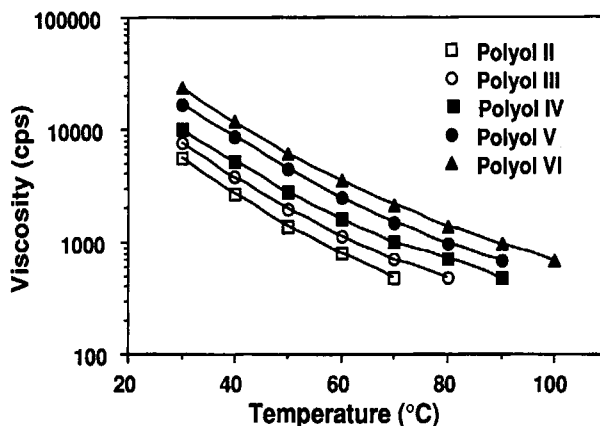


Figure 4 Viscosity of polyester-modified diols.

Table VI Molecular Weight Advancement Data for Adipic Acid-modified Poly(Ethylene Ether Carbonate) Diol

Pot Temp (°C)	Distillate ^a (Wt %)	Distillate Assay (Wt %)				Molecular Weight Data			
		EC	DEG	TriEG	TetraEG	Peak	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
25	—	—	—	—	—	565	455	673	1.48
100	—	—	—	—	—	225	390	618	1.58
170	5.6	19.2	76.2	3.2	—	544	428	638	1.49
197	8.3	4.0	83.5	12.2	—	673	506	773	1.53
221	10.7	0.9	48.6	47.3	1.2	873	621	1013	1.63
238	12.1	0.7	44.9	48.3	2.6	1137	784	1349	1.72
250	13.3	0.9	48.7	42.8	3.1	1398	888	1600	1.80
262	16.0	0.9	53.8	34.2	4.8	2119	1183	2315	1.96

^a Weight percent of reactants charged present as distillate.

glycols)], reflux stopped. The vacuum was reduced, the pot temperature increased, and distillate removal begun. It was necessary to run the initial reaction at total reflux since dimethyl adipate (boiling point 109–110°C/10 mmHg) is more volatile than is diethylene glycol (boiling point 134°C/10 mmHg).¹² 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.

Distillate was removed until the pot temperature reached 250°C. The number-average molecular weight is plotted vs. pot temperature in Figure 6. There was a systematic increase in molecular weight with increasing pot temperature. The amount of distillate removed controls the molecular weight build (Fig. 7). The distillate was predominately DEG (Table VIII). Only very small amounts of dimethyl adipate were present in the distillate (Table VIII).

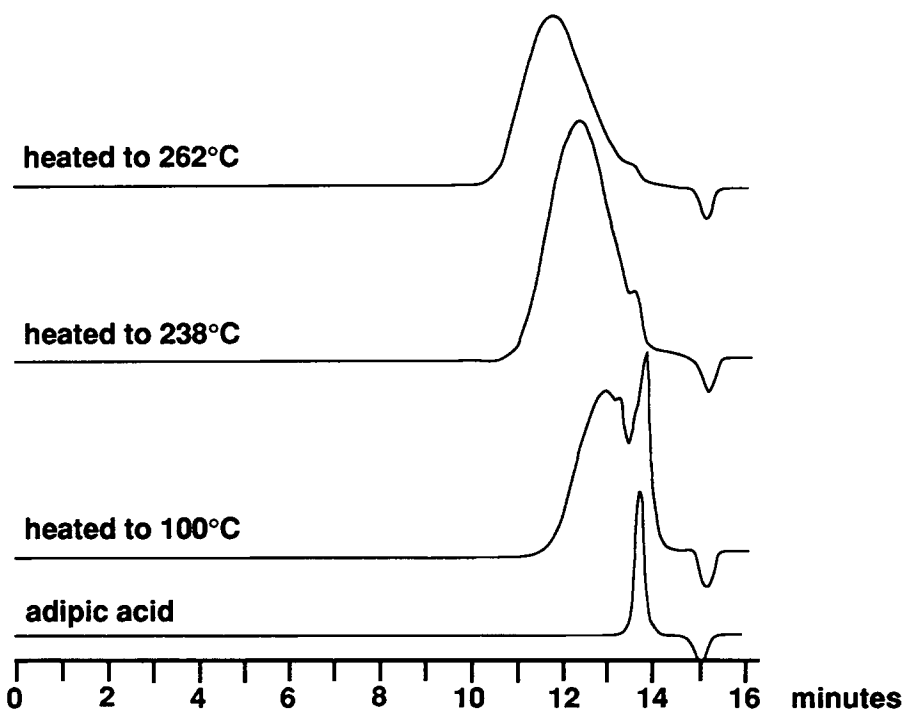


Figure 5 SEC traces for adipic acid-modified poly(ethylene ether carbonate) diols.

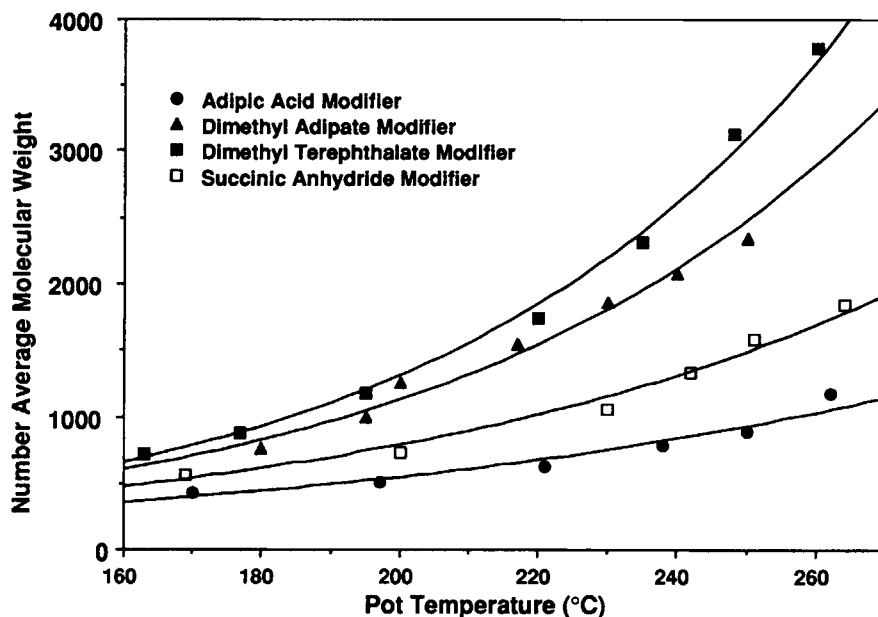


Figure 6 Effect of modifier on molecular weight build.

The mass balance and product molecular weight data are given in Table VII; the distillate and dry-ice trap compositions are given in Table VIII. The product (IX) accounted for 70.5 wt % of the reactants charged, contained adipate moieties, and had a number-average molecular weight of 2338 by SEC.

The byproduct methanol was present in the dry-ice trap.

Representative SEC traces for the dimethyl adipate-modified, molecular weight-advanced poly(ethylene ether carbonate) diol are given in Figure 8. ^{13}C -NMR structural assignments are given in Ta-

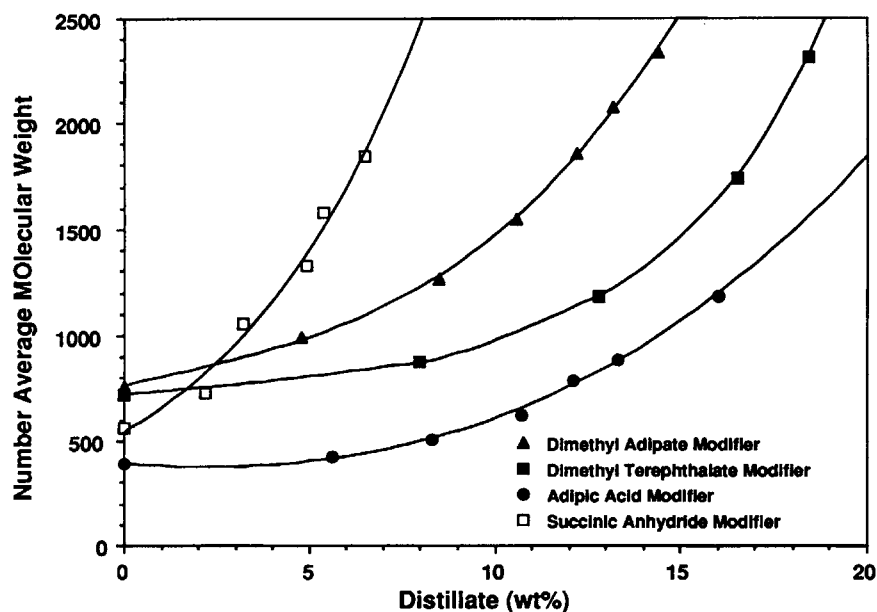


Figure 7 Effect of modifier and distillate level on molecular weight build of modified poly(ethylene ether carbonate) diols.

Table VII Products Formed by Reactions of Selected Modifiers with Poly(Ethylene Ether Carbonate) Diols under Molecular Weight Advancement Conditions

Polyol No.	Modifier	Pot Temp (°C)	Mass Balance (Wt %)				Molecular Weight Data				Product Brookfield Viscosity (cps; 25°C)
			Distillate Trap	-78°C Trap	Unaccounted For ^a	Product	Peak	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	
VII	Adipic acid	262	16.0	5.0	4.7	74.3	2119	1183	2315	1.96	9,700
VIII	Adipic acid	240	11.7	4.5	3.5	80.3	1209	848	1530	1.80	ND ^b
IX	Dimethyl adipate	250	14.4	8.5	6.6	70.5	4623	2338	5331	2.28	58,800
X	Dimethyl terephthalate	260	22.0	7.2	8.8	62.0	8886	3778	9259	2.45	875,000
XI	Succinic anhydride	264	6.5	5.0	5.8	82.7	3701	1843	4086	2.22	54,200

^a Many samples removed for analysis.

^b ND = not determined.

Table VIII Analysis of Material in the Distillate Trap and Dry-ice Trap as a Result of Reaction with Selected Modifiers under Molecular Weight Advancement Conditions

Polyol No.	Modifier	Distillate ^a (Wt %)	Distillate Assay ^a (Wt %)						Dry-ice Trap Assay (Wt %)			
			Dioxane	EC	DEG	TriEG	TetraEG	Modifier	Acetone	Dioxane	MeOH	H ₂ O
VII	Adipic acid	16.0	—	8.1	63.7	22.7	1.4	—	37.2	3.8	—	51.1
VIII	Adipic acid	11.7	—	8.9	70.7	18.6	0.3	—	38.0	1.6	—	60.7
IX	Dimethyl adipate	14.4	0.6	4.3	79.8	9.6	0.4	0.9	31.8	3.6	44.5	4.7
X	Dimethyl terephthalate	22.0	1.0	4.3	76.2	7.9	0.7	5.0	35.4	15.5	30.3	6.3
XI	Succinic anhydride	6.5	—	24.9	67.7	4.3	—	—	32.7	2.0	—	61.8

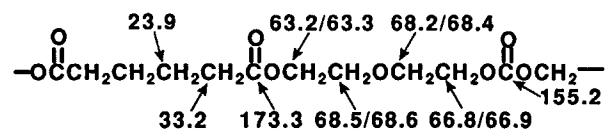
^a Material trapped by water-chilled condenser.

Table IX ^{13}C -NMR Structural Assignments of Adipic Acid-modified Poly(Ethylene Ether Carbonate) Diol

Chemical Shift ^a (ppm)	Structural Assignments
175.1	—CH ₂ CH ₂ C(O)OH
173.3	—CH ₂ OC(O)CH ₂ CH ₂ —
155.2	—CH ₂ CH ₂ OC(O)OCH ₂ CH ₂ —
72.5/72.6	—CH ₂ OCH ₂ CH ₂ OH
69.9	—CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ —
68.5/68.6	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
68.2/68.4	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
66.8/66.9	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
63.2/63.3	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
60.4/60.5	—CH ₂ OCH ₂ CH ₂ OH
33.4	—CH ₂ CH ₂ C(O)OH
33.2	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
24.1	—CH ₂ CH ₂ C(O)OH
23.9	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —

^a ppm from tetramethylsilane (TMS = 0); DMSO-*d*₆.

ble XI; all expected features are present. Adipic acid esters with poly(ethylene glycols) are indicated by the following structural unit (in addition to the consumption of dimethyl adipate and the formation of methanol):



Dimethyl Terephthalate as a Modifier

A poly(ethylene ether carbonate) diol (70.5 g, 0.310 eq OH) and dimethyl terephthalate (10.0 g, 0.103

eq ester) were combined and heated to 260°C at 10 mmHg. 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 XII.

Representative SEC traces for the terephthalate-modified, molecular weight-advanced poly(ethylene ether carbonate) diol are given in Figure 9. There is a systematic increase in molecular weight with increasing pot temperature and a corresponding decrease in the dimethyl terephthalate peak. The number-average molecular weight is plotted vs. pot temperature in Figure 6. The amount of distillate

Table X Molecular Weight Advancement Data for Dimethyl Adipate-modified Poly(Ethylene Ether Carbonate) Diol

Pot Temp (°C)	Vacuum (mmHg)	Distillate ^a (Wt %)	Distillate Assay (Wt %)						Molecular Weight Data			
			Dioxane	EC	DEG	TriEG	TetraEG	DMA	Peak	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
25	—	—	—	—	—	—	—	—	565	455	673	1.48
157	50	—	—	—	—	—	—	—	587	521	735	1.41
180	50	—	—	—	—	—	—	—	1048	762	1252	1.64
195	14	4.8	1.0	10.6	75.3	8.8	—	1.5	1616	990	1814	1.83
200	10	8.5	—	1.3	82.3	12.8	0.3	0.5	2209	1261	2442	1.94
217	10	10.6	—	0.3	86.5	8.2	—	0.3	2776	1546	3156	2.04
230	10	12.2	0.5	0.6	78.9	10.3	—	0.9	3553	1855	4004	2.16
240	10	13.2	0.5	0.8	78.2	9.4	0.3	0.6	4181	2074	4241	2.04
250	10	14.4	0.7	0.9	70.5	12.6	0.4	0.3	4623	2338	5331	2.28

^a Weight percent of reactants charged present as distillate.

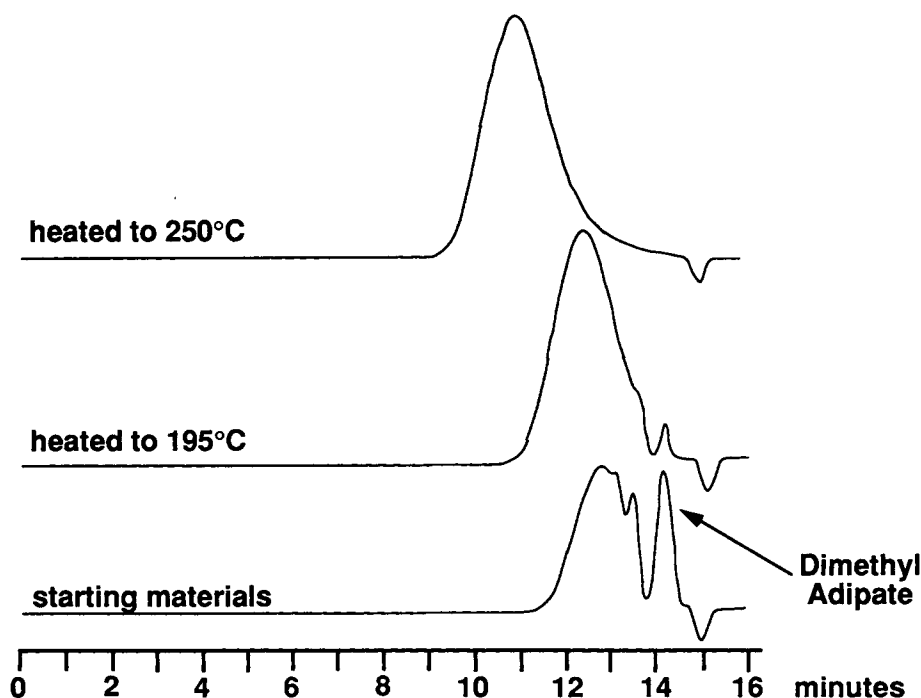


Figure 8 SEC traces for dimethyl adipate-modified poly(ethylene ether carbonate) diols.

removed controls the molecular weight build (Fig. 7). The distillate was predominately DEG (Table VIII); 5.0 wt % of the distillate was dimethyl terephthalate (Table VIII).

The mass balance and product molecular weight data are given in Table VII; the distillate and dry-ice trap compositions are given in Table VIII. The product (X) accounted for 62.0 wt % of the reactants charged, contained terephthalate moieties, and had a number-average molecular weight of 3778 by SEC. The byproduct methanol was present in the dry-ice trap.

^{13}C -NMR structural assignments are given in Table XIII; all expected features are present. Terephthalate acid esters with poly(ethylene glycols) are indicated by the following structural unit (in addition to the consumption of dimethyl terephthalate and the formation of methanol):

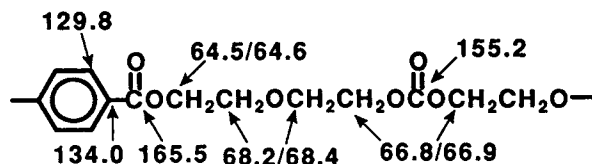


Table XI ^{13}C -NMR Structural Assignments of Dimethyl Adipate-modified Poly(Ethylene Ether Carbonate) Diol

Chemical Shift ^a (ppm)	Structural Assignments
173.3	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ O—
155.2	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ O—
72.5/72.6	—CH ₂ OCH ₂ CH ₂ OH
69.9	—CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ —
68.5/68.6	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
68.2/68.4	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
66.8/66.9	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
63.2/63.3	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
60.4/60.5	—CH ₂ OCH ₂ CH ₂ OH
33.2	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
23.9	—CH ₂ CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —

^a ppm from tetramethylsilane (TMS = 0); DMSO-*d*₆.

Table XII Molecular Weight Advancement Data for Dimethyl Terephthalate-modified Poly(Ethylene Ether Carbonate) Diol

Pot Temp (°C)	Distillate ^a (Wt %)	Distillate Assay (Wt %)					Molecular Weight Data			
		Dioxane	EC	DEG	TriEG	DMT	Peak	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
25	—	—	—	—	—	—	565	455	673	1.48
140	—	—	—	—	—	—	544	441	647	1.47
163	—	—	—	—	—	—	1048	720	1212	1.68
177	8.0	—	8.5	73.6	6.3	9.6	1369	874	1563	1.79
195	12.8	—	3.6	77.6	9.1	7.5	1991	1180	2288	1.94
220	16.5	0.6	1.0	84.8	8.1	2.7	3481	1738	3711	2.14
235	18.4	1.8	0.7	79.9	10.5	1.0	5107	2308	5185	2.25
248	20.4	4.5	1.0	67.9	10.0	1.1	7242	3130	7451	2.38
260	22.0	7.5	1.4	47.9	11.4	1.5	8886	3778	9259	2.45

^a Weight percent of reactants charged present as distillate.

Succinic Anhydride as a Modifier

The use of a cyclic acid anhydride such as succinic anhydride as an ester modifier introduces a series of reactions into the overall process. Cyclic acid anhydrides will ring open by reaction with hydroxyl

moieties to form the corresponding succinate ester acid under mild conditions. This acid will further react with hydroxyl moieties at higher temperatures to give direct esterification products. In addition, transesterification will occur around the carbonate and succinate ester moieties and transesterifica-

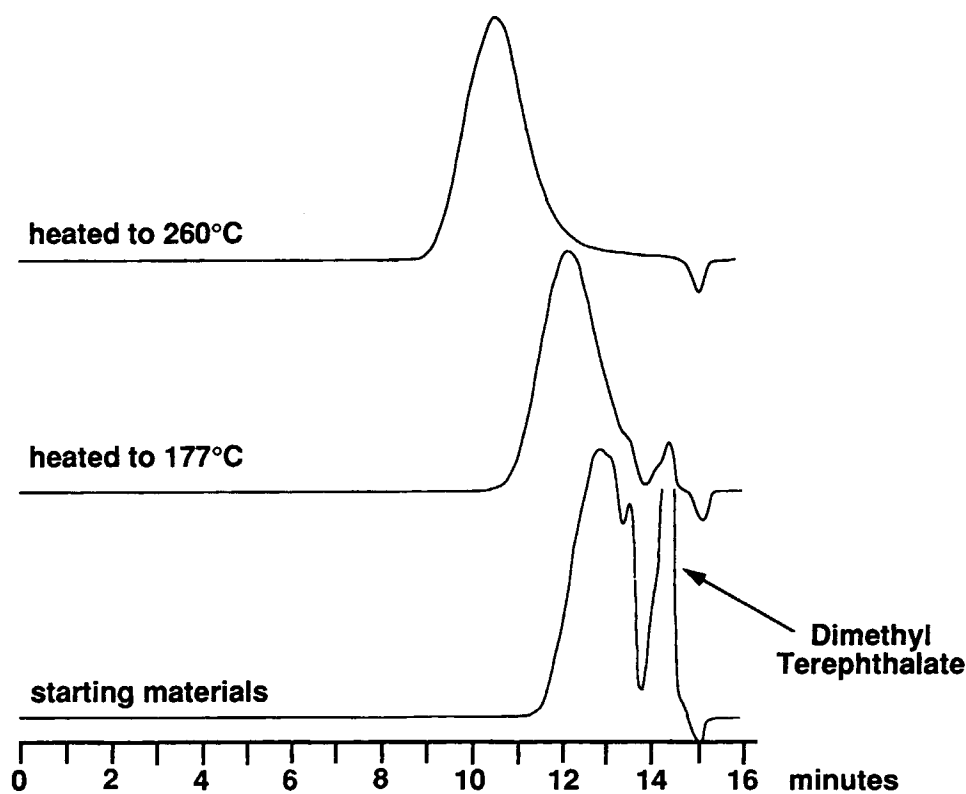


Figure 9 SEC traces for dimethyl terephthalate-modified poly(ethylene ether carbonate) diols.

Table XIII ^{13}C -NMR Structural Assignments of Dimethyl Terephthalate-modified Poly(Ethylene Ether Carbonate) Diol

Chemical Shift ^a (ppm)	Structural Assignments
165.5	— ArC(O)OCH ₂ CH ₂ O —
155.2	— OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ O —
134.0	C1 and C4 aromatic
129.8	C2 and C3 aromatic
72.5/72.6	— CH ₂ OCH ₂ CH ₂ OH
69.9	— CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ —
68.2/68.4	— OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
66.8/66.9	— OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
64.5/64.6	— ArC(O)OCH ₂ CH ₂ O —
60.4/60.5	— CH ₂ OCH ₂ CH ₂ OH

^a ppm from tetramethylsilane (TMS = 0); DMSO-*d*₆.

tion/advancement will occur at higher temperatures as volatile hydroxyl compounds (DEG, TriEG, etc.) are removed as distillate.

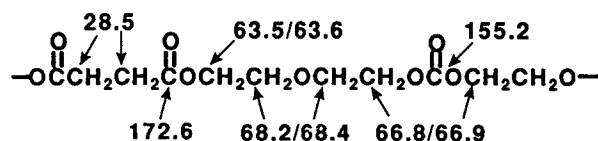
A poly(ethylene ether carbonate) diol (65.4 g, 0.288 eq OH) and succinic anhydride (150.0 g, 0.150 mol) were combined and heated to 264°C at 10 mmHg. No fractionating column was used. The distillate was removed, weighed, and analyzed at various pot temperatures. In addition, samples of the product were removed for molecular weight measurement. The results are listed in Table XIV.

Representative SEC traces for the succinate-modified, molecular weight-advanced poly(ethylene ether carbonate) diol (XI) are given in Figure 10. The succinic anhydride was essentially gone at the 169°C pot temperature sample (by SEC). There was a systematic increase in molecular weight with increasing pot temperature. The number-average molecular weight is plotted vs. pot temperature in Figure 6. The amount of distillate removed controls the

molecular weight build (Fig. 7). The distillate was predominately DEG (Table VIII).

The mass balance and product molecular weight data are given in Table VII; the distillate and dry-ice trap compositions are given in Table VIII. The product (XI) accounted for 82.7 wt % of the reactants charged, contained succinate moieties, and had a number-average molecular weight of 1843 by SEC. The byproduct water was present in the dry-ice trap.

^{13}C -NMR structural assignments are given in Table XV; all expected features are present. Esterification of the succinic anhydride with poly(ethylene glycols) is indicated by the following structure (in addition to the consumption of succinic anhydride and the formation of water):

**Table XIV** Molecular Weight Advancement Data for Succinic Anhydride-modified Poly(Ethylene Ether Carbonate) Diol

Pot Temp (°C)	Distillate ^a (Wt %)	Distillate Assay (Wt %)				Molecular Weight Data			
		MEG	EC	DEG	TriEG	Peak	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
25	—	—	—	—	—	565	455	673	1.48
90	—	—	—	—	—	565	425	657	1.48
169	—	—	—	—	—	714	568	863	1.52
200	2.2	0.4	47.9	48.3	1.6	1026	733	1222	1.67
230	3.2	0.4	13.9	77.5	3.1	1794	1058	2001	1.89
242	4.9	—	5.7	78.6	8.4	2303	1329	2671	2.00
251	5.4	0.4	2.9	78.4	8.2	3273	1583	3391	2.14
264	6.5	—	2.7	73.2	13.2	3701	1843	4086	2.22

^a Weight percent of reactants charged present as distillate.

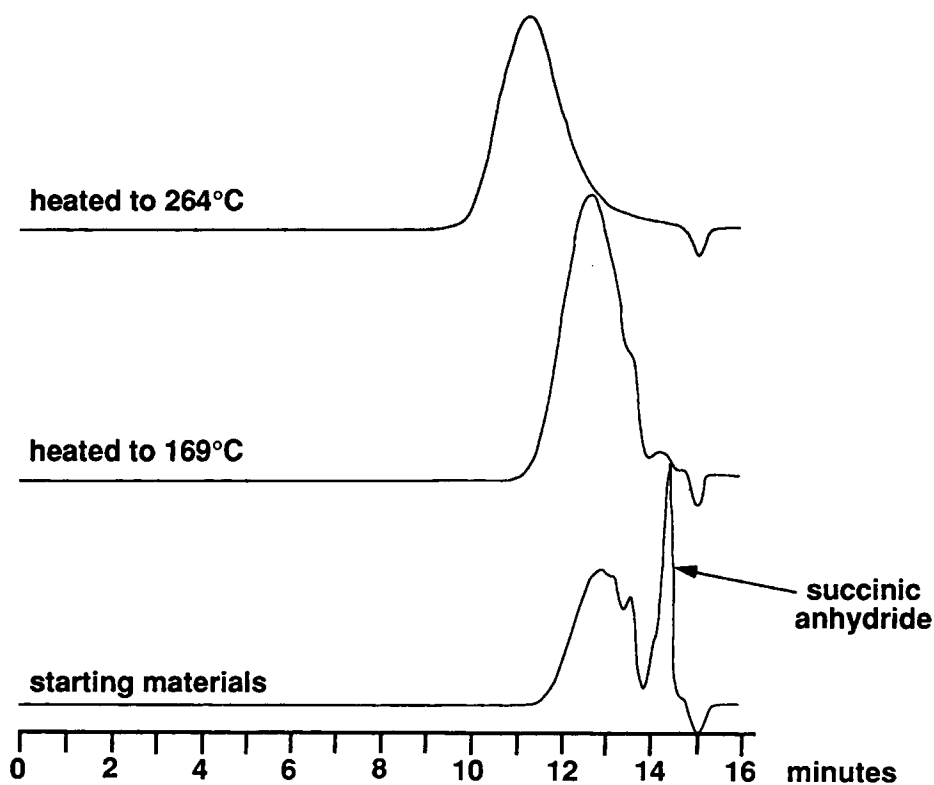


Figure 10 SEC traces for succinic anhydride-modified poly(ethylene ether carbonate) diols.

CONCLUSIONS

Poly(ethylene ether carbonate) polyols can be modified by chemical reactions with polyester polyols, poly(carboxylic acids), poly(carboxylic acid) esters, or poly(carboxylic acid) cyclic anhydrides under conditions of elevated temperatures and reduced pressures to give ester-modified poly(ethylene

ether carbonate) polyols. Polyester polyols and poly(carboxylic acid) ester are incorporated into the polymer backbone by transesterification/advance-ment reactions. Poly(carboxylic acids) and poly(carboxylic acid) cyclic anhydrides first undergo esterification and then transesterification/advance-ment reactions. Molecular weight builds in a predictable manner and can be controlled by the

Table XV ^{13}C -NMR Structural Assignments of Succinic Anhydride-modified Poly(Ethylene Ether Carbonate) Diol

Chemical Shift ^a (ppm)	Structural Assignments
172.6	—OCH ₂ CH ₂ OC(O)CH ₂ CH ₂ C(O)OCH ₂ —
155.2	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ O—
72.5/72.6	—CH ₂ OCH ₂ CH ₂ OH
69.9	—CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ —
68.2/68.4	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
66.8/66.9	—OCH ₂ CH ₂ OC(O)OCH ₂ CH ₂ OCH ₂ —
63.5/63.6	—OC(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —
60.4/60.5	—CH ₂ OCH ₂ CH ₂ OH
28.5	—OC(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₂ OCH ₂ —

^a ppm from tetramethylsilane (TMS = 0); DMSO-*d*₆.

amount of distillate removed. It is important that the modifier have a higher boiling point than that of DEG. Since dimethyl adipate is more volatile than is DEG, it is converted to the adipate ester of poly(ethylene glycols) prior to distillate removal.

The processes have been characterized by following the distillate formation and composition as a function of reactor temperature and product molecular weight build. The products have been characterized by molecular weight and ^{13}C -NMR spectroscopy.

A new family of ester-modified poly(ethylene ether carbonate) polyols has been prepared, most of which were not available with prior technology. The modification procedure permits the control of properties such as modifier type and content, molecular weight, viscosity, T_g , and density in the resultant polyols. These polyols are useful in polyurethane applications, where the degree and type of polyol modification can be used to adjust polyurethane properties.

REFERENCES

1. R. F. Harris, *J. Appl. Polym. Sci.*, **37**, 183 (1989).
2. R. F. Harris and L. A. McDonald, *J. Appl. Polym. Sci.*, **37**, 1491 (1989).
3. R. F. Harris, U.S. Pat. 4,709,069 (1987).
4. R. F. Harris, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.*, **29**(2), 418 (1988).
5. R. F. Harris, *J. Appl. Polym. Sci.*, **38**, 463 (1989).
6. R. F. Harris, *J. Appl. Polym. Sci.*, **40**, 1265 (1990).
7. R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.*, **30**(2), 235 (1989).
8. R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 487 (1990).
9. R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 509 (1990).
10. R. F. Harris, M. D. Joseph, C. Davidson, and C. D. DePorter, *J. Appl. Polym. Sci.*, **42**, 3241 (1991).
11. R. F. Harris, U.S. Pat. 4,861,909 (1989).
12. R. F. Harris, *J. Appl. Polym. Sci.*, **41**, 1937 (1990).
13. R. F. Harris, U.S. Pat. 4,686,273 (1987).
14. R. F. Harris, U.S. Pat. 4,795,810 (1989).
15. R. F. Harris, U.S. Pat. 4,948,862 (1990).
16. R. F. Harris, M. D. Joseph, and C. Davidson, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **33**(2), 132 (1992).
17. R. F. Harris, M. D. Joseph, and C. Davidson, *J. Appl. Polym. Sci.*, **46**, 1843 (1992).
18. R. F. Harris, U.S. Pat. 4,816,529 (1989).
19. R. F. Harris, U.S. Pat. 5,084,528 (1992).
20. M. O. Myers, U.S. Pat. 4,686,276 (1986).
21. D. G. Prior, U.S. Pat. 4,528,364 (1985).
22. C. Delides, R. A. Pethrick, A. V. Cunliffe, and P. G. Klein, *Polymer*, **22**, 1205 (1981).

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