Modification of Poly(Ethylene Ether Carbonate) Polyols by Transesterification

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SYNOPSIS

Poly(ethylene ether carbonate) polyols are the reaction products of alkylene carbonates or alkylene oxides and CO_2 with alcoholic initiators. These polyols can be modified with aliphatic hydroxyl compounds by transesterification reactions. The modifier becomes chemically bound into the polymer during reaction and modifies the properties of the polyol. The extent of reaction is very easy to follow by size exclusion chromatography. Molecular weight is controlled by the molecular weight of the reactants and by their stoichiometry. This transesterification process is compared to the previously described transesterification/advancement process. The transesterification process has the advantage of using milder temperature conditions and runs at ambient pressures. Therefore, modifiers can be used in the transesterification process that are unstable or undergo different chemistry under the reaction conditions of the transesterification/advancement process. Although the modifiers used in the transesterification/advancement process must be less volatile than DEG, more volatile modifiers can be used in the transesterification process. The two processes compliment each other, allowing the preparation of a wide variety of modified poly(ethylene ether carbonate) polyols. These polyols are useful in polyurethane applications.

INTRODUCTION

Poly(ethylene ether carbonate) polyols have been formed by the reactions of ethylene carbonate (EC), dialkyl carbonates, diphenyl carbonate, ethylene oxide and carbon dioxide or phosgene with polyether polyol initiators in the presence of appropriate catalysts. These poly(ethylene ether carbonate) polyols are polymers that contain alternating blocks of carbon dioxide units and poly(ethylene glycol) units in their backbones when polyglycol initiators are employed. When these polyols are prepared from ethylene carbonate (or ethylene oxide and carbon dioxide) and diethylene glycol (DEG) using sodium stannate trihydrate as the catalyst, backbone hydrolysis studies,[1] and ^{13}C nuclear magnetic resonance (NMR) studies[2] have shown that these polyols contain predominantly carbon dioxide units and diethylene glycol units with small quantities of triethylene glycol (TriEG) units and have $-OC(O)OCH_2CH_2OCH_2CH_2OH$ end groups.

When these polyols are heated to elevated temperatures (> 180°C) at reduced pressures under distillation conditions, volatile impurities are removed, followed by molecular weight advancement and formation of DEG.[3-5] 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. Low levels of certain catalysts effectively enhance reaction rates without causing serious product decomposition at these elevated temperatures.[6] These advanced polyols form rapidly with high CO_2 retention, relatively low polydispersity, and high purity.

If a second polyol, having a boiling point greater than the boiling point of DEG, is present in the reaction mixture, it acts as a coreactant and becomes chemically incorporated into the polymer to form a new class of polyols.[7-9] Since poly(ethylene ether

Journal of Applied Polymer Science, Vol. 44, 605–617 (1992)
CCC 0021-8995/92/040605-13$04.00

carbonate) polyols have predominantly polyester polyol properties, modification with polyether polyols can be used to adjust properties.[9] Poly(ethylene ether carbonate) polyols are useful in polyurethane applications.[10-13]

This study extends this work to include the modification of poly(ethylene ether carbonate) polyols by the direct transesterification with polyols under milder conditions.[14] Polyamine and polycarboxylic acid modifiers are also introduced.

EXPERIMENTAL

Adipic acid, 1,4-butanediol, sodium stannate trihydrate, triethylene tetramine, titanium isopropoxide, and *N*-methylbis(2-hydroxyethyl)amine were obtained from Aldrich Chemical Co. Tetraethylene glycol (TetraEG), E-4500 (a polyethylene glycol of 4500 molecular weight), P-425 (a polypropylene glycol of 425 molecular weight), and P-1200 (a polypropylene glycol of 1200 molecular weight) were manufactured by Dow Chemical Co. K-Flex 188-50 (a polyester diol of dodecanedioic acid and 1,4-hydroxymethylcyclohexane) was manufactured by King Industries. Jeffamine D-400 (an aminated polypropylene glycol of 400 molecular weight) was manufactured by Texaco. The molecular weights and distribution were determined by size exclusion chromatography (SEC) on Waters Ultrastyragel 1000-Å and 10,000-Å columns, in series, using tetrahydrofuran (THF) as the mobile phase and calibrated with narrow molecular weight poly(ethylene glycols) using a refractive index detector. The CO_2 content of the poly(ethylene ether carbonate) polyols was measured by quantitative proton NMR using dimethylsulfoxide as the internal standard.

Poly(Ethylene Ether Carbonate) Polyol Synthesis

Poly(ethylene ether carbonate) polyols were prepared from EC and monoethylene glycol (MEG) or DEG using sodium stannate trihydrate (0.5 wt %) as catalyst.[1,2] One poly(propylene ether carbonate) polyol was prepared from propylene carbonate and DEG.[2] A polyol was also prepared from ethylene oxide, CO_2, and MEG.[15] The catalyst was removed from all samples by dissolving the polyol in acetone, stirring with Florisil, filtering, and acetone stripping.[16]

Transesterification Procedure

The poly(ethylene ether carbonate) polyol (catalyst removed), modifier, and catalyst (if used) were weighed into a reactor equipped with overhead stirring, thermometer, condenser, heating control system, and maintained under a nitrogen atmosphere. When titanium isopropoxide was used as catalyst, it was added by syringe to the reactor. The reaction temperature was established and small samples were removed from the reactor at appropriate times, diluted with THF, and analyzed by SEC.

RESULTS AND DISCUSSION

Tetraethylene Glycol (TetraEG) as Modifier

TetraEG was first evaluated as a modifier since it has much better compatibility with poly(ethylene ether carbonate) polyols than poly(propylene glycols). A poly(ethylene ether carbonate) diol (**1**, $\bar{M}_n$ of 2889, 15.85 g) having 29.3 wt % CO_2 and TetraEG (10.04 g) were combined and heated to 175°C (no catalyst). Samples were analyzed by SEC after reaching 175°C (Table I). The TetraEG and **1** are

Table I Transesterification of a Poly(Ethylene Ether Carbonate) Diol with Tetraethylene Glycol at 175°C

		Molecular Weight Data			
Conditions	Titanium Isopropoxide	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	—	6919	2889	4663	1.61
Heated to 175°C	No	228	508	3485	6.86
30 min at 175°C	No	207	519	2687	5.17
15 min at 175°C	Yes	841	517	848	1.64
30 min at 175°C	Yes	841	523	878	1.62
45 min at 175°C	Yes	841	508	838	1.66
60 min at 175°C	Yes	841	523	863	1.65

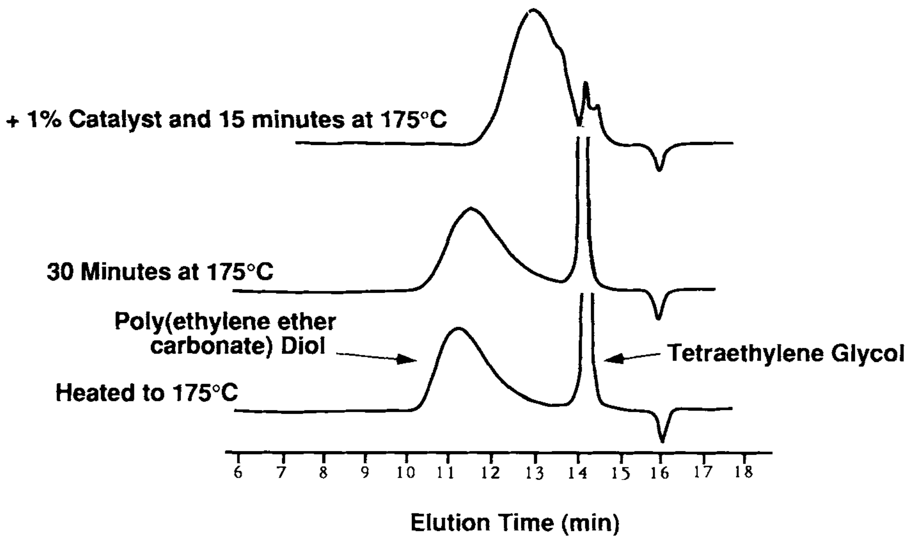

Figure 1 SEC traces of the transesterification of a poly(ethylene ether carbonate) diol with tetraethylene glycol at 175°C.

clearly resolved in the SEC traces (Fig. 1). After 30 min at 175°C, 1.0 wt % titanium isopropoxide was added as catalyst and samples were removed for SEC analysis at 15, 30, 45, and 60 min after catalyst addition. A small amount of reaction had occurred after 30 min at 175°C without catalyst (note shift in $\bar{M}_w$), but reaction was complete in less than 15 min after catalyst addition. No further change occurred in molecular weight as heating was continued.

Transesterification produced a new composition in which the TetraEG was chemically bound into the poly(ethylene ether carbonate) diol backbone and/or as end groups (Fig. 1). The product contained 17.5 wt % CO_2. Dilution effects alone lead to a calculated weight percent CO_2 of 17.9, indicating very little loss of CO_2 content during transesterification. At the same time, the molecular weight of the poly(ethylene ether carbonate) diol was reduced to a molecular weight between that of the two starting materials. The $\bar{M}_n$ should be unaffected by this transesterification, but the process can bring about changes in the molecular weight distribution.[17] A product $\bar{M}_n$ of 542 was calculated based on the mole fraction and $\bar{M}_n$ of the reactants.

Poly(Propylene Glycols) as Modifier

A poly(propylene glycol) (P-425, $\bar{M}_n$ of 429) was evaluated as a modifier since it is immiscible with poly(ethylene ether carbonate) polyols. A poly(ethylene ether carbonate) diol (**1**, $\bar{M}_n$ of 2889, 16.02 g) having 29.3 wt % CO_2 and P-425 (10.19 g) were combined and heated to 175°C (no catalyst). Samples were analyzed by SEC after reaching 175°C (Table II). The P-425 and **1** are clearly resolved in the SEC traces (Fig. 2). After 30 min at 175°C, 1.0

Table II Transesterification of a Poly(Ethylene Ether Carbonate) Diol with Poly(Propylene Glycol) ($\bar{M}_n$ = 425) at 175°C

Conditions	Titanium Isopropoxide	Molecular Weight Data			
		Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	—	6919	2889	4663	1.61
Heated to 175°C	No	394	752	2687	3.57
30 min at 175°C	No	1502	803	1549	1.93
15 min at 175°C	Yes	1151	705	1268	1.80
30 min at 175°C	Yes	1151	728	1261	1.73

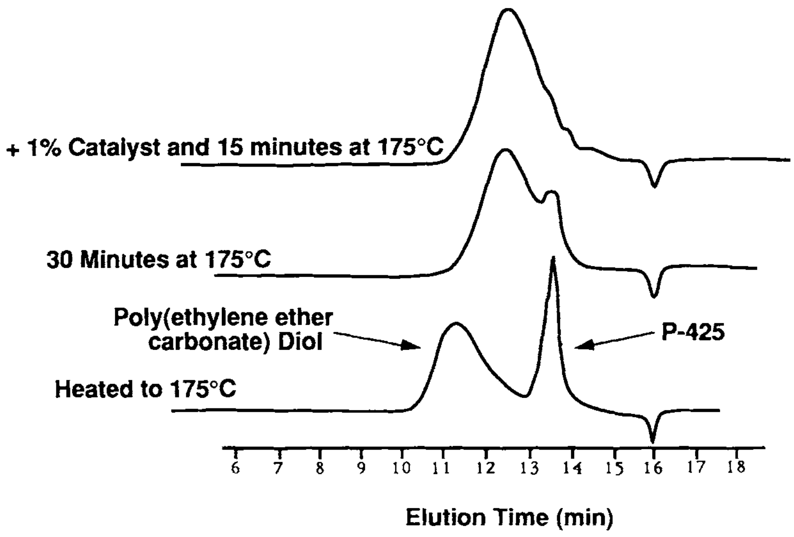

Figure 2 SEC traces of the transesterification of a poly(ethylene ether carbonate) diol with P-425 at 175°C.

wt % titanium isopropoxide was added as catalyst, and samples were removed for SEC analysis at 15 and 30 min after catalyst addition. Appreciable reaction had occurred after 30 min at 175°C without catalyst, but reaction was complete in less than 15 min after catalyst addition. No further change occurred in molecular weight as heating was continued.

The two starting materials were immiscible at ambient temperature and at 175°C. After 30 min at 175°C, the reaction progressed to the point where only one phase was present. The final product is one phase at ambient temperature. The CO_2 content cannot be accurately determined due to the poly(propylene glycol) blocks. However, the lack of gas evolution observed during reaction and the product weight after reaction indicate very little, if any, CO_2 loss.

A probing experiment was run to see if transesterification can occur at a reasonable rate at 135°C. A poly(ethylene ether carbonate) diol (**2**, $\bar{M}_n$ of 2942, 25.0 g, 0.153 mol carbonate) having 26.9 wt % CO_2, P-425 (7.64 g, 0.0382 mol hydroxyl), and sodium stannate trihydrate (0.5 wt %) were combined and heated to 135°C. This mixture (two phases) gives a molar ratio of carbonate in the poly(ethylene ether carbonate) diol to hydroxyl in the P-425 of 4.0 : 1. Samples were taken every 30 min (at 135°C) for 3 h and analyzed by SEC (Table III). Transesterification is complete in about 2 h. The product is a single-phase liquid containing very little free P-425.

Table III Transesterification of a Poly(Ethylene Ether Carbonate) Diol with Poly(Propylene Glycol) ($\bar{M}_n$ = 425) at 135°C Using 0.5 wt % Sodium Stannate Trihydrate as Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	5132	2942	4492	1.53
30 min at 135°C	3697	974	3161	3.25
1.0 h at 135°C	2727	964	2650	2.75
1.5 h at 135°C	2461	960	2390	2.49
2.0 h at 135°C	2221	951	2287	2.41
2.5 h at 135°C	2221	942	2291	2.43
3.0 h at 135°C	2221	958	2287	2.39

Table IV Transesterification of a Poly(Ethylene Ether Carbonate) Diol with Poly(Propylene Glycol) ($\bar{M}_n$ = 1200) at 175°C Using 0.5 wt % Sodium Stannate Trihydrate as Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	5132	2942	4492	1.53
Heated to 175°C	1053	1055	2525	2.39
15 min at 175°C	1151	1099	2551	2.32
45 min at 175°C	2771	1119	2835	2.53
75 min at 175°C	3021	1247	2966	2.38
105 min at 175°C	3021	1160	2969	2.55

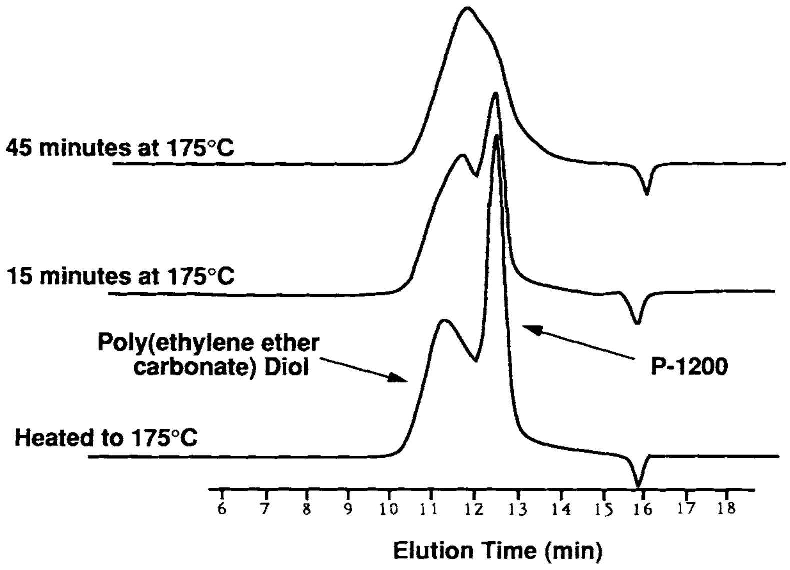

Figure 3 SEC traces of the transesterification of a poly(ethylene ether carbonate) diol with P-1200 at 175°C.

A second probing experiment was run using a higher molecular weight poly(propylene glycol) (P-1200, $\bar{M}_n$ of 1200). A poly(ethylene ether carbonate) diol (**2**, $\bar{M}_n$ of 2942, 16.10 g, 0.099 mol carbonate) having 26.9 wt % CO_2, P-1200 (9.99 g, 0.0167 mol hydroxyl), and sodium stannate trihydrate (0.5 wt %) were combined and heated to 175°C. This mixture (two phases) gives a molar ratio of carbonate in the poly(ethylene ether carbonate) diol to hydroxyl in the P-1200 of 5.9 : 1. Samples were taken at selected times and analyzed by SEC (Table IV and Fig. 3). Transesterification is complete in about 75 min. The product is a single-phase liquid containing very little free P-1200. The majority of the P-1200 was chemically incorporated into the oligomeric product.

1,4-Butanediol as Modifier

A poly(ethylene ether carbonate) diol (**4**, $\bar{M}_n$ of 3103, 423.3 g) and 1,4-butanediol (47.03 g) were combined (miscible) and heated to 175°C (no catalyst). Samples were analyzed by SEC (Table V). Reaction is complete on reaching 175°C. Reaction rates are rapid even in the absence of a catalyst when the two reactants are miscible. The product is a straw-colored viscous liquid containing 10.0 wt % 1,4-butanediol chemically incorporated into the oligomeric product. The Brookfield viscosity at 24°C is 2350 Hz.

High Molecular Weight Poly(Ethylene Glycol) as Modifier

A probing study was made to explore the transesterification when the poly(ethylene ether carbonate) diol and the modifier have comparable molecular weights. A poly(ethylene ether carbonate) diol (**2**, $\bar{M}_n$ of 2942, 3.64 g, 0.00611 mol carbonate) having 26.9 wt % CO_2, a poly(ethylene glycol) (E-4500, $\bar{M}_n$ of 4500, 25.00 g, 0.0111 mol hydroxyl), and sodium stannate trihydrate (0.5 wt %) were combined and heated to 175°C. This mixture (two phases) gives a molar ratio of carbonate in the poly(ethylene ether carbonate) diol to hydroxyl in the E-4500 of 2.0 : 1. Samples were taken at selected times and analyzed by SEC (Table VI). After equilibrium was estab-

Table V Transesterification of a Poly(Ethylene Ether Carbonate) Diol with 1,4-Butanediol; No Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	6285	3103	6715	2.16
Heated to 175°C	1397	936	1653	1.77
30 min at 175°C	1375	915	1563	1.71
60 min at 175°C	1397	925	1576	1.71

Table VI Transesterification of a Poly(Ethylene Ether Carbonate) Diol with Poly(Ethylene Glycol) ($\bar{M}_n$ = 4500) at 175°C Using 0.5 wt % Sodium Stannate Trihydrate as Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Carbonate–Hydroxyl Ratio = 2				
Starting diol	5132	2942	4492	1.53
Heated to 175°C	[a]	2684	4033	1.50
15 min at 175°C	[a]	3040	4935	1.63
30 min at 175°C	[a]	3574	5787	1.62
60 min at 175°C	[a]	3183	6673	2.13
90 min at 175°C	[a]	2699	6618	2.45
Carbonate–Hydroxyl Ratio = 4				
Heated to 175°C	[a]	2283	6728	2.95
15 min at 175°C	[a]	1973	6419	3.25
30 min at 175°C	[a]	2335	6607	2.83
60 min at 175°C	[a]	2300	6164	2.68
90 min at 175°C	[a]	2300	6299	2.74
Carbonate–Hydroxyl Ratio = 8				
Heated to 175°C	[a]	2010	6227	3.10
15 min at 175°C	[a]	1807	5971	3.30
30 min at 175°C	[a]	1870	5983	3.20
60 min at 175°C	[a]	1651	6052	3.67
Carbonate–Hydroxyl Ratio = 16				
Heated to 175°C	[a]	1596	5433	3.40
15 min at 175°C	[a]	1383	5111	3.70
30 min at 175°C	[a]	1428	5113	3.58
60 min at 175°C	[a]	1399	5029	3.60
90 min at 175°C	[a]	1444	5223	3.62

[a] Peak molecular weight is meaningless due to number of peaks.

lished, additional poly(ethylene ether carbonate) diol (3.64 g) was added to adjust the carbonate–hydroxyl molar ratio to what would have been 4.0 : 1 at the start of the reaction. This was continued, to adjust the initial carbonate–hydroxyl molar ratio to 8.0 : 1 (7.28 g) and 16.0 : 1 (14.56 g), respectively. Equilibrium was established after each addition. SEC results are tabulated in Table VI; the final SEC trace at each molar ratio are given in Figure 4.

Three distinct molecular weight bands are evident, and each increases with increasing carbonate–hydroxyl molar ratio (Fig. 4). Band 1 (239–2727 peak molecular weight) cannot contain any E-4500 (molecular weight too low) and must come from the lower molecular weight portion of the poly(ethylene ether carbonate) diol after equilibrium. Band 2 (6030–7963 peak molecular weight) can contain only one E-4500 unit per molecule, while band 3 (12,224–13,235 peak molecular weight) can contain two E-4500 units per molecule. Some higher molecular weight materials are also present (unresolved) at the high end of the distribution. It is apparent that as the modifier molecular weight increases, a polynodal molecular weight distribution is obtained after transesterification.

Polyester Polyol as Modifier

One polyester polyol was evaluated as a modifier with a poly(ethylene ether carbonate) diol to see if it underwent similar transesterification chemistry when heated under the same conditions as polyether polyols. A poly(ethylene ether carbonate) diol (**2**, $\bar{M}_n$ of 2942, 16.02 g, 0.099 mol carbonate) having 26.9 wt % CO_2, a polyester diol (K-Flex 188-50, $\bar{M}_n$ of 442, 9.94 g, 0.045 mol hydroxyl), and sodium stannate trihydrate (0.5 wt %) were combined and heated to 175°C. This mixture (two phases) gives a molar ratio of carbonate in the poly(ethylene ether carbonate) diol to hydroxyl in the K-Flex 188-50 of 2.2 : 1. Samples were taken at selected times and analyzed by SEC (Table VII). Selected SEC traces are given in Figure 5. Transesterification is complete within 15 min. The product is a single-phase liquid material containing very little free K-Flex 188-50. The majority of the polyester polyol was chemically incorporated into the oligomeric product.

Table VII Transesterification of a Poly(Ethylene Ether Carbonate) Diol with a Polyester Polyol (K-Flex 188-50) at 175°C Using 0.5 wt % Sodium Stannate Trihydrate as Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	5132	2942	4492	1.53
K-Flex 188-50	360	464	592	1.28
Heated to 110°C	394	716	2273	3.17
Heated to 175°C	1502	797	1746	2.19
15 min at 175°C	1791	787	1811	2.30
30 min at 175°C	1641	745	1706	2.29
75 min at 175°C	1640	847	1750	2.07

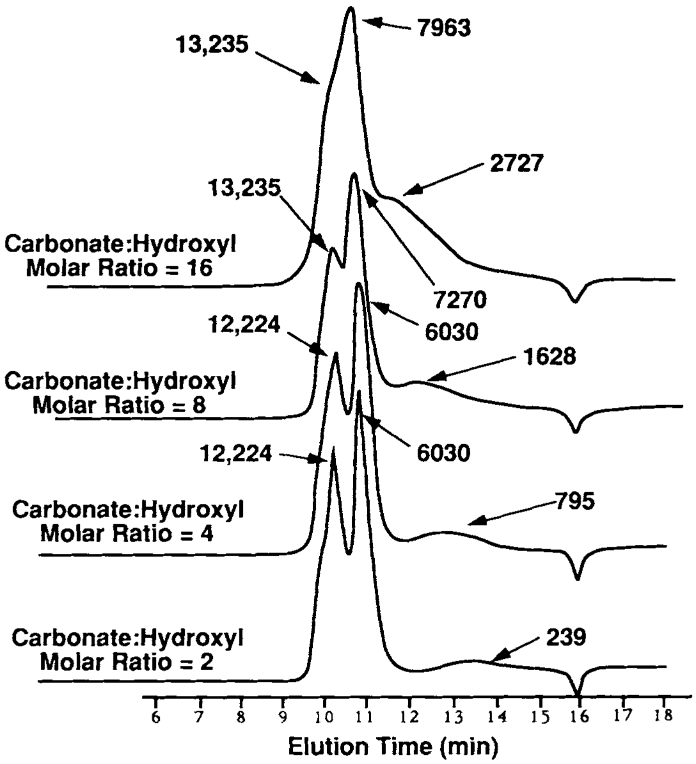

Figure 4 SEC traces of the transesterification of a poly(ethylene ether carbonate) diol with E-4500 at 175°C and various reactant ratios.

Poly(Propylene Ether Carbonate) Polyols as Modifiers

A poly(propylene ether carbonate) diol was evaluated as a modifier for a poly(ethylene ether carbonate) diol to form a hybrid system. A poly(ethylene ether carbonate) diol (**1**, $\bar{M}_n$ of 2889, 15.71 g), a poly(propylene ether carbonate) diol (based on a 10 : 1 molar ratio of propylene carbonate–diethylene glycol, $\bar{M}_n$ of 383, 10.0 g), and sodium stannate tri-

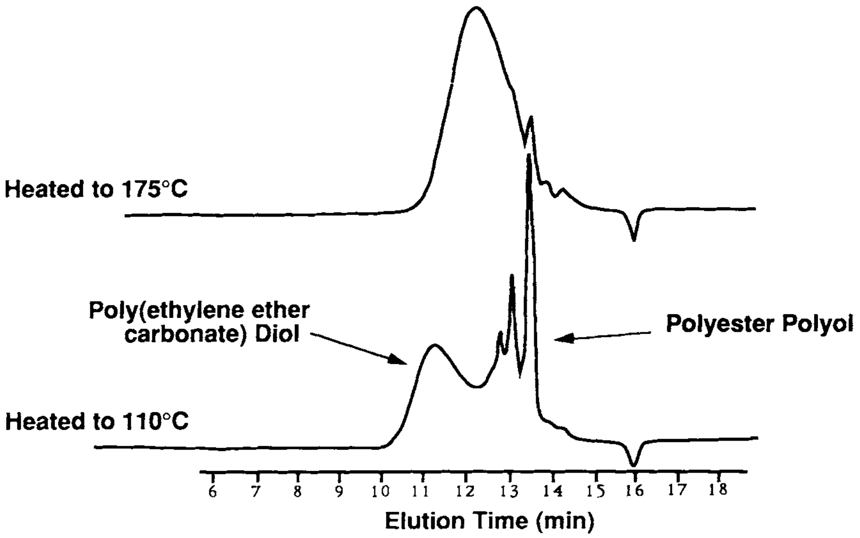

Figure 5 SEC traces of the transesterification of a poly(ethylene ether carbonate) diol with a polyester polyol at 175°C.

Table VIII Transesterification of a Poly(Ethylene Ether Carbonate) Diol with a Poly(Propylene Ether Carbonate) Diol ($\bar{M}_n$ = 383) at 175°C Using 0.5 wt % Sodium Stannate Trihydrate as Catalyst

Conditions	Molecular Weight Data			
	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	6219	2889	4663	1.61
Starting modifier	417	383	1479	3.91
Heated to 100°C	5035	673	3023	4.49
Heated to 175°C	1641	637	1419	2.23
15 min at 175°C	1151	594	1199	2.02
30 min at 175°C	1258	641	1416	2.21
45 min at 175°C	1258	655	1283	1.96

Table IX Transesterification of a Poly(Ethylene Ether Carbonate) Diol with a Poly(Ethylene Ether Carbonate) Polyol ($\bar{M}_n$ = 353) at 175°C Using 0.5 wt % Sodium Stannate Trihydrate as Catalyst

Conditions	Molecular Weight Data			
	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	5132	2942	4492	1.53
Starting modifier	375	354	641	1.81
Ambient temperature	4628	550	2573	4.67
Heated to 175°C	1151	557	1326	2.43
15 min at 175°C	1053	566	1313	2.32
30 min at 175°C	1053	586	1332	2.27

hydrate (0.5 wt %) were combined and heated to 175°C. Samples were analyzed by SEC at selected times (Table VIII); selected traces are given in Figure 6. Transesterification is essentially complete in 15 min to form a new poly(alkylene ether carbonate) diol containing the elements of the two reactants.

Other Poly(Ethylene Ether Carbonate) Polyols as Modifiers

A poly(ethylene ether carbonate) diol (**2**, $\bar{M}_n$ of 2942, 16.10 g), a poly(ethylene ether carbonate) polyol (based on the glycerine-initiated reaction of ethylene oxide with carbon dioxide,[15] $\bar{M}_n$ of 354, 9.99 g), and sodium stannate trihydrate (0.5 wt %) were combined and heated to 175°C. Samples were analyzed by SEC (Table IX); selected SEC traces are given in Figure 7. Transesterification is complete in less than 15 min to form a new poly(ethylene ether carbonate) polyol containing the elements of the two reactants.

Aminated Poly(Propylene Glycols) as Modifier

A probing experiment was run to see if transesterification-type reactions can occur using diamines as modifier. In this case some of the carbonate moieties in a poly(ethylene ether carbonate) polyol would be converted to urethane and/or urea moieties. A poly(ethylene ether carbonate) diol (**3**, $\bar{M}_n$ of 1070, 21.28 g, 0.133 mol carbonate), Jeffamine D-400 (an aminated polypropylene glycol manufactured by Texaco, $\bar{M}_n$ of 400, 13.34 g, 0.0667 mol amine), and

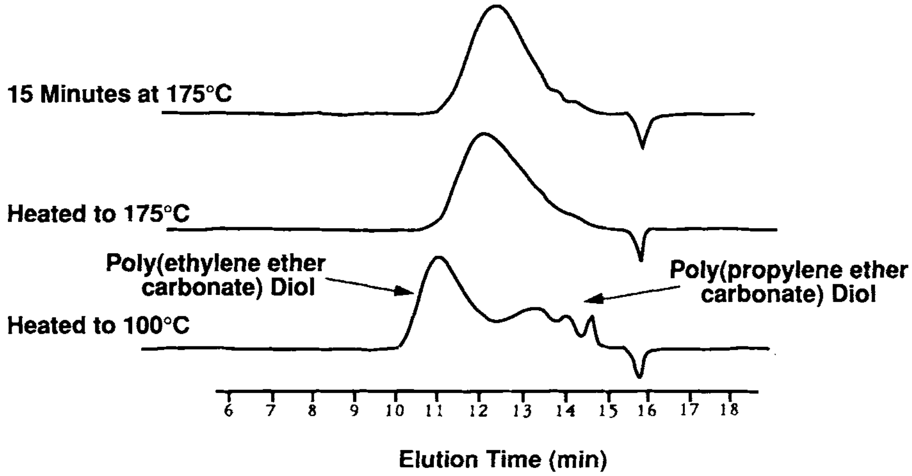

Figure 6 SEC traces of the transesterification of a poly(ethylene ether carbonate) diol with a propylene carbonate based poly(propylene ether carbonate) diol at 175°C.

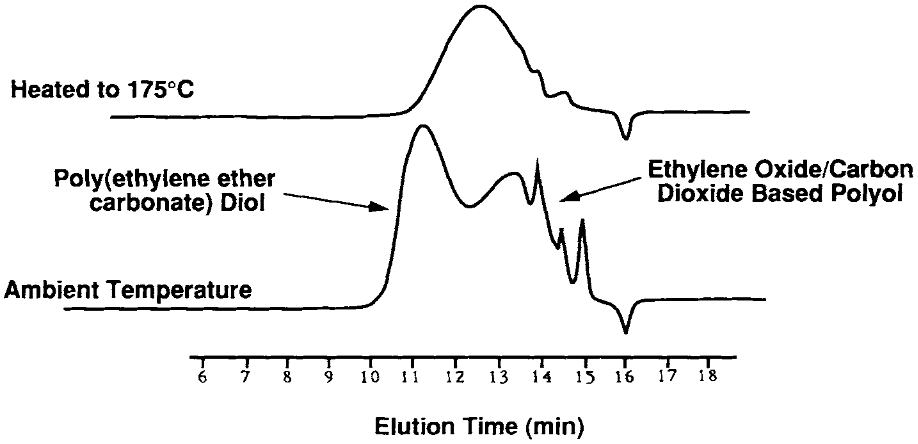

Figure 7 SEC traces of the transesterification of a poly(ethylene ether carbonate) diol with an ethylene oxide/carbon dioxide based poly(ethylene ether carbonate) polyol at 175°C.

sodium stannate trihydrate (1.0 wt %) were combined and heated to 175°C. This mixture (two phases) gives a carbonate–amine molar ratio of 2.0 : 1. Samples were analyzed by SEC (Table X); the SEC traces are given in Figure 8. The product is a single-phase liquid material containing very little free Jeffamine D-400 and contains 12.8 wt % CO_2 by NMR analysis. This represents a 76% CO_2 retention after reaction under the conditions employed. This experiment shows that a polyamine can function as the modifier and become chemically incorporated into the oligomeric product.

Triethylene Tetramine as Modifier

A poly(ethylene ether carbonate) diol (**2**, $\bar{M}_n$ of 2942, 25.92 g, 0.159 mol carbonate), triethylene tetramine (2.90 g, 0.0397 mol primary amine), and sodium stannate trihydrate (1.0 wt %) were combined and heated to 175°C. This mixture gives a carbonate–amine molar ratio of 4.0 : 1. Samples were analyzed by SEC (Table XI). Reaction is complete between 30 and 60 min at 175°C. The product is a single-phase liquid material containing very little free triethylene tetramine and containing 19.8% CO_2 by NMR analysis. This represents an 83% CO_2 retention after reaction under the conditions employed.

Hydroxyl-Functional Tertiary Amines as Modifier

A series of probing experiments were run to study the transesterification of poly(ethylene ether carbonate) polyols with hydroxyl-functional tertiary amines. *N*-Methylbis(2-hydroxyethyl)amine was chosen as a model compound. A poly(ethylene ether carbonate) diol (**2**, $\bar{M}_n$ of 2942, 27.88 g, 0.171 mol carbonate), *N*-methylbis(2-hydroxyethyl)amine (2.54 g, 0.0427 mol amine), and sodium stannate trihydrate (1.0 wt %) were combined and heated to 175°C. This mixture gives a carbonate–hydroxyl molar ratio of 4.0 : 1. Samples were analyzed by SEC after heating to 175°C and after 30 min at 175°C (Table XII). Gas was evolved during the reaction and the product was dark brown. Conditions were too severe; backbone degradation had occurred.

The same poly(ethylene ether carbonate) diol and *N*-methylbis(2-hydroxyethyl)amine (carbonate–hydroxyl molar ratio = 4.0 : 1; no catalyst) were

Table X Reaction of a Poly(Ethylene Ether Carbonate) Diol with an Aminated Poly(Propylene Glyol) ($\bar{M}_n$ = 400[a]) at 175°C Using 1.0 wt % Sodium Stannate Trihydrate as Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	4086	1071	3623	3.38
Starting modifier	307	257	613	2.39
Heated to 175°C	3343	589	2376	4.03
30 min at 175°C	368	521	1208	2.32
60 min at 175°C	368	442	832	1.88
90 min at 175°C	795	495	875	1.77

[a] By acid titration.

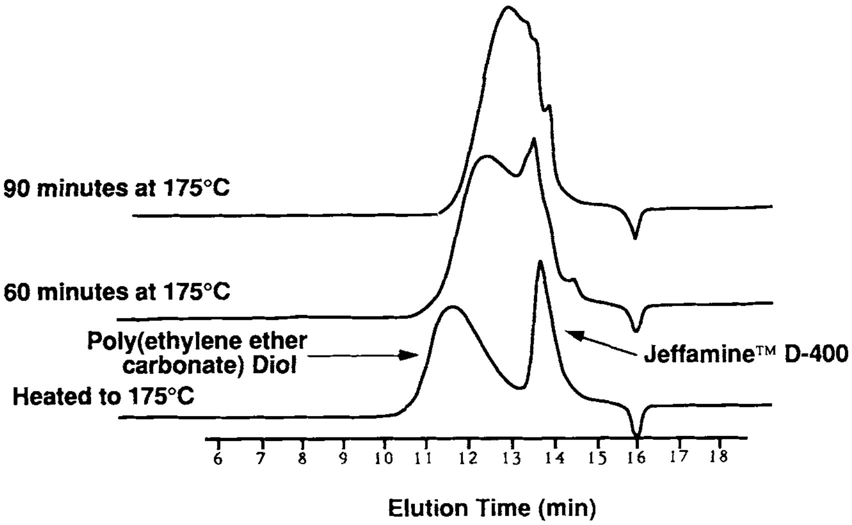

Figure 8 SEC traces of the reaction of a poly(ethylene ether carbonate) diol with Jeffamine D-400 at 175°C.

combined and heated to 135°C. Samples were analyzed by SEC at selected times (Table XII). Some degradation had occurred, but it was much less severe than in the previous experiment.

A third experiment was carried out using the same poly(ethylene ether carbonate) diol and *N*-methylbis(2-hydroxyethyl)amine (carbonate–hydroxyl molar ratio = 4.0 : 1; no catalyst) at 80°C. Samples were analyzed by SEC at selected times (Table XII). Reaction appears to be complete in about 4 h and the product is pale yellow.

The number average molecular weight versus time for each of the three reactions of a poly(ethylene ether carbonate) diol with *N*-methylbis(2-hydroxyethyl)amine is plotted in Figure 9. Clearly the final molecular weight of each system is different. The

Table XI Reaction of a Poly(Ethylene Ether Carbonate) Diol with Triethylene Tetramine at 175°C Using 1.0 wt % Sodium Stannate Trihydrate as Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	5132	2964	4492	1.53
Heated to 175°C	1729	772	1750	2.27
30 min at 175°C	981	517	1127	2.18
60 min at 175°C	877	473	980	2.07
90 min at 175°C	877	452	914	2.02

Table XII Transesterification of a Poly(Ethylene Ether Carbonate) Diol with *N*-Methylbis(2-hydroxyethyl)amine under Various Conditions

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
175°C; 1.0 wt % Sodium Stannate Trihydrate				
Starting diol	5132	2942	4492	1.53
Heated to 175°C	1377	678	1395	2.06
30 min at 175°C	1098	578	1125	1.95
135°C; No Catalyst				
Heated to 135°C	2431	795	2363	2.97
30 min at 135°C	1543	738	1672	2.26
1 h at 135°C	1543	726	1593	2.20
2 h at 135°C	1377	686	1475	2.15
3 h at 135°C	1377	671	1430	2.13
80°C; No Catalyst				
Heated to 80°C	3800	861	3682	4.27
30 min at 80°C	3403	818	2980	3.64
1 h at 80°C	2721	817	2495	3.05
1.5 h at 80°C	2431	823	2261	2.75
2 h at 80°C	1938	772	1974	2.56
3 h at 80°C	1938	790	1874	2.37
4 h at 80°C	1729	773	1977	2.56
5 h at 80°C	1729	776	1735	2.24
7 h at 80°C	1729	785	1788	2.28

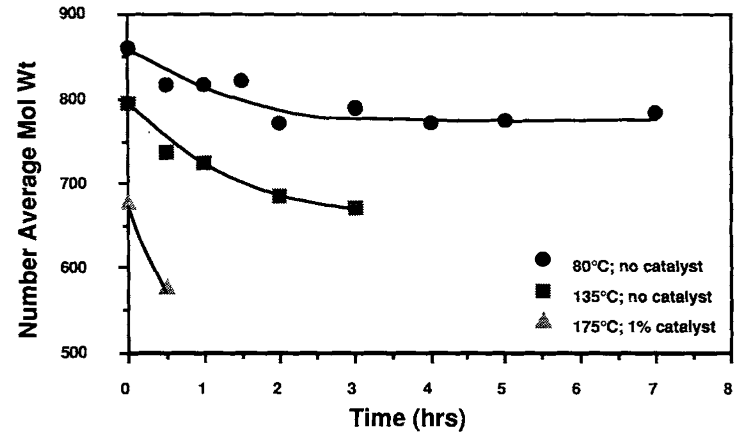

Figure 9 Transesterification of a poly(ethylene ether carbonate) diol with *N*-methylbis(2-hydroxyethyl)amine.

lower molecular weight with more severe conditions is a consequence of more degradation of the polymer backbone and leads to a more highly colored product. The tertiary amine center acts as its own catalyst and a more favorable product is obtained after 4 h at 80°C without any added catalyst. However, some degradation is still occurring under these conditions (calculated $\bar{M}_n = 988$).

Adipic Acid as Modifier

A probing experiment was run using adipic acid to see if transesterification-like reactions can occur with polycarboxylic acids as modifiers. A poly(ethylene ether carbonate) diol (**2,** $\bar{M}_n$ of 2942, 24.30 g, 0.149 mol carbonate), adipic acid (4.00 g, 0.0548 mol carboxylic acid), and sodium stannate trihydrate (1.0 wt %) were combined and heated to 175°C. This mixture gives a carbonate–carboxylic acid molar ratio of 2.7 : 1. Samples were analyzed by SEC (Table XIII); selected SEC traces are given in Figure 10. Reaction is complete between 2.0 and 2.5 h at 175°C. The majority of the adipic acid was chemically incorporated into the oligomeric product.

Table XIII Reaction of a Poly(Ethylene Ether Carbonate) Diol with Adipic Acid at 175°C Using 1.0 wt % Sodium Stannate Trihydrate as Catalyst

	Molecular Weight Data			
Conditions	Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Starting diol	5132	2942	4492	1.53
Heated to 175°C	182	796	3985	5.18
30 min at 175°C	4723	917	3721	4.06
1.0 h at 175°C	3800	976	3358	3.44
1.5 h at 175°C	3403	1028	3115	3.03
2.0 h at 175°C	3044	1011	2785	2.76
2.5 h at 175°C	2721	1002	2796	2.79
3.0 h at 175°C	2721	1002	2691	2.63
3.5 h at 175°C	2721	1040	2629	2.58
4.0 h at 175°C	2721	960	2496	2.60

Process Alternatives for Preparing Modified Poly(Ethylene Ether Carbonate) Polyols

Previous work has shown that when poly(ethylene ether carbonate) polyols are heated to elevated temperatures (> 180°C) at reduced pressures under distillation conditions, volatile impurities are removed, followed by molecular weight advancement and formation of DEG (transesterification/advancement process).[3-5] In this process molecular weight is controlled by DEG removal. If a modifier, having a boiling point greater than the boiling point of DEG, is present in the reaction mixture, it acts as a coreactant and becomes chemically incorporated into the polymer to form a modified poly(ethylene ether carbonate) polyol.[7-9]

The transesterification process described in this study is an alternative process to prepare modified poly(ethylene ether carbonate) polyols and compliments the transesterification/advancement process. The transesterification process has the advantage of using milder temperature conditions and runs

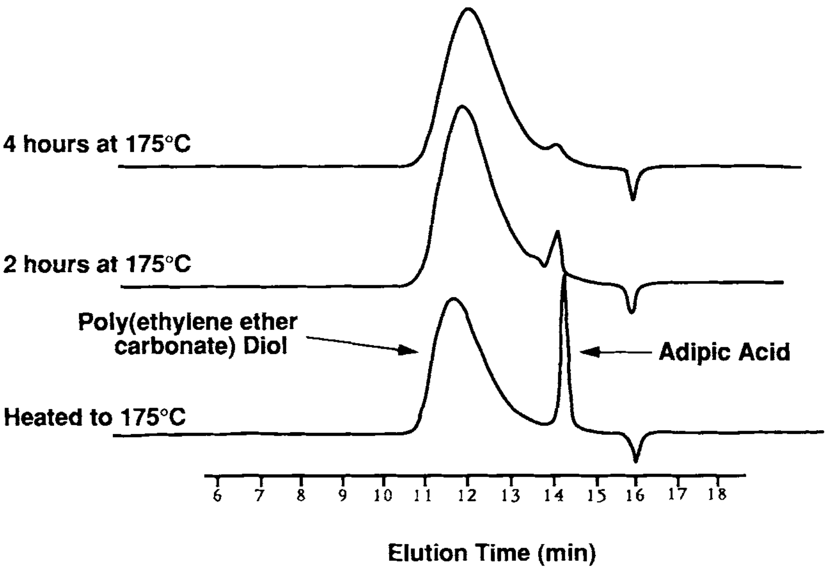

Figure 10 SEC traces of the reaction of a poly(ethylene ether carbonate) diol with adipic acid at 175°C.

at ambient pressures. Therefore, modifiers can be used in the transesterification process that are unstable or undergo different chemistry under the reaction conditions of the transesterification/advancement process. Although the modifiers used in the transesterification/advancement process must be less volatile than DEG, more volatile modifiers can be used in the transesterification process. The transesterification process is also a good way to fine tune molecular weight.

The transesterification/advancement process has the advantage of requiring only relatively low molecular weight poly(ethylene ether carbonate) polyol starting materials. No catalyst is required. Molecular weight is controlled by the advancement process, allowing the preparation of a wide variety of modified poly(ethylene ether carbonate) polyols that are independent of the molecular weight of the reactants. Both processes are rapid and can proceed with high CO_2 retention.

In practice, the fact that the transesterification/advancement process can use low molecular weight feed and make a wide variety of modified poly(ethylene ether carbonate) polyols, which are independent of the molecular weight of the reactants, makes it the method of choice when thermally stable, high-boiling modifiers are used. The transesterification process offers a viable option with more volatile and/or less stable modifiers.

CONCLUSIONS

Poly(ethylene ether carbonate) polyols can be modified with aliphatic hydroxyl compounds, amines, and carboxylic acids by transesterification-like reactions. The modifier becomes chemically bound into the polymer during reaction, and only low levels (or none) of the modifier remains unreacted when the transesterification equilibrium has been established. The extent of reaction is very easy to follow by size exclusion chromatography when the starting poly(ethylene ether carbonate) polyol and modifier are chosen to be well resolved under SEC conditions. In most of the cases studied, the poly(ethylene ether carbonate) polyol and the modifier were not compatible. However, the modified poly(ethylene ether carbonate) polyol products were single-phase viscous liquids.

The transesterification reaction is thought to involve the reaction of a carbonate moiety on the poly(ethylene ether carbonate) polyol with an active hydrogen moiety on the modifier. The modifier moieties retain their molecular weight during transesterification. However, the poly(ethylene ether carbonate) moieties undergo fragmentation around the carbonate centers. The carbonate–modifier molar ratio is important in reaction control. The CO_2 content of the poly(ethylene ether carbonate) polyol, its molecular weight, and the molecular weight of the modifier are important variables. Three possibilities can exist:

1. The poly(ethylene ether carbonate) polyol molecular weight is large and the modifier molecular weight is small.
2. The poly(ethylene ether carbonate) polyol and the modifier have about the same molecular weight.
3. The poly(ethylene ether carbonate) polyol molecular weight is small and the modifier molecular weight is large.

Most examples of transesterification studied in this work were of type 1. In this case a high molecular weight poly(ethylene ether carbonate) polyol and a low molecular weight modifier equilibrate to form a modified poly(ethylene ether carbonate) polyol with an intermediate molecular weight. In the case where polyglycol E-4500 was used as modifier, the poly(ethylene ether carbonate) polyol and the modifier had very similar molecular weights (type 2). Under these circumstances the modified poly(ethylene ether carbonate) polyol had a polynodal molecular weight distribution. Type 3 transesterifications are of limited value due to the relatively low CO_2 levels available for reaction.

This transesterification process for preparing modified poly(ethylene ether carbonate) polyols is complimentary to the previously described transesterification/advancement process.

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Received January 23, 1991
Accepted April 17, 1991