Formation of Poly(ethylene ether carbonate) Diols: Proposed Mechanism and Kinetic Analysis

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ABSTRACT: The ring-opening polymerization of ethylene carbonate (EC), using organotin-based catalysts such as dibutyltin diacetate, dibutyltin dilaurate, and dibutyltin dimethoxide as well as the inorganic catalyst sodium stannate trihydrate, was investigated. The soluble organotin catalysts at 2 mol % concentration produced an ultimate conversion which leveled to about 80% after 72 h. The use of dibutyltin diacetate and dibutyltin dilaurate resulted in the formation of an insoluble byproduct which was removed by column chromatography. The heterogenous sodium stannate trihydrate catalyst yielded higher polymerization rates and ultimate conversions >90%. Since alcohols act as initiators in EC polymerization, molecular weights higher than $\bar{M}_n$ = 4600 were not attained due to the adventitious presence of ethylene glycol (MEG) in the monomer, at a prevailing concentration, $[MEG]_{in\ situ}$. Ethylene carbonate polymerization using glycols as initiators and sodium stannate trihydrate as catalyst was proposed to proceed by a mixed mechanism, consisting of ring-opening steps in which carbonyl and alkylene attack are competitive and transcarbonation steps which are responsible for the steady-state concentrations of oligo(ethylene glycol) condensates. The latter, principally ethylene and bis(ethylene glycol), due to their high boiling points remain in equilibrium with the polymer product throughout the polymerization. A kinetic interpretation of the mechanism was developed and analyzed. The polymerization was found to be first order in [EC], and a pseudo rate constant of polymerization was extracted from the kinetic analysis and found to be 1.8 × 10⁻⁴ M⁻¹ s⁻¹ at 165 °C. The prevailing level of adventitious ethylene glycol in the monomer was found to be 0.12 M.

Introduction

The use of CO_2 as a comonomer in polymer synthesis is highly desirable from the standpoint of economy and ecology. There are generally two modes of CO_2 incorporation, either the direct copolymerization of cyclic ethers with CO_2 (1) or the ring-opening polymerization (2) of a
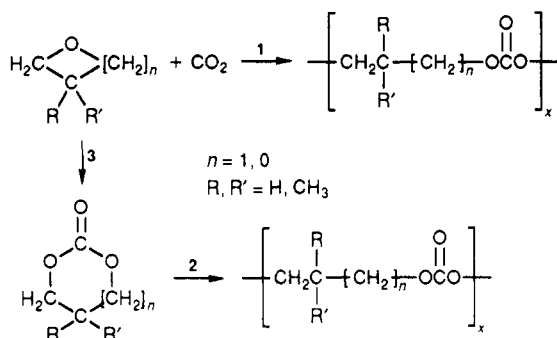

cyclic carbonate which contains the desired polycarbonate backbone structure. The latter route still represents a direct utilization of CO_2 since the cyclic carbonate is generally also produced by the reaction of a cyclic ether with CO_2 (3).[1,2]

Inoue et al. first reported the synthesis of high molecular weight poly(propylene carbonate) by the alternating copolymerization of propylene oxide and carbon dioxide.[3,4] Since then the copolymerization of cyclic ethers and CO_2 has been reported quite extensively.[5] The applicability of the reaction is quite extensive as carbon dioxide undergoes copolymerization with unsubstituted oxirane ($n = 0$) and oxetane ($n = 1$) as well as their mono- and disubstituted analogues. The mechanism for the alternating copolymerization catalyzed by dialkylzinc systems has been proposed to be of a coordinated anionic nature,[6] with propagation occurring by monomer insertion between

the polymer chain end and a catalyst fragment. In specific cases the catalyst fragment remains attached to the polymer chain after polymer work-up procedures.[7] The recent discovery of *immortal* polymerization has expanded the utility of CO_2 as a comonomer since well-defined copolymers are now possible.[8]

The ring-opening polymerization of six-membered cyclic carbonates is well-known to produce copolymers comprised of repeat units which are identical to those which would have derived from the perfectly alternating copolymerization of the corresponding cyclic ether and CO_2.[9–12] Decarboxylation is not observed unless aromatic rings are fused to the six-membered ring.[13] Although the polymerizations of six-membered ring cyclic carbonates are relatively uncomplicated, the polymerizations of five-membered cyclic carbonates are not.
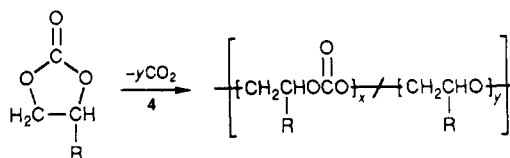
The ring-opening polymerization of propylene carbonate (4, where R = CH_3) has been reported to lead to loss of CO_2 during the course of the reaction to produce a copolymer comprised of propylene oxide and propylene carbonate repeat units.[14] The ring-opening polymerization of ethylene carbonate (4, where R = H) using appropriate catalysts also proceeds with partial decarboxylation, resulting in the formation of a copolymer comprised of ethylene oxide and ethylene carbonate repeat units, poly(ethylene ether carbonate) (PEEC). The synthesis of PEEC has been reported by several workers.[15–33] The presence of labile carbonate linkages in PEEC allows for its facile backbone hydrolysis, and the composition of the degradation products can be utilized to deduce the structural composition of the polymer. Soga et al.[23] and Vogdanis et al.[29] have employed this technique and

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examined the residues by gas chromatography (GC) and gel permeation chromatography (GPC), respectively. Soga et al. found that when Al(acac)$_3$ and Ti(OBu)$_4$ were used as catalysts, the sole hydrolysis product was diethylene glycol. This implies that the structure of PEEC is mostly an alternating copolymer of ethylene carbonate and ethylene oxide, resulting from the evolution of carbon dioxide from every other repeat unit. They proposed a mechanism in which 1,4,6,9-tetraoxaspiro[4.4]nonane (TON) is an intermediate for ethylene carbonate and 2,7-dimethyl-1,4,6,9-tetraoxaspiro[4.4]nonane (DTN) an intermediate for propylene carbonate polymerization, respectively. The formation of TON and DTN was proposed to result from the dimerization (5) of the respective cyclic
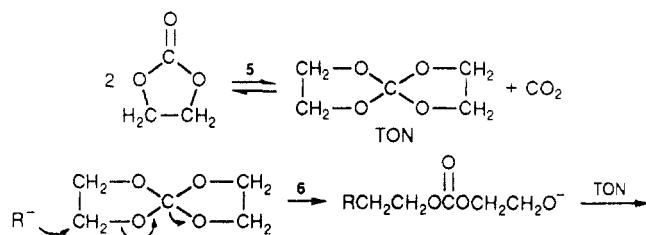

carbonate accompanied by the loss of 1 equiv of CO$_2$. Soga et al.[23] suggested that anionic polymerization of TON (6) will result in the formation of an alternating copolymer of ethylene carbonate and ethylene oxide, while DTN will yield an alternating copolymer of propylene carbonate and propylene oxide; however, they did not detect the intermediates, TON or DTN, in the respective polymerization mixtures.

Vogdanis et al.[29] found that when organotin compounds, such as dibutyltin dimethoxide (DBTDM), were used as catalysts, the major hydrolysis product was again diethylene glycol (DEG) with smaller amounts of higher glycols but never ethylene glycol. They also reported that the composition of PEEC was strongly dependent on the catalyst chosen and that the degree of CO$_2$ retention decreased as the relative basicity of the catalyst increased. Thus, the ethylene carbonate content in the copolymer could be varied from 0.10 to 0.50 mole fraction; however, in no case was the mole fraction of ethylene carbonate higher than 0.50. Their explanation was that the polymerization occurred above the ceiling temperature (T_c) for pure poly(ethylene carbonate) formation and that propagation occurred via monomer insertion between the growing polymer chain end and a catalyst fragment (cat). The mechanistic explanation presented by Vogdanis et al.[29] is without detail and thus somewhat open to interpretation; however, it appears that the authors envisioned the reaction to proceed as described below.
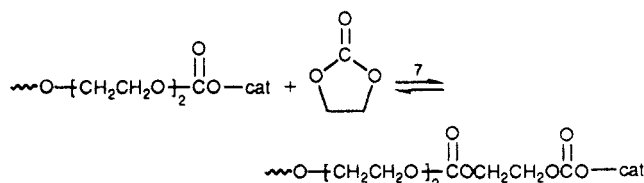

Above T_c the equilibrium (7) must lie to the left side since the sequence length of ethylene carbonate units cannot exceed one; however, the small population of chain ends with back-to-back EC units (2-carbonatoethyl carbonate end groups, right side of equilibrium 7) may undergo decarboxylation of the chain end via reaction 8a to form a 2-alkoxyethyl carbonate chain end. The 2-carbonatoethyl ether end group (species on the left side
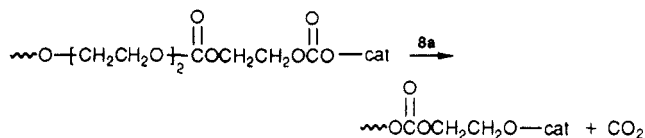
of equilibrium 7) can also under decarboxylation (8b) to
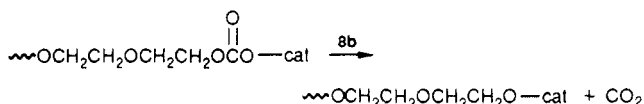
form a 2-alkoxyethyl ether chain end, and this reaction is competitive with the forward direction of equilibrium 7. Either type of alkoxide chain end can proceed to propagate by addition of ethylene carbonate (9) According to their
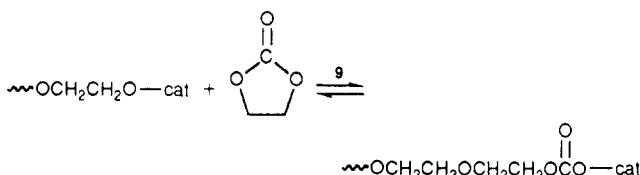
mechanism then, the amount of CO$_2$ retained in the copolymer is governed by the relative rate of reaction 8b compared to the forward reaction of equilibrium 7. If the rate of 8b is greater than or comparable to that of the forward reaction of 7, the CO$_2$ content will be low; if the rate of 8b is relatively small, the fraction of CO$_2$ retention will approach the ideal of 0.5. The rates of the various reactions should depend on the catalyst used, and this may explain the dependence of PEEC composition on the catalyst system. Recently, Vogdanis et al. have investigated the thermodynamics of ethylene carbonate polymerization and attributed the loss of CO$_2$ not to a low ceiling temperature but to a large positive enthalpy of polymerization (ΔH_p = 125.6 kJ/mol).[33]

Harris has also used backbone hydrolysis and subsequent GC analysis to examine the structural composition of PEEC synthesized using inorganic salts such as sodium stannate trihydrate (SS) as catalysts.[31] The structure of PEEC was again found to consist of alternating ethylene carbonate and ethylene oxide units. Direct GC analysis of aliquots removed from the reaction medium indicated the presence of a homologous series of oligo(ethylene glycols) which were actual intermediates in the polymerization reaction (as opposed to hydrolytic degradation products). These oligo(ethylene glycols) consisted mainly of DEG with smaller amounts of ethylene glycol (MEG) and triethylene glycol (TEG) present, along with trace amounts of higher glycols depending on the initial EC-initiator ratio and the catalyst chosen.[31]

Harris and McDonald used GC analysis in conjunction with ^{13}C NMR to elucidate the structure of certain polymer end-group structures and other intermediates formed during the ring-opening polymerization of ethylene carbonate.[32] They observed that both 2-hydroxyethyl carbonate (10) and 2-hydroxyethyl ether (11) end groups are
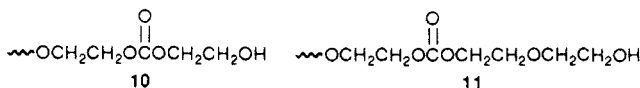
present initially; however, only 11 is present during the latter stages of the polymerization. They also found that diethylene glycol was an important reaction intermediate and was present in steady-state concentration, independent of which glycol was used as the initiator.[32]

We became interested in PEEC as a highly oxygenated prepolymer for cross-linked polyurethane network formation.[34,35] Such materials are potential solid rocket propellant binders, and compared to the commonly used hydrocarbon polymeric binders, such as hydroxy-terminated polybutadiene (HTPB), simple aliphatic polycarbonates possess a high oxygen content, and thus usually display a low heat of combustion,[6] and incorporate CO_2 as a cheap building block. In the course of our PEEC syntheses we found some interesting features of the polymerization system, not previously reported. Although the previous workers have contributed greatly to our understanding of EC polymerization, in particular Harris's important and careful elucidation of the major polymerization intermediates, they have yet to put forth a mechanism completely consistent with all the experimental results. It is our goal in this paper to report our results and to propose a mechanism which fully explains these results as well as results previously reported in the literature.

Experimental Section

Materials. Ethylene carbonate (EC, 99.5%; Texaco Chemical Co.) was distilled from calcium hydride under vacuum prior to use. Ethylene glycol (MEG, anhydrous, 99+%; Aldrich Chemical Co.) and sodium stannate trihydrate (SS; Pfaltz & Bauer) were used as received. Dibutyltin diacetate (DBTDA) and dibutyltin dilaurate (DBTDL) from Aldrich Chem Co. and dibutyltin dimethoxide (DBTDM; Pfaltz & Bauer) were dried in vacuo at 80 °C for 24 h before use. Poly(ethylene oxide) (PEO) of 300, 600, 1500, 2000, 8000, and 14 000 molecular weight from Aldrich Chemical Co. and a PEO of 4000 molecular weight from Polysciences Inc. were used as received. Methanol and acetone (J.T. Baker) were used as received.

Procedures. Synthesis of Poly(ethylene ether carbonate) Using Organotin Catalysts. All polymerizations were conducted in the bulk under a flow of nitrogen at 165 °C. A typical reaction setup was as follows: a 250-mL three-neck flask was flame-dried under nitrogen, charged with 50.0 g (0.567 mol) of ethylene carbonate and 7.20 g (0.0114 mol) of DBTDL, and placed in a constant-temperature bath. Aliquots of approximately 1 g were removed from the reaction vessel at different intervals and analyzed for EC conversion and CO_2 retention in the polymer using ^{1}H NMR and for molecular weight and molecular weight distribution using GPC. The final PEEC oligomer was purified by filtration through a medium glass frit funnel to remove insoluble catalyst residues, and the filtrate was dissolved in a minimal amount of chloroform, followed by precipitation into a 10-fold excess of methanol. The methanol layer was decanted, and the oily residue was rinsed thrice more with methanol and freed of solvents to leave a yellow liquid polymer. The polymer dissolved in methylene chloride was eluted through a silica gel column. Solvent evaporation yielded a clear, light-yellow product.

Synthesis of Poly(ethylene ether carbonate) Using Sodium Stannate Trihydrate Catalyst. A typical polymerization was as follows: a 500-mL three-neck flask equipped with mechanical stirrer was oven-dried and cooled under a stream of dry nitrogen. The vessel was charged with 100 g (1.13 mol) of EC, 0.50 g (2.6 × 10⁻³ mol) of SS, and 2.11 g (3.40 × 10⁻² mol) of MEG and immersed in a 165 °C oil bath, and polymerization was conducted under a nitrogen flow. The reaction was analyzed using ^{1}H NMR to monitor EC conversion and CO_2 retention in the copolymer and by GPC to determine molecular weight and molecular weight distribution. After approximately 90% conversion (9 h for the above recipe) the flask was removed from the oil bath and allowed to cool to about 50 °C, at which time the reaction mixture was dissolved in 300 mL of acetone and the solution cooled to room temperature. To remove the catalyst, 5 g of magnesium silicate was added, the solution was stirred for 2 h and then filtered through a 3-cm bed of Celite held within a medium glass frit funnel, and the acetone was removed using a rotary evaporator. The residual monomer was removed by dissolving the reaction mixture in a minimum amount of
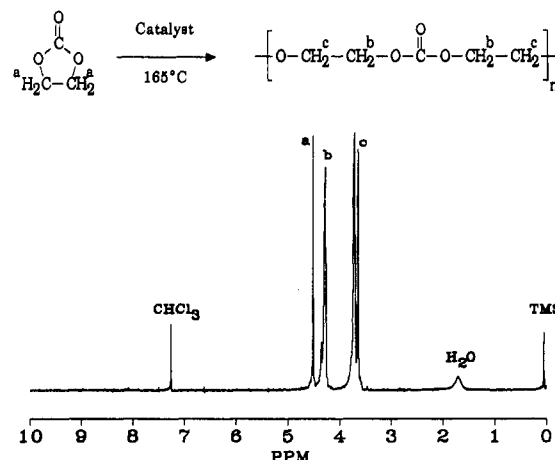

Figure 1. 300-MHz ^{1}H NMR spectrum of a PEEC reaction mixture and peak assignments.

chloroform followed by precipitation into a 10-fold excess of methanol. The methanol layer was decanted off and the polymer washed thrice more with methanol. Finally, the polymer was dried in an 80 °C air oven for 3 days followed by 24 h at 80 °C in vacuo to remove any residual solvent.

^{13}C NMR Monitor of Mono(ethylene glycol)-Ethylene Carbonate Model Reaction. Into a 5-mm NMR tube equipped with a sealed DMSO-d_6 insert and vented cap was charged through a tissue filter approximately 1 g of a 1:1 mass ratio (1.4:1 molar ratio) MEG-EC solution prepared by gently warming the two compounds. After an 8-h equilibration period, the ^{13}C NMR spectrum was taken at room temperature. SS catalyst (5 mg) was added to the tube, and the ^{13}C NMR spectrum was obtained at room temperature after a 1-h equilibration period.

The sample temperature was initially raised from 25 to 57 °C using one 12 °C and then two 10 °C incremental steps spaced 3 min apart; the sample was then heated to a final temperature of 135 °C using 5 °C increments every 3 min, with the final increment being 8 °C. After equilibrating at 135 °C for 3 min, the ^{13}C NMR spectrum was obtained. Thereafter, additional spectra were acquired every 30 min.

Variable-temperature ^{13}C NMR spectra were acquired on a Bruker AC-300 NMR spectrometer equipped with a BVT-1000 temperature controller. The acquisition parameters were as follows: the [13]C 90° pulse width was 4.5 s, the recycle delay was 2 s, the number of scans for each spectrum was 512, and WALTZ-16 decoupling was used during data acquisition. The samples were run neat, with a sealed DMSO-d_6 insert used for lock and peak reference.

Characterization. ^{1}H NMR spectra were recorded on a Varian EM-360 (60 MHz for ^{1}H) or a Burker Model AC-300 spectrometer (300 MHz for ^{1}H). ^{13}C NMR spectra were recorded on a Bruker Model AC-300 spectrometer (75 MHz for ^{13}C). CDCl₃ containing TMS for shift referencing purposes was the NMR solvent.

GPC was performed on a Waters Associates system employing 100, 500, 10⁴, and 10⁵ Å Ultrastyragel columns and a differential refractometer. Poly(ethylene oxide) molecular weight standards were used to obtain a calibration curve. Thermal analysis was performed using a Du Pont 9900 thermal analyzer equipped with a 951 TGA module. Temperature scans (5–20-mg samples) were performed at a heating rate of 10 °C/min in air.

Results and Discussion

Synthesis of Poly(ethylene ether carbonate) Using Organotin Catalysts. A ^{1}H NMR spectrum of an EC polymerization mixture along with the reaction scheme and peak assignments[23] is shown in Figure 1. During polymerization, a fraction of the EC units decarboxylate so that one actually obtains a copolymer of ethylene oxide and ethylene carbonate; however, there are only three peaks in the spectrum, and thus the monomer conversion and EC incorporation, i.e., CO_2 retention, can be calculated

Table I
Conversion, Composition, and Molecular Weight Results for PEEC Catalyzed by 1 mol % DBTDA

sampling time (h)	conversion[a] (%)	EC incorporation[a] (mol %)	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
24	40.0	45.1	2030	4500	2.22
48	56.6	44.6	2410	4560	1.89
72	60.7	44.0	2550	4690	1.84

[a] Determined by ^{1}H NMR. [b] Determined by GPC.

Table II
Conversion, Composition, and Molecular Weight Results for PEEC Catalyzed by 2 mol % DBTDA

sampling time (h)	conversion[a] (%)	EC incorporation[a] (mol %)	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
24	54.0	44.1	1120	1880	1.68
48	67.3	43.6	1170	1960	1.68
72	76.2	44.0	1240	2070	1.66

[a] Determined by ^{1}H NMR. [b] Determined by GPC.

Table III
Conversion, Composition, and Molecular Weight Results for PEEC Catalyzed by 1 mol % DBTDL

sampling time (h)	conversion[a] (%)	EC incorporation[a] (mol %)	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
24	39.9	43.6	2010	3320	1.65
48	51.2	42.2	2140	3450	1.61
72	58.0	40.4	2230	3570	1.60

[a] Determined by ^{1}H NMR. [b] Determined by GPC.

Table IV
Conversion, Composition, and Molecular Weight Results for PEEC Catalyzed by 2 mol % DBTDL

sampling time (h)	conversion[a] (%)	EC incorporation[a] (mol %)	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
24	56.4	44.0	1500	2490	1.66
48	67.8	43.6	1620	2630	1.62
72	83.4	43.7	1710	2750	1.61

[a] Determined by ^{1}H NMR. [b] Determined by GPC.

Table V
Conversion, Composition, and Molecular Weight Results for PEEC Catalyzed by 1 mol % DBTDM

sampling time (h)	conversion[a] (%)	EC incorporation[a] (mol %)	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
24	43.8	33.1	3560	5700	1.60
48	51.9	30.8	4150	6270	1.51
72	63.3	29.5	4290	6440	1.50
92	64.0	28.9	4390	6590	1.50

[a] Determined by ^{1}H NMR. [b] Determined by GPC.

Table VI
Conversion, Composition, and Molecular Weight Results for PEEC Catalyzed by 2 mol % DBTDM

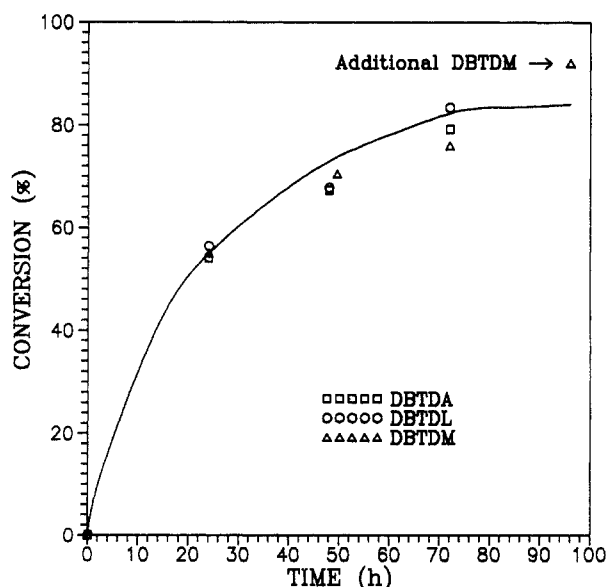| sampling time (h)	conversion[a] (%)	EC incorporation[a] (mol %)	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
24	56.4	30.4	2190	3570	1.63
48	73.5	28.1	2340	3740	1.60
72	82.5	27.3	2560	4040	1.58
96	84.1	27.1	2590	4040	1.56

[a] Determined by ^{1}H NMR. [b] Determined by GPC.

Figure 2. Conversion vs time curves for PEEC formation catalyzed by (O) 2 mol % DBTDA, (□) 2 mol % DBTDL, and (Δ) 2 mol % DBTDM at 165 °C.

by integration of the relative peak areas A_a, A_b, and A_c, as outlined in eqs 1 and 2. The spectrum in Figure 1

$$\text{conversion } (\%) = \frac{A_b + A_c}{A_a + A_b + A_c} \times 100 \qquad (1)$$

$$\text{EC incorporation (mol \%)} = \frac{A_c}{A_b + A_c} \times 100 \qquad (2)$$

indicates a monomer conversion of 50.9% and an ethylene carbonate incorporation of 45.6 mol %.

The conversion, EC incorporation, and molecular weight versus time results for DBTDA-, DBTDL-, and DBTDM-catalyzed polymerizations at catalyst levels of 1 and 2 mol % are shown in Tables I–VI, respectively. In all cases conversion increased with time and was then observed to approach an asymptotic value at longer reaction times (48 h). This effect is seen more clearly in Figure 2, which is

a plot of conversion versus time for the three catalysts at 2 mol % concentration. The attainment of an *ultimate* conversion below 100%, even after reaction times as long as 240 h, has been observed by several workers.[23,29,33] This effect may be due to the attainment of an equilibrium monomer concentration ($[M]_e$); however, the appearance of an intractable, white precipitate during polymerizations catalyzed by DBTDL or DBTDA suggests that incomplete conversions may be due to cumulative decomposition of the catalyst. To address this question, a polymerization using DBTDM as catalyst (which produces no visible byproduct) was conducted for 72 h (polymerization was essentially finished), and then additional DBTDM (0.5 mol % based on the initial amount of EC) was added and the conversion monitored. As shown in Figure 2 the addition of extra DBTDM resulted in resumption of polymerization and higher conversion, a result that was also seen for the other two catalysts. The addition of further catalyst should not affect the value of $[M]_e$ if the system is truly at equilibrium, and this is one reason that we feel the leveling off of conversion with time is due to catalyst decomposition and not polymerization–depolymerization equilibrium. A second reason for our claim is outlined in Figure 3 where there are shown the ^{13}C NMR spectra of (A) a reaction mixture of PEEC catalyzed by DBTDL, (B) lauric acid, and (C) the above PEEC sample purified by column chromatography to remove the intractable reaction byproduct. In spectrum A the peaks centered about 40 ppm (a) correspond with those found (b) in the spectrum of lauric acid (B); however, the carbonyl carbons, a′ and b′ from spectra A and B, respectively, are vastly different. Thus, we do not feel the byproduct is lauric acid due to this difference in ^{13}C NMR spectra as
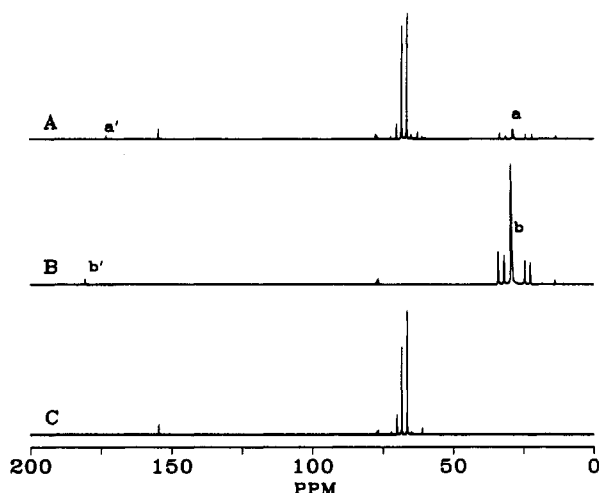
Figure 3. 75-MHz ^{13}C NMR spectra of (A) PEEC catalyzed by DBTDL, (B) lauric acid, and (C) PEEC catalyzed by DBTDL after purification by column chromatography.

well as the difference in melting point and solubility. Furthermore, in switching to DBTDA we did not recover acetic acid as would be expected by analogy. We have not yet identified this impurity unequivocally, but we suspect that it may be a Sn(II) species, i.e., tin(II) diacetate and tin(II) dilaurate from DBTDA and DBTDL, respectively. Conceivably, a soluble byproduct is produced with DBT-DM, which explains why it also yields less-than-quantitative conversions yet does not show a visible decomposition product.

The degree of EC incorporation in the copolymer was found to be catalyst dependent as expected.[22] The use of DBTDM resulted in about 30 mol % EC incorporation, while the use of DBTDA and DBTDL resulted in 40–44 mol % EC incorporation. The use of DBTDM previously has been reported to give 43–49 mol % EC incorporation,[29] and we have no explanation why our polymerizations yielded a lower EC incorporation.

The molecular weights of the resulting polymers were in the range $\bar{M}_n = 1200$–3600. Molecular weights increased with increasing time and displayed a dependence on catalyst concentration, i.e., higher molecular weights resulted from lower catalyst concentrations. The polymers produced using DBTDA and DBTDL possessed lower molecular weights than those using DBTDM at identical concentrations. In Figure 4 are shown GPC chromatograms at differing reaction times for an EC polymerization mixture catalyzed by DBTDA at 1 mol % concentration. The increase in size of the peak due to polymer (broad peak occurring from 28 to 35 mL of elution volume) compared to the peak due to EC (44.5 mL) shows the increase in conversion with time. Along with increasing conversion, the shift of the polymer peak to higher elution volumes with time indicates an increase in molecular weight. These same trends may be observed in Figures 5 and 6 which show GPC chromatograms at various reaction times for EC polymerization mixtures catalyzed by DBTDL and DBTDM at 2 mol % concentration, respectively. In Figure 6 the chromatogram labeled D is that of the polymerization mixture where extra catalyst was added after 72 h as discussed previously. Clearly, upon addition of extra catalyst, the increase in conversion is evident since the polymer peak grows with respect to the monomer peak; however, the polymer peak shifts to higher elution volumes as well showing an increase in molecular weight with increasing conversion. This results suggests that at this stage of the reaction DBTDM is a
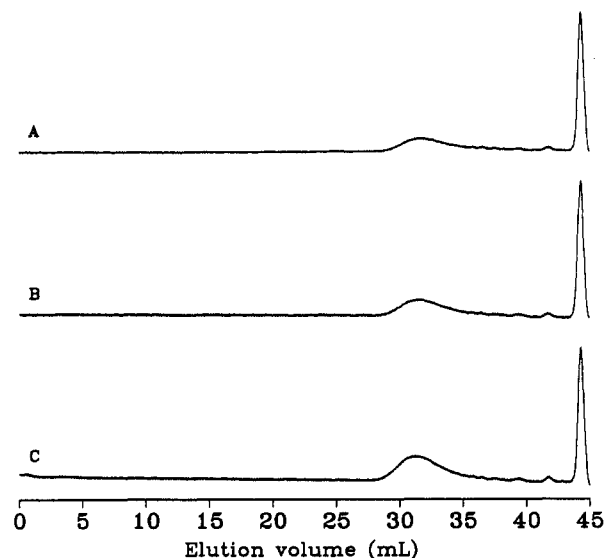

Figure 4. GPC chromatograms of EC reaction mixtures catalyzed by DBTDA at 1 mol % concentration: (A) 24, (B) 48, and (C) 72 h.
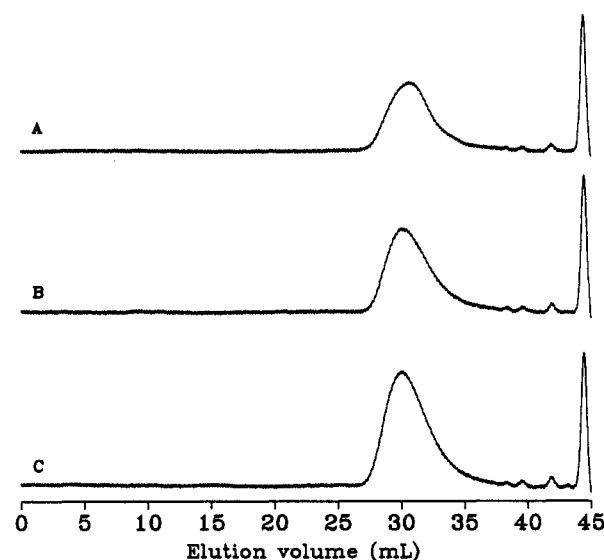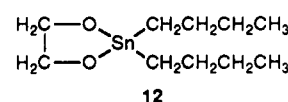

Figure 5. GPC chromatograms of EC reaction mixtures catalyzed by DBTDL at 2 mol % concentration: (A) 24, (B) 48, and (C) 72 h.

catalyst and not an initiator since low molecular weight polymer would have been expected upon further addition of initiator. The dependence of molecular weight on the initial concentration of DBTDA, DBTDL, and DBTDM, however, suggests that they act not only as catalysts but also as initiators. Investigations of the mechanism of lactone polymerizations in the presence of these catalysts were carried out by Kricheldorf et al.,[36,37] and they proposed that the compounds act as initiators since the chain end was found to contain a catalyst fragment. Vogdanis et al.[33] have suggested that these compounds play a similar role in EC polymerization, since they reported achieving defined molecular weights by varying the ratio of monomer to initiator and by taking into account all of the alkoxide substituents on the catalyst. For example, in dibutyl(ethylenedioxy)tin (12) the alkoxide

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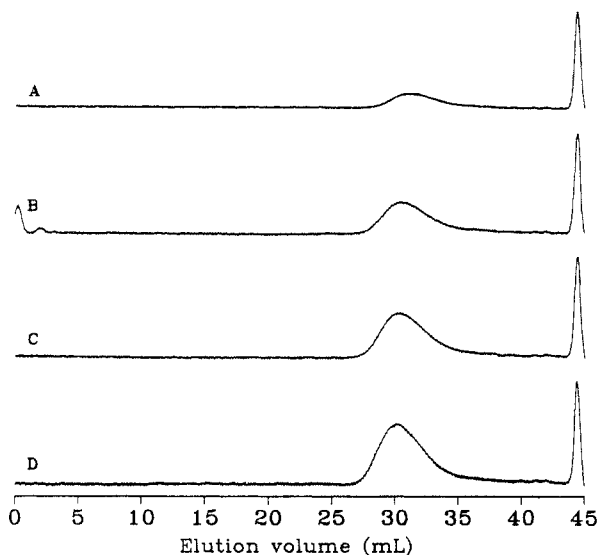groups are connected, and because of this the authors

Figure 6. GPC chromatograms of EC reaction mixtures catalyzed by DBTDM at 2 mol % concentration: (A) 24, (B) 48, (C) 72, and (D) 96 h (additional 0.5 mol % based on initial moles EC added after 72 h).

envisioned that the polymer chains grow in the form of macrocycles until they are hydrolyzed to open chains sometime during polymerization.[33] This implies that the two alkoxide groups only result in the generation of one polymer chain, which in fact consists of two kinetic chains coupled through the ethylene moiety. In DBTDM (13)

$$H_3C-O \diagdown Sn \diagup CH_2CH_2CH_2CH_3$$
$$H_3C-O \diagup \diagdown CH_2CH_2CH_2CH_3$$

13
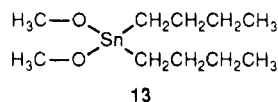
the alkoxide substituents are not joined, and therefore it is expected that each alkoxide group will generate one polymer chain. At equal concentrations then, the use of 12 should lead to higher molecular weights.[33] Sakai et al.[38] observed that DBTDM reacted instantaneously with EC at room temperature in high yields to form 12, implying that 12 is the true catalyst even when DBTDM is used. This observation may suggest that the differing polymer molecular weights reported by Vogdanis et al.[33] were not due to differences in the number of alkoxides units attached to the catalyst but perhaps other factors such as impurities introduced with the monomer or catalyst. This discussion raises the question as to what, then, is the true initiator in these polymerizations. We propose that it is residual ethylene glycol (MEG). Vogdanis et al. have characterized MEG as a chain-transfer agent since they have observed that its addition lowers the molecular weight of the polymer;[33] however, this observation is equally in harmony with the proposition that MEG acts as an initiator. The consistent presence of residual MEG in the reaction mixture most probably results from the known azeotrope between ethylene carbonate and ethylene glycol[39] which would defeat attempts to completely remove ethylene glycol from the monomer via distillation. Further addition of hydroxyl sources, e.g., moisture from the catalysts, would increase MEG levels through hydrolysis of EC.

Returning to Figures 4–6, a further feature of these chromatograms is the presence of a peak located at 42 mL, which is apparently due to DEG which is formed during the polymerizations. This is illustrated in Figure 7 in which the GPC chromatograms of (A) PEEC catalyzed by DBTDL, (B) ethylene carbonate, and (C) diethylene glycol are shown. In chromatogram C, the peak due to DEG
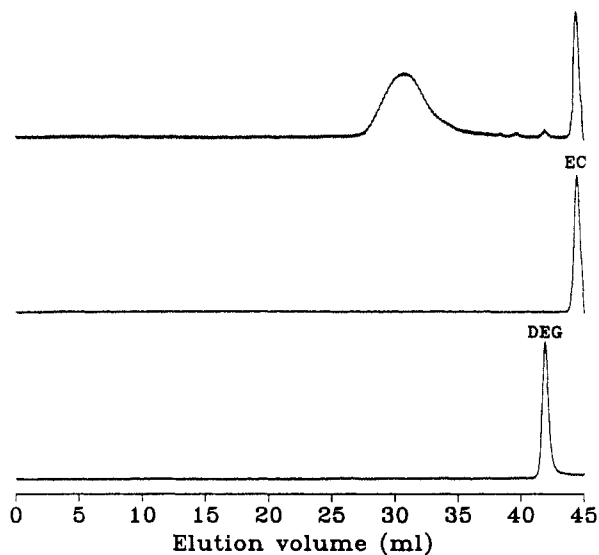

Figure 7. GPC chromatograms of (A) an EC reaction mixture catalyzed by DBTDL, (B) ethylene carbonate, and (C) diethylene glycol.
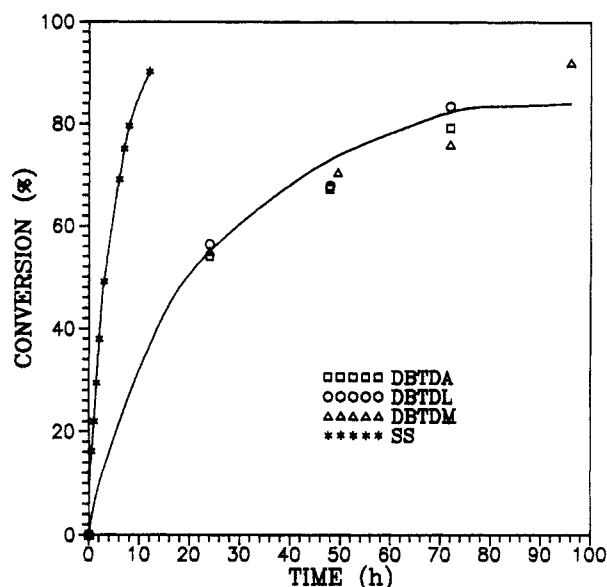

Figure 8. Conversion vs time curves for PEEC formation catalyzed by (O) 2 mol % (DBTDA, (□) 2 mol % DBTDL, (△) 2 mol % DBTDM, and (*) 0.50 wt % SS at 165 °C.

occurs in the same position as the peak assigned to DEG in the reaction mixture (A). At this time we have not quantified the level at which DEG is present although it is interesting that, for polymerizations using DBTDA and DBTDL, the highest DEG content was noticed (size of the peak at 42 mL in chromatograms) and the lowest molecular weights resulted. Harris has reported DEG to be an important reaction intermediate, whose concentration is constant and nearly equal to the initial initiator concentration, when sodium stannate trihydrate is used as catalyst in EC polymerization.[32]

Synthesis of Poly(ethylene ether carbonate) Using Sodium Stannate Trihydrate Catalyst. The ring-opening polymerization of EC was conducted using sodium stannate trihydrate (SS) as the catalyst to eliminate the problem of reaction byproducts formed when DBTDA or DBTDL are used as catalysts, and since SS itself can be easily removed from the reaction mixture.[40] Sodium stannate trihydrate is a heterogeneous catalyst but under our conditions yields a higher rate of polymerization than the organotin catalysts, as shown by the conversion versus time plot in Figure 8. When SS was used at a 0.5 wt %
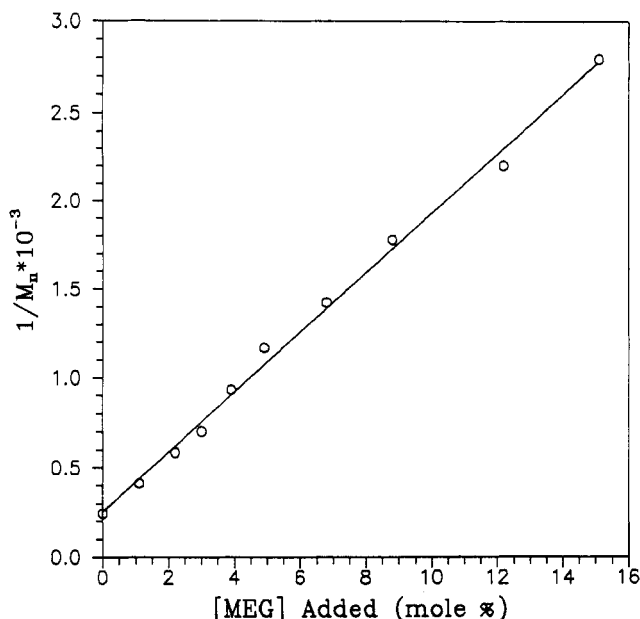
Figure 9. Reciprocal resultant number-average molecular weight $(1/\bar{M}_n)$, catalyzed by 0.50 wt % SS at 165 °C after 90% yield, vs the purposefully added MEG ([MEG]$_{added}$) in mole percent.
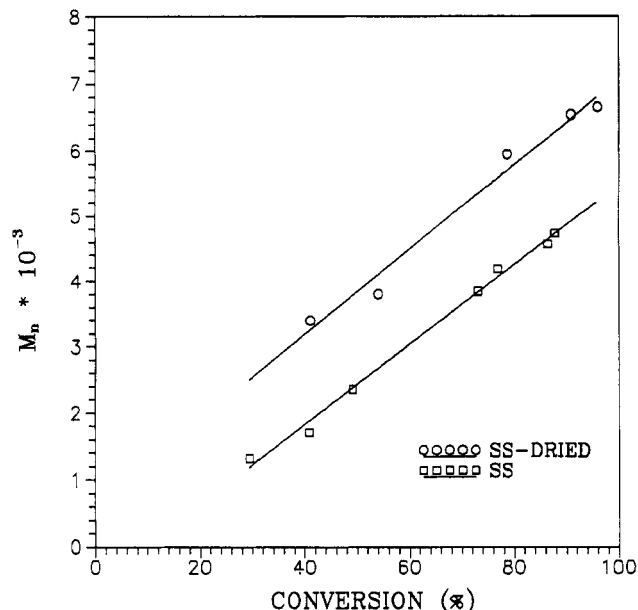

Figure 10. $\bar{M}_n$ vs conversion for PEEC formation at 0 mol % MEG purposefully added and 0.50 wt % SS (O) dried at 100 °C for 7 days and (□) as received.
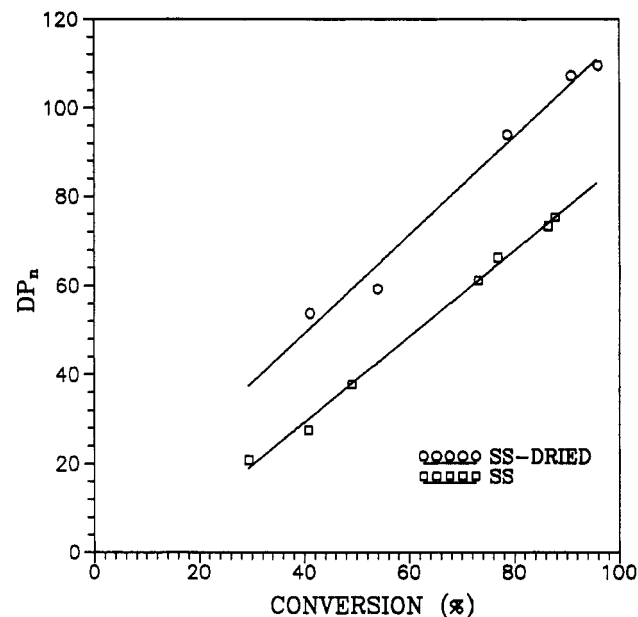

Figure 11. $\overline{DP}_n$ vs conversion for PEEC formation at 0 mol % MEG purposefully added and 0.50 wt % SS (O) dried at 100 °C for 7 days and (□) as received.

level with 1 mol % ethylene glycol externally added, 90% conversion was reached after 9 h, while 72 h was required to attain only 80% conversion for the organotins at 2 mol % (~12.5 wt % DBTDL).

It has been reported by Harris[31] that diols, and in particular MEG, serve as initiators in this polymerization and may thus be used to control the molecular weight of PEEC. We investigated the role of the initiator, MEG, in the polymerization, and the results are shown in Figure 9 which is a plot of the reciprocal resultant number-average molecular weight $(1/\bar{M}_n)$, after a 90% yield, versus the amount of externally added MEG ([MEG]$_{added}$) in mole percent. The observed linearity and positive slope of the plot confirms that MEG does apparently behave as a conventional initiator in this polymerization; however, the polymerization is atypical because of the finite intercept in the plot, where no ethylene glycol was added, suggesting a limiting value of $\bar{M}_n$ and an unexplained source of additional initiator. Considering the nature of the mono-mer, we strongly suspect that this source consists of MEG which either is present initially in the monomer as an impurity or is formed from the monomer during the course of the polymerization. Thus we feel the true initiator concentration in a given polymerization in which MEG is purposefully added will always be given by [MEG]$_{added}$ + [MEG]$_{in\ situ}$, and therefore the prevailing [MEG]$_{in\ situ}$ will limit the attainable molecular weight. The presence of [MEG]$_{in\ situ}$ in the reaction mixture can again be accounted for by considering the existence of an ethylene carbonate–ethylene glycol azeotrope which would defeat attempts to completely separate ethylene glycol via distillation and would account for a characteristic prevailing concentration.

Adventitious H_2O may also contribute to [MEG]$_{in\ situ}$ since the hydrolysis of EC forms MEG, and this reaction would be expected to be catalyzed by SS and in fact has been shown to be catalyzed by alkaline compounds.[41] Since SS is available as a trihydrate, we felt it was probably hygroscopic and could represent a source of unaccounted moisture. The catalyst was dried in a 150 °C air oven for 7 days, which changed the physical appearance of the catalyst from a sticky to a granular powder. Two poly-merizations were run with [MEG]$_{added}$ = 0, one using the dried SS and the other using SS as received. The result

is shown in Figure 10 which is a plot of $\bar{M}_n$ versus conversion for each polymerization. Interestingly enough, both of the curves were observed to be straight lines but neither was observed to extrapolate through the origin. Harris has also observed a linear growth of $\bar{M}_n$ with conversion.[32] Since the molecular weight of PEEC is dependent on the degree of CO_2 retention, the preferred method of examining the effect of conversion on the polymerization is plotting the degree of polymerization $(\overline{DP}_n)$ versus conversion as shown in Figure 11. A linear relationship is also observed in this case. A linear relationship for $\bar{M}_n$ or $\overline{DP}_n$ versus conversion indicates that the number of growing chains is constant throughout the polymerization.[42] The polym-erization conducted with the dried SS shows higher molecular weight polymer at all conversions which is indicative of a lesser number of growing chains, compared to that of the undried SS. Although yielding a slight increase in $\bar{M}_n$, the dried SS still produced relatively low
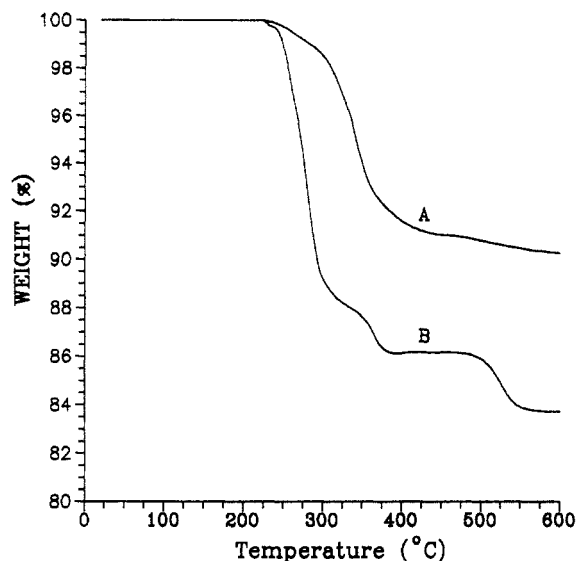
Figure 12. Thermogravimetric analysis curves of SS (A) dried at 100 °C for 7 days and (B) as received.

molecular weight polymer (ultimately $\bar{M}_n \sim 6600$).
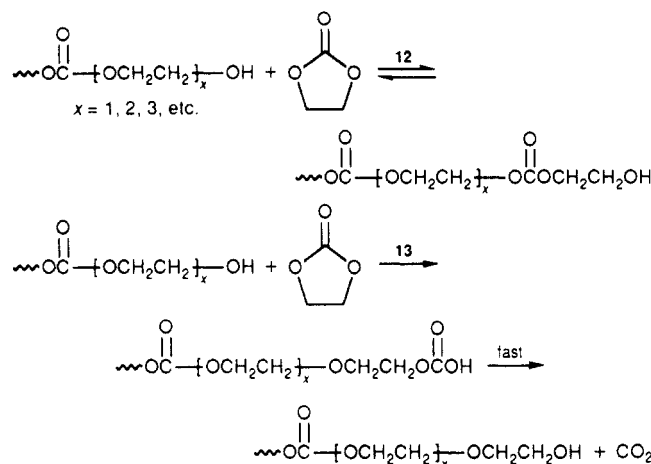
The effect of drying the catalyst may be understood by examining the TGA curves of SS before and after drying, shown in Figure 12. The undried SS (B) shows an initial weight loss of 16.5% beginning at about 300 °C; however, the dried SS (A) shows an initial weight loss of less than 10%. We feel that our heat treatment of the catalyst, while not affecting the waters of hydration,[43] did tend to drive off absorbed moisture, which if present, could lead to the formation of MEG through hydrolysis of ethylene carbonate. Thus the true initiator concentration ([MEG]$_0$) in a given polymerization will always be given by eq 3, and

$$[MEG]_0 = [MEG]_{added} + [MEG]_{in\ situ} \qquad (3)$$

the prevailing [H_2O] will contribute to [MEG]$_{in\ situ}$, since every molecule of water is able to initiate a polymer chain by forming, in situ, a molecule of MEG.

Proposed Mechanism. In an attempt to explain our experimental results, in particular the limiting value of $\bar{M}_n$, we have proposed a mechanism of ethylene carbonate polymerization initiated by glycols and catalyzed by sodium stannate trihydrate. Its development has been guided in part by a report by Harris which shows that diethylene glycol is an important reaction intermediate and is maintained at a steady-state concentration.[32] We envision the polymerization to proceed by a mixed mechanism, consisting of ring-opening steps in which carbonyl attack and alkylene attack are competitive and transcarbonation steps which are necessary to explain the steady-state concentrations of oligo(ethylene glycol) intermediates during the polymerization. The central feature of the ring-opening process is that carbonyl attack (12) is favored kinetically over alkylene attack (13); however, carbonyl attack is reversible, but alkylene attack is not, because of rapid loss of CO_2. A very important further feature of the process is that the position of equilibrium 12 is highly dependent on the value of x; if $x = 1$, it lies far to the left, effectively preventing the incorporation of consecutive ethylene carbonate units.

To begin, let us consider the case of a truly alternating copolymer of ethylene ether and ethylene carbonate repeat units formed using MEG as the initiator. Our proposed mechanism for this idealized case is shown in Figures 13 and 14. The mechanism does not explain the precise role of the catalyst; however, SS may act by complexing with the carbonyl group of the monomer and thus enhancing the reactivity of both the acyl and alkylene groups. Another possible action of the catalyst is to form a small equilibrium concentration of stannyl ether chain ends which, although very low in concentration, are responsible for the bulk of the polymerization.

Starting with Figure 13, the first step in the polymerization is the reversible reaction, K, of ethylene glycol, either added purposefully and/or present in situ, with ethylene carbonate to form the symmetrical dimer bis(2-hydroxyethyl) carbonate (I). I can react with EC at either the carbonyl group, k_{car}, or the alkylene group, k_{alk}, but only attack at the alkylene group, to form IA, is observed since attack at the carbonyl group is rapidly reversible and would result in two consecutive ethylene carbonate repeat units in the polymer backbone, which does not occur spontaneously at typical polymerization temperatures.[15-33] The alkyl hydrogen carbonate (carbonic acid monoester) end group of IA decarboxylates rapidly to form the asymmetrical trimer II, which contains two distinctly different end groups, a 2-hydroxyethyl carbonate end group ($x = 1$ above) and a 2-hydroxyethyl ether end group ($x = 2$). These end groups will be hereafter referred to as type 1 and 2, respectively. Now, Harris[32] reported that the reaction of MEG with EC at a 1:1 ratio produced DEG in over 90% yield, with the remaining components comprised mostly of triethylene glycol. To account for this observation, we propose the reaction of II with additional MEG in a transcarbonation process which liberates DEG and produces another molecule of I.

The alternative and more direct explanation for the production of DEG, i.e., attack of MEG at the alkylene group of EC followed by decarboxylation, cannot be completely eliminated from consideration; however, we feel that it is only marginally competitive with the proposed mechanism for two reasons. First, the central premise of the proposed mechanism is that carbonyl attack is faster than alkylene attack, except when the attacking nucleophile is a type 1 end group. Thus, it is expected that MEG will react more readily at the carbonyl group of EC to form I than with the alkylene group to form DEG (after decarboxylation). Of course, MEG is unique, i.e., it is neither a type 1 nor a type 2 end group; however, it is reasonable to assume that since the reaction of MEG at the carbonyl group of EC does not lead to the incorporation of two consecutive ethylene carbonate units, MEG reacts faster with the carbonyl group than with the alkylene group. This proposition is supported by ^{13}C NMR evidence which showed that, upon reaction of MEG and EC, intermediate I was formed and maintained at a relatively level concentration during conversion of the reactants to DEG.
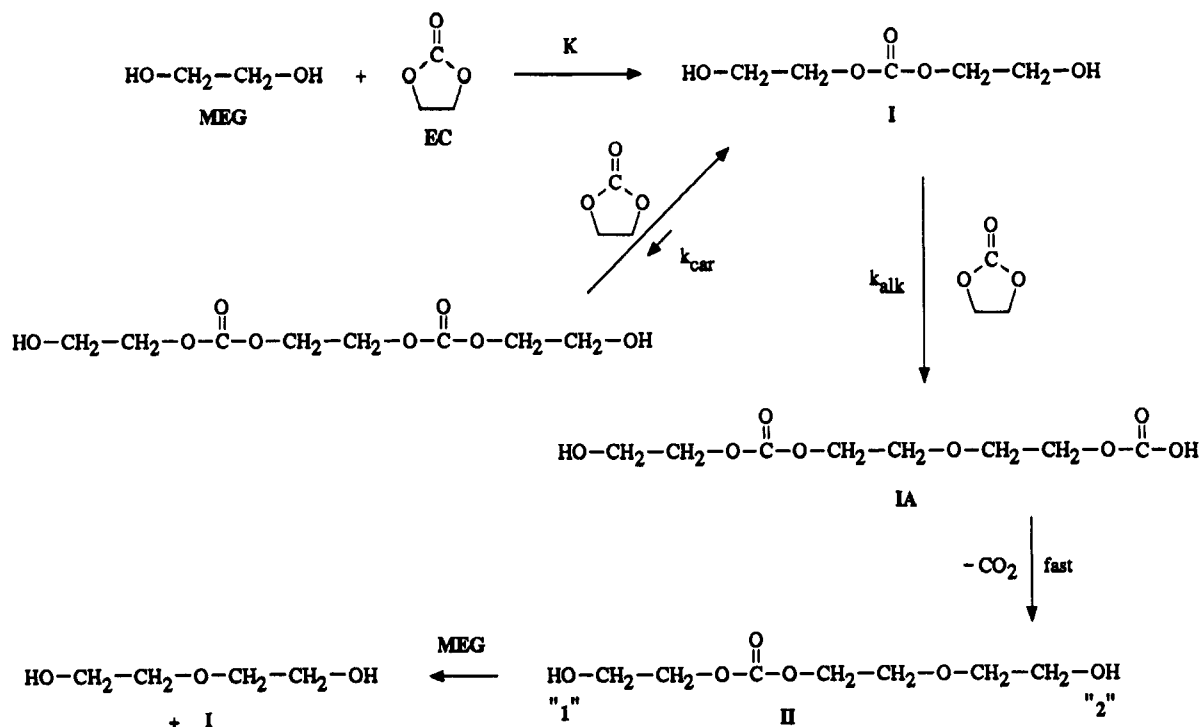
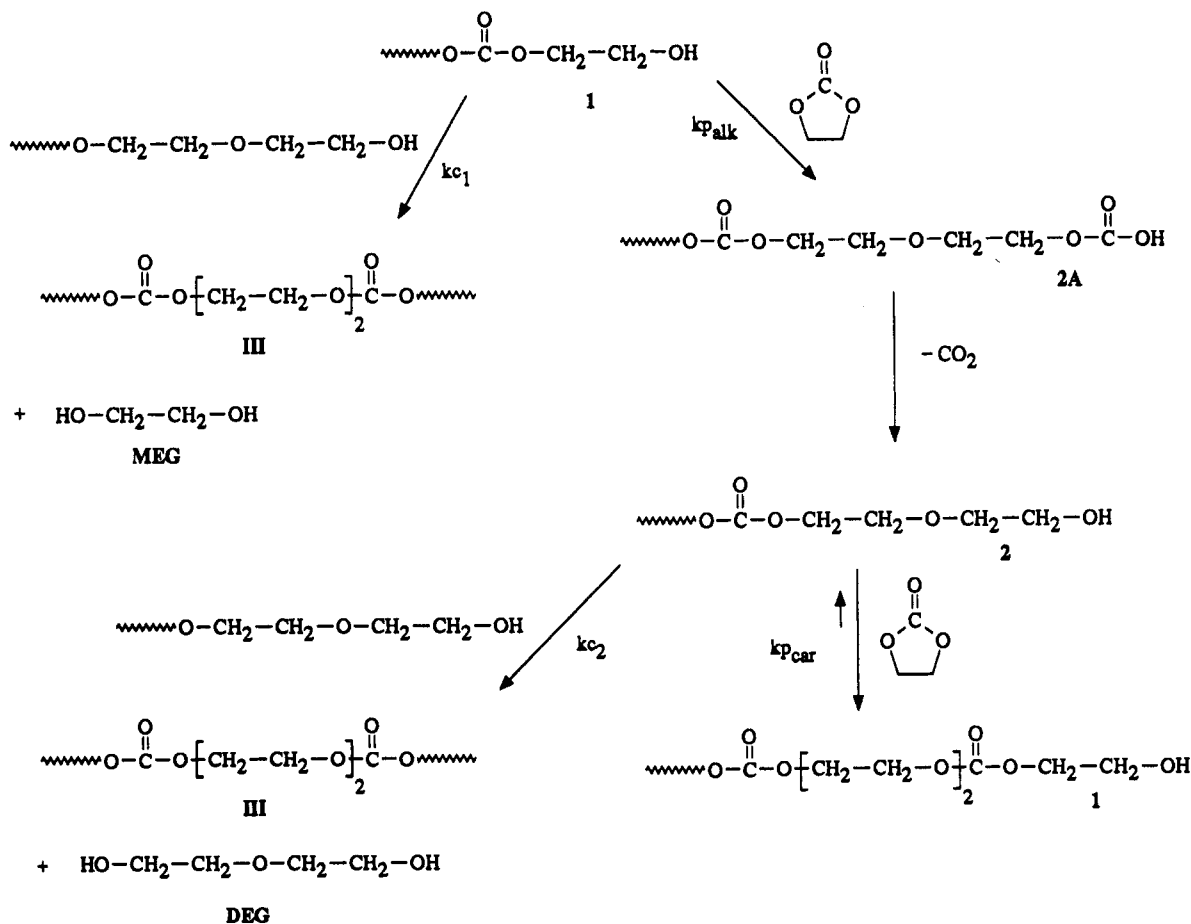**Figure 13.** Proposed mechanism of PEEC formation (part 1).

Figure 14. Proposed mechanism of PEEC formation (part 2).

MEG and EC were reacted under various stoichiometric conditions designed to eliminate polymer formation, and the reaction for MEG–EC of 1:1 mass ratio (1.4:1 molar ratio) is representative of the general behavior. Figure 15A is the ^{13}C NMR spectrum of the 1:1 mixture of MEG and EC, without catalyst, after standing at room temperature for 8 h. In addition to the two reactants, one can

discern a small concentration of intermediate I, evidenced by the resonances at 59.0 (–CH$_2$OH), 68.6 (–CH$_2$–), and 154.7 ppm (C=O); these resonances are identified as a–c, respectively, in the upper (B) spectrum, where they can be observed more clearly. The presence of I indicates that reaction K, Figure 13, takes place at a very slow rate, uncatalyzed at room temperature. After addition of the
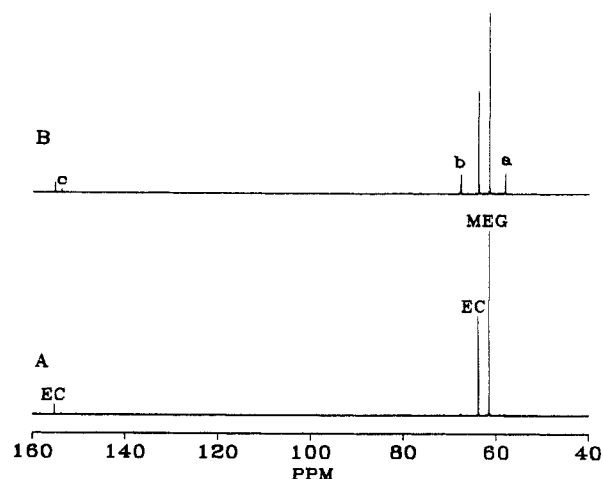
Figure 15. ^{13}C NMR spectra of MEG–EC (1.4:1, mole–mole) at room temperature, with no catalyst present (A) and 1 h after addition of 0.5% sodium stannate (B).
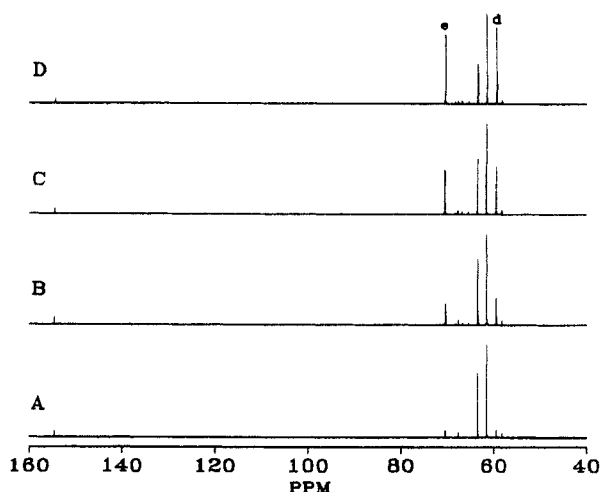

Figure 16. ^{13}C NMR spectra of MEG–EC (1.4:1, mole–mole) at 135 °C with 0.5% sodium stannate: 0 (A), 30 (B), 60 (C), 90 min (D).

catalyst and a 1-h equilibration at room temperature, the spectrum in Figure 15B was obtained. Here an appreciable concentration of intermediate I was observed, and in fact this was reckoned to be the equilibrium concentration at this temperature. Importantly, little or no DEG was observed in this spectrum. Harris[32] also observed the resonances at 59 and 69 ppm and suggested that they could be due to the formation of type 1 end groups during the early stages of the polymerization reaction.

The reaction mixture was next heated to 135 °C, and the ^{13}C NMR spectrum shown in Figure 16A was obtained immediately after temperature stabilization. It was observed that the formation of DEG had begun as evidenced by the resonances at 59.5 (–CH$_2$OH) and 70.5 ppm (–CH$_2$O–); these resonances are identified as d and e, respectively, in the uppermost (D) spectrum, where they can be observed most clearly. It was also apparent that the equilibrium concentration of I was less at the higher temperature. Now, DEG can only be formed by some process involving alkylene attack; the only question is whether it forms by direct attack by MEG or indirectly through I, or both. The proposed route via I, involving a transcarbonation step, is in greater harmony with Harris' finding that DEG exists in steady-state concentration throughout the polymerization, and it is simply unreasonable to assume that I is formed first but then assumes no further role in the process. The reaction was allowed to proceed at 135 °C, and spectra were obtained after 30,

60, and 90 min, as shown in parts B–D of Figure 16. It was observed that the concentration of DEG steadily increased with time and the concentration of I very slowly diminished with time. Several additional resonances of very low intensity were observed in the ranges 67–71 and 154–155 ppm; these were postulated to be due to higher oligomers such as triethylene glycol and species II in Figure 13.

Essentially the same results outlined above were observed for model reactions in which the MEG–EC ratio ranged anywhere from 1:1 to 7:1 (mole–mole). These model reactions make clear several important points which lend support for the proposed mechanism. First, they show that I is the first-formed (kinetic) product of the reaction of MEG and EC. The formation of I, which is viewed as a model for ring opening via carbonyl attack (equilibrium 12), is very rapid even at room temperature and does appear to be a reversible equilibrium. Second, the reaction of I with EC to produce IA, which involves alkylene attack (reaction 13), is much slower since it could not be detected at room temperature. At 135 °C the presence of IA is implied because of the production of DEG; however, since it could not be observed in the NMR spectra, the decarboxylation reaction must be very fast.

Under normal polymerization conditions there is much less MEG present, and the formation of higher oligomers and polymers is favored. Figure 14 outlines the general polymerization mechanism involving the basic end-group types 1 and 2, which may be attached to molecules of any degree of polymerization. The reaction of ethylene carbonate with a type 1 end group, kp_{alk}, must proceed via attack at the alkylene group, resulting in an alkyl hydrogen carbonate end group (2A) which is unstable and decarboxylates to form the stable type 2 end group. Reaction of a type 2 end group with EC, kp_{car}, proceeds via attack at the carbonyl position to regenerate a type 1 end group, and thus one can imagine a continual buildup of molecular weight by this monomer addition/decarboxylation/monomer addition reaction scheme. This scenario, though, does not account for the maintenance of steady-state concentrations of MEG and DEG throughout the polymerization. To account for this experimental fact,[32] one must postulate the operation of random transcarbonation reactions during the polymerization, catalyzed by SS. Returning to the top to Figure 14, the carbonate function of the type 1 end group can also undergo a transcarbonation condensation reaction, kc_1, with any hydroxyl function within the reaction mixture, except for a type 1. The greatest probability is for reaction with a type 2 end group, which produces the stable ethylene ether-*alt*-ethylene carbonate repeat unit III, leads to molecular weight buildup, and liberates a molecule of MEG. Since polymerization occurs below the boiling point of MEG (bp = 196 °C), it remains in the polymerization vessel and can react with EC as shown earlier in Figure 13, beginning a new polymer chain. Of course, the carbonate functions of type 2 end groups can also undergo transcarbonation reactions, kc_2, as shown in Figure 14, forming the stable alternating copolymer repeat unit III and liberating DEG, which can then react further with EC. Note that transcarbonation reactions involving the hydroxyl function of type 1 end groups must not occur since it would produce, in effect, consecutive EC units in the polymer, which are not observed experimentally.[15-33]

The above mechanism deals only with a truly alternating copolymer, and this is not the actual situation in SS-catalyzed polymerizations, since the CO$_2$ retention is less than 50 mol %. To approach the real situation, we must
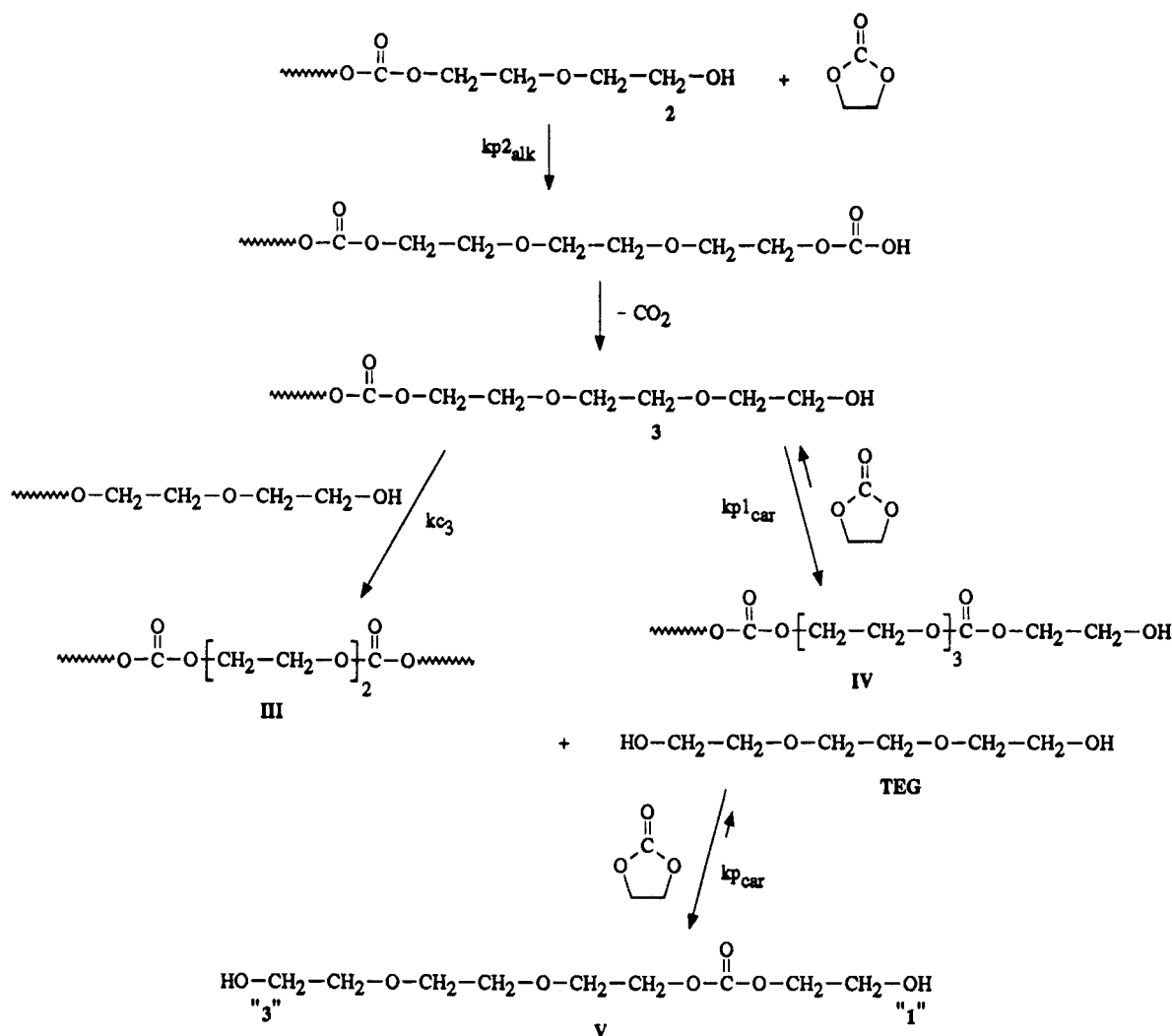
wwwwO—C(=O)—O—CH₂—CH₂—O—CH₂—CH₂—OH   +   (ethylene carbonate)
2

$kp2_{alk}$ ↓

wwwwwO—C(=O)—O—CH₂—CH₂—O—CH₂—CH₂—O—CH₂—CH₂—O—C(=O)—OH

↓ $-CO_2$

wwwwwO—C(=O)—O—CH₂—CH₂—O—CH₂—CH₂—O—CH₂—CH₂—OH
3

wwwwwO—CH₂—CH₂—O—CH₂—CH₂—OH   /kc_3

$kp1_{car}$ (ethylene carbonate)

wwwwO—C(=O)—O[CH₂—CH₂—O]C(=O)—O wwww
III

wwwwO—C(=O)—O[CH₂—CH₂—O]₃C(=O)—O—CH₂—CH₂—OH
IV

+   HO—CH₂—CH₂—O—CH₂—CH₂—O—CH₂—CH₂—OH
TEG

(ethylene carbonate) /kp_{car}

HO—CH₂—CH₂—O—CH₂—CH₂—O—CH₂—CH₂—O—C(=O)—O—CH₂—CH₂—OH
"3"   "1"
V

Figure 17. Proposed mechanism of PEEC formation accounting for CO_2 retentions of <50 mol %.

account for triethylene glycol (and possibly higher glycol) formation, as well as the incorporation of trioxyethylene (and higher) repeat units in the polymer backbone. We have accounted for this by expanding our proposed mechanism as shown in Figure 17. Infrequently (depending on the catalyst system[32]) an end group of type 2 will open the EC ring by alkylene attack, $kp2_{alk}$, resulting in the formation of a stable triethylene glycol-type end group 3. (This reaction is analogous to alkylene attack by MEG discussed earlier.) The type 3 end group behaves similarly to a type 2 end group in the sense that it opens the EC ring primarily through carbonyl attack, and it may analogously enter the pathways outlined for type 2 end groups in Figures 13 and 14. This process leads to the incorporation into the polymer of internal trioxyethylene units IV and accounts for the observation of triethylene glycol upon backbone hydrolysis and for PEEC retaining less than 50 mol % CO_2. When an end group of type 3 undergoes a condensation reaction at its carbonate linkage, with the hydroxyl function of a type 2 end group, kc_3, it produces the stable ethylene ether-*alt*-ethylene carbonate repeat unit III, leading to molecular weight buildup and a molecule of triethylene glycol. As discussed earlier in regard to the other liberated glycols (MEG and DEG), TEG can reinitiate a chain by reaction with EC to produce intermediate V, which contains end-group types 1 and 3. The proposed mechanism also readily accounts for the presence of higher poly(ethylene glycols), both as reaction intermediates and as stable chain segments between carbonate linkages in PEEC. Thus, PEEC's characterized

by very low carbonate retention are formed under conditions for which alkylene attack is more likely for all species. A type 3 end group would produce a tetrakis-(ethylene glycol) (TTEG) segment by this process, a TTEG segment would produce a pentakis(ethylene glycol) segment, and so on.

As mentioned earlier, in MEG-initiated EC polymerization both type 1 and type 2 end groups are present initially; however, only type 2 end groups are present during the latter stages of the polymerization, and our proposed mechanism accounts for this observation. Returning to Figure 13, the first step is the reaction of ethylene glycol with ethylene carbonate to form the intermediate I which contains two 2-hydroxyethyl carbonate (type 1) end groups. Since Harris has shown that MEG is consumed rapidly,[32] this implies high concentrations of I early in the polymerization; however, as the polymerization proceeds the concentration of I will decrease and the concentration of type 1 end groups will decrease. Initially, the reported[32] lack of type 1 end groups at the latter stages of the polymerization appears to be contradictory to the mechanism since they are important intermediates throughout the polymerization; however, we feel type 1 end groups are undoubtedly still present, but at a level below the levels detectable by NMR. Furthermore, if they are at a low level, then the mechanism would also predict a corresponding low level of MEG, which is reported to be the case.[32]

The above mechanism does not explicitly discuss the occurrence of transcarbonation reactions at carbonate
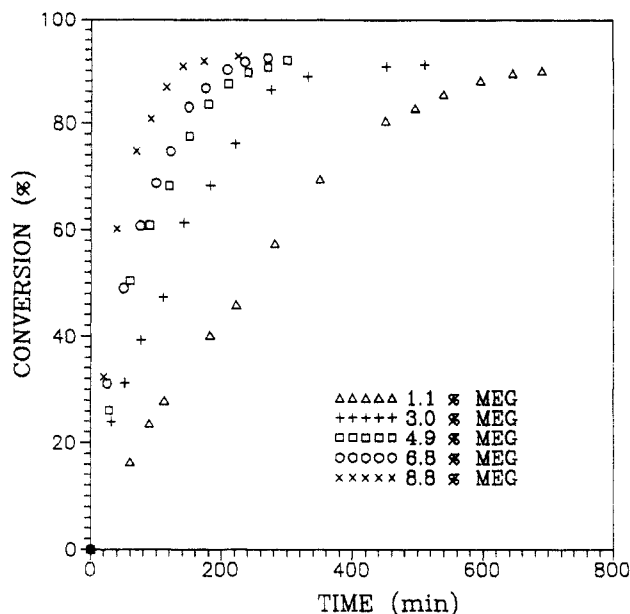
Figure 18. Conversion vs time curves for PEEC formation initiated by varying the [MEG]$_{added}$ and catalyzed by 0.50 wt % SS at 165 °C: [MEG]$_{added}$ = (△) 1.1, (+) 3.0, (□) 4.9, (○) 6.8, and (×) 8.8 mol %.

Figure 19. −ln ([EC]/[EC]$_0$) vs time for [MEG]$_{added}$ = 6.8 mol % at 165 °C.

linkages other than those at the chain termini. It is likely that all carbonate linkages undergo such reactions; however, since such interchain reactions do not alter the number of molecules in the system, the resultant $\bar{M}_n$ is not affected, although the molecular weight distribution, $\bar{M}_w/\bar{M}_n$, would be affected.[44] The kinetics of the polymerization, i.e., the disappearance of EC, will not be affected by interchain reactions, since monomer is not consumed or generated during these processes.

Kinetic Analysis of Polymerization. A series of polymerizations was conducted in which the [MEG]$_{added}$ was varied from 1.1 to 8.8 mol %. Figure 18 shows conversion versus time plots for the series. In all cases an ultimate conversion of about 92% was reached, and then a leveling off of conversion with time was observed. The rate of the polymerizations clearly increased with increasing [MEG]$_{added}$, confirming the suspected role of ethylene glycol as initiator in this polymerization. These results were found to yield linear first-order kinetic plots, and the result for the reaction with [MEG]$_{added}$ = 6.8 mol % is shown in Figure 19. A linear relationship exists up to about 220 min, implying first-order behavior during this reaction time. After 220 min a deviation from linearity was observed which is characteristic of the reaction becoming diffusion controlled.[45] Deviation from first-order behavior during the latter stages of the polymerization was seen for all reactions in the series of ([MEG]$_{added}$ from 1.1 to 8.8 mol %). Plots for all reactions in the series are shown in Figure 20, and for clarity only portions where first-order behavior was followed are shown. The linearity of the plots confirms that the polymerization is first order with respect to [EC] at the studied concentrations, and the absence of an appreciable y-intercept indicates that no induction period was present.

We next sought to establish whether our proposed mechanism was consistent with first-order kinetics. For the ideal case, i.e., truly alternating copolymer (Figures 13 and 14), and when reverse reactions are ignored, the disappearance of EC is due to four elementary steps, represented by the four terms on the right-hand side of eq 4. Here, as before, EC = ethylene carbonate, MEG = ethylene glycol, DEG = diethylene glycol, (1) = a PEEC oligomer of any size which carries a 2-hydroxyethyl
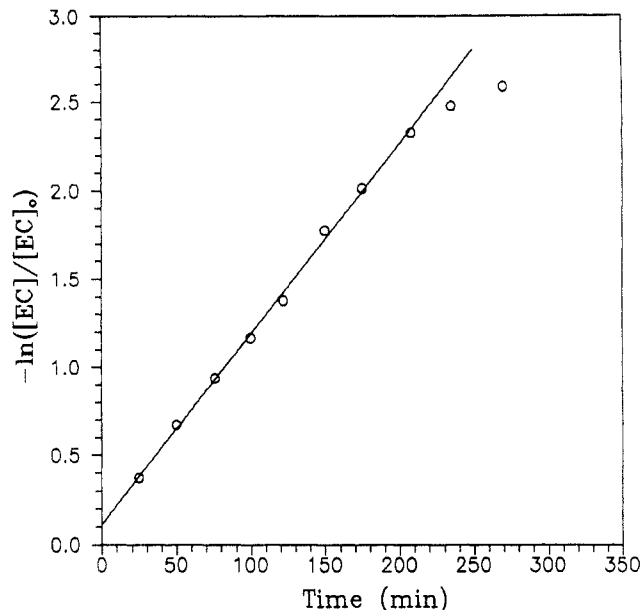

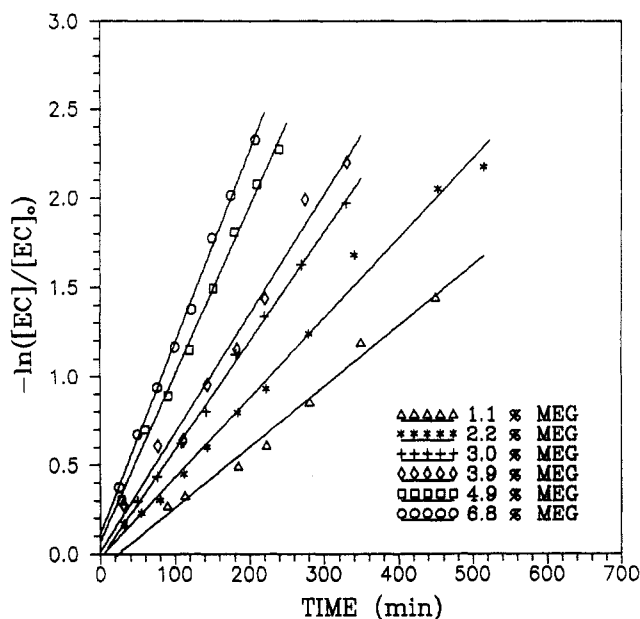**Figure 20.** −ln ([EC]/[EC]$_0$) vs time curves for varying [MEG]$_{added}$ at 165 °C: [MEG]$_{added}$ = (△) 1.1, (*) 2.2, (+) 3.0, (◇) 3.9, (□) 4.9 and (○) 6.8 mol %.

$$-d[EC]/dt = k_M[MEG][EC][C^*] +$$
$$k_D[DEG][EC][C^*] + k_{car}[(2)][EC][C^*] +$$
$$k_{alk}[(1)][EC][C^*] \quad (4)$$

carbonate, or type 1 end group, (2) = a PEEC oligomer of any size which carries a 2-hydroxyethyl ether, or type 2 end group, and [C*] = the active catalyst concentration. This relationship can be reduced to a simple form by making the assumption shown in eq 5, i.e., by assuming

$$k_p' = k_M = k_D = k_{car} \gg k_{alk} \quad (5)$$

that all three propagation rate constants involving carbonyl attack are essentially equal and represented by k_p' and are much larger than k_{alk}. This relative order of magnitudes of the rate constants is completely consistent with the central premise of the proposed mechanism, and it allows combination of the first three terms and elimination of the last term of eq 4. Elimination of the last term is

further justified considering the experimental fact[32] that type 1 end groups exist in very low concentrations except during the very early stages of the polymerization. At this stage it should be pointed out that if the hydroxyl functions of type 3 (and higher) end groups are similar in reactivity to type 2 end groups, eq 5 also holds for PEEC formation in which the CO_2 incorporation is less than 50 mol %.

Further simplification is achieved by defining a *pseudo* rate constant, k_p, which incorporates the concentration of the catalyst, ([C*]), eq 6. Since the reaction is hetero-

$$k_p = k_p'[C*] \qquad (6)$$

geneous, [C*] is difficult to calculate and in such cases is usually estimated by labeling the growing chain end,[46] a technique which is not amenable to our system. We tried to eliminate the question of [C*] by running the polymerizations in identical vessels with equal amounts of SS, which hopefully presents the same surface area to each polymerization. By thus attempting to maintain a constant catalyst concentration, we feel justified to assume that the active catalyst concentration, [C*], is approximately constant and can be incorporated into k_p.

Referring back to eq 4 and substituting in the simplifying relationships in eqs 5 and 6, the disappearance of EC with respect to time now reduces to eq 7.

$$-d[EC]/dt = k_p[EC]([MEG] + [DEG] + [(2)]) \qquad (7)$$

This relationship may be further simplified by assuming that the concentration of hydroxyl groups remains constant throughout the polymerization, as indicated in eq 8, a claim

$$[\sim OH] = \text{constant} \simeq [MEG] + [DEG] + [(2)] \qquad (8)$$

which is supported by our data shown earlier in Figures 10 and 11, i.e., that the number of growing chains is constant throughout the polymerization. Since the polymerizations were run below the boiling point of MEG, DEG, and other higher boiling glycols, then the total hydroxyl concentration should be equal to the initial ethylene glycol concentration, $[MEG]_0$, as shown in eq 9.

$$[MEG]_0 = [\sim OH] \simeq [MEG] + [DEG] + [(2)] \qquad (9)$$

Substituting eq 9 into eq 7 yields eq 10 which indicates that the reaction is first order with respect to EC. Upon

$$-d[EC]/dt = k_p[EC][MEG]_0 \qquad (10)$$

integration of eq 10 we obtain eq 11, which is the basis for the plots in Figure 20.

$$-\ln ([EC]/[EC]_0) = k_p[MEG]_0 t \qquad (11)$$

According to eq 11, the slope of the lines in Figure 20 is equal to $k_p[MEG]_0$. This quantity, as discussed earlier, is actually the sum of two terms as shown in eq 12. A plot

$$k_p[MEG]_0 = k_p[MEG]_{added} + k_p[MEG]_{in\ situ} \qquad (12)$$

of $k_p[MEG]_0$ versus $[MEG]_{added}$ is shown in Figure 21, where $[MEG]_{added}$ is expressed in terms of moles per liter; a linear relationship was observed with the slope equal to k_p and the intercept equal to $k_p[MEG]_{in\ situ}$. Solving for the slope and intercept simultaneously yields a value of k_p equal to $1.8 \times 10^{-4}\ M^{-1}\ s^{-1}$ and $[MEG]_{in\ situ}$ equal to 0.12 mol/L. In terms of mol %, $[MEG]_{in\ situ} = 0.79$ mol %, meaning that MEG is present initially at 0.56 wt %. The reported purity of EC is 99.5 wt %, with the remaining 0.5

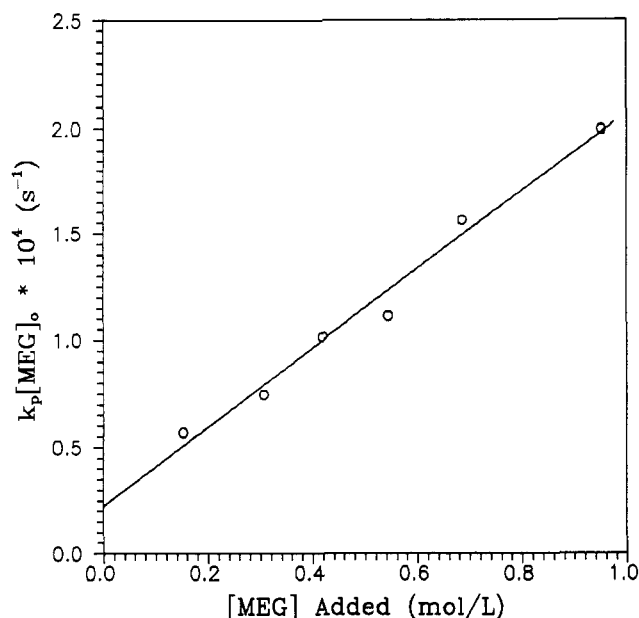**Figure 21.** Plot of $k_p[MEG]_0$ vs $[MEG]_{added}$ (mol/L) for PEEC formation at 165 °C.

wt % being mostly ethylene glycol.[47] This corresponds very well with our experimental results, suggesting that the proposed mechanism and kinetic treatment are valid.

Conclusions

The ring-opening polymerization of ethylene carbonate was investigated using DBTDA, DBTDL, DBTDM, and SS as catalysts. The organotin catalysts produced a kinetically slow reaction in all cases, and an ultimate conversion well below 100%. The introduction of additional catalyst produced higher conversions, suggesting catalyst decomposition during the course of polymerization which in the case of both DBTDA and DBTDL was confirmed by the presence of an intractable reaction byproduct. The GPC chromatograms of the organotin reaction mixtures indicated that DEG was formed throughout the course of the polymerization, and, although it was not quantified, its concentration may be related to the initial initiator concentration and perhaps nearly equal to it.

The use of SS resulted in a heterogeneous polymerization that was kinetically faster and more easily freed of catalyst residues. Ethylene glycol was shown to be an efficient initiator of the polymerization since the resultant $\bar{M}_n$ was inversely proportional to the initial concentration of purposefully added MEG, $[MEG]_{added}$. For the cases when $[MEG]_{added} = 0$, a limiting $\bar{M}_n$ was observed, suggesting that the initial ethylene glycol concentration is equal to the ethylene glycol externally added plus that initially present or generated in situ ($[MEG]_0 = [MEG]_{added} + [MEG]_{in\ situ}$). Drying of the SS catalyst resulted in the formation of higher molecular weight polymer which suggests that moisture also acts as an effective initiator, perhaps by hydrolyzing ethylene carbonate to form MEG. A mechanism was proposed to explain the limit on $\bar{M}_n$, as well as the steady-state formation of glycols throughout the polymerization. It consists of ring-opening steps in which carbonyl and alkylene attack are competitive and transcarbonation steps which are responsible for the steady-state concentrations of oligo(ethylene glycol) condensates. The mechanism is valid for the polymerization regardless of the glycol used as initiator since the steady-state formation of DEG is unaffected by the initiating species. The polymerization was shown to be first order

in [EC], and a kinetic treatment consistent with the proposed mechanism was put forward to explain this result. A *pseudo*-first-order rate constant of polymerization, k_p, was found to be equal to 1.8×10^{-4} M^{-1} s^{-1}, and the [MEG]$_{in\ situ}$ was found to be equal to 0.12 M, which is consistent with the reported purity of EC.

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