The hydrolytic polymerization of ε-caprolactone by triphenyltin acetate

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ABSTRACT
    The polymerization of ε-caprolactone (CL) using triphenyltin acetate has
been investigated. Polymers with broad MWD were obtained in almost quanti-
tative yield. After an initial induction period, the polymerization showed
zero order kinetics with respect to monomer and nearly first order with
respect to catalyst. The mechanism of the propagation reaction is proposed
to proceed via an ester alcoholysis, with initiation by traces of water.
The zero order kinetics are explained as follows: the tin catalyst is
coordinated by the cyclic lactone, monomer addition to the polymer chain in
the rate-determining step results in formation of an acyclic ester link,
which is no longer a strong donor, and leads to a coordinatively
unsaturated tin species.

INTRODUCTION
    Previous workers have studied the mechanism of lactone ring-opening
polymerization by organotin compounds (1-5). Organotin alkoxides react by
insertion at the ester bond, forming ester tail groups. Organotin
carboxylates cannot react with ester cleavage, as this would form a high
energy anhydride. Accordingly, organotin carboxylates do not initiate or
insert, but catalyze the reactions of alcohols or water with the lactone
ring.
    As yet no kinetics studies of organotin carboxylate - catalyzed lactone
polymerization have been reported. It seemed possible that tin(IV) carbo-
xylate, in which the available coordination sites would be fewer than in
tin(II) carboxylates, might provide a narrow molecular weight distribution.
Triphenyltin acetate was selected as the catalyst because of its availa-
bility and convenient physical properties. This paper is concerned with
the mechanism and kinetics of the polymerization of ε-caprolactone (CL)
using triphenyltin acetate as a catalyst.

EXPERIMENTAL
Instrumentation - Molecular weight data were obtained with size exclusion
chromatography, using a Waters Associates R-401 differential refractometer
and DuPont Zorbax PSM 1000-S, Zorbax PSM 300-S, Zorbax PSM 60-S, and IBM 10
μ-pore Type A columns.

Reagents - ε-Caprolactone CL (Aldrich or Fluka) was dried over molecular
sieves or calcium hydride, distilled under vacuum (b.p. 67°C/1 mmHg), and
stored over 4Å molecular sieves under nitrogen. Monomer dryness was
confirmed by the absence of a hydroxyl peak at 3610 cm^{-1} in the infrared
spectrum, which had been observed before the drying procedure.

Triphenyltin acetate (Morton Thiokol, Alfa Products) was used as received.

Standard Procedure for Polymerization - Triphenyltin acetate (37mg, 0.50 mole percent) and 2g of CL were placed in a polymerization tube. The reaction mixture was degassed via two successive freeze-thaw cycles and placed under nitrogen. The polymerization tube was placed in a 130°C silicon oil bath for the desired length of time. At the end of the reaction, the tube was quickly placed in a beaker of ice water to stop polymerization. The cooled polymer was dissolved in chloroform and precipitated into petroleum ether, filtered and dried under vacuum at room temperature. Each data point in the rate study had to be obtained individually because the viscosities of the polymers at high conversion prevented the removal of aliquots for study.

RESULTS
   The bulk polymerization of CL was investigated by performing seven reaction series in which the amounts of catalyst and added water or acetic acid were varied, as shown in Table 1. In each series, yield and molecular weight were determined as functions of time.

Table 1. Polymerization Runs of ε-Caprolactone in Bulk Catalyzed by Triphenyltin Acetate

Series	Mole% Cat.	Additive (mole%)	Zero Order Rate Constant Mole.$L^{-1}s^{-1}$ x 10^3
A	0.25	none	0.84
B	0.50	none	1.47
C	1.00	none	3.35
D	2.00	none	7.37
E	0.50	H_2O (0.25)	1.05
F	0.50	H_2O (0.50)	1.25
G	0.50	HOAc (0.25)	0.78

Conditions: 2g CL, 130°, bulk, under nitrogen atmosphere

Rates: Effect of Tin Concentration - In Series A, triphenyltin acetate (0.25 mole %) was used. As shown in Figure 1, the conversion increases linearly with time following a short induction period. Linearity continues until 90% conversion, indicating zero order kinetics with respect to monomer. The non-linear area of the curve above 90% yield is attributed to increased viscosity at high conversion, low monomer concentrations and experimental inaccuracies in this region.
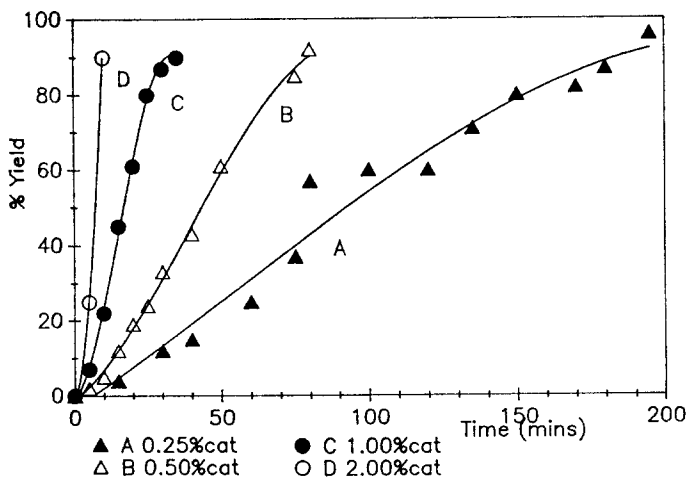
Figure 1. Zero order time-conversion curves for the polymerization of CL
initiated by Ph$_3$SnOAc at 130°C.

Series B, C, and D were performed using increasing amounts of
triphenyltin acetate. Figure 1 shows that the linear increase in percent
conversion after the induction period with time is general at all catalyst
concentrations, and shows the dependence of the polymerization rate on the
concentration of triphenyltin acetate. The rate constants k$_o$ are
calculated from the linear slopes and are listed in Table 1. A log-log
plot of k$_o$ versus the concentration of triphenyltin acetate gives a
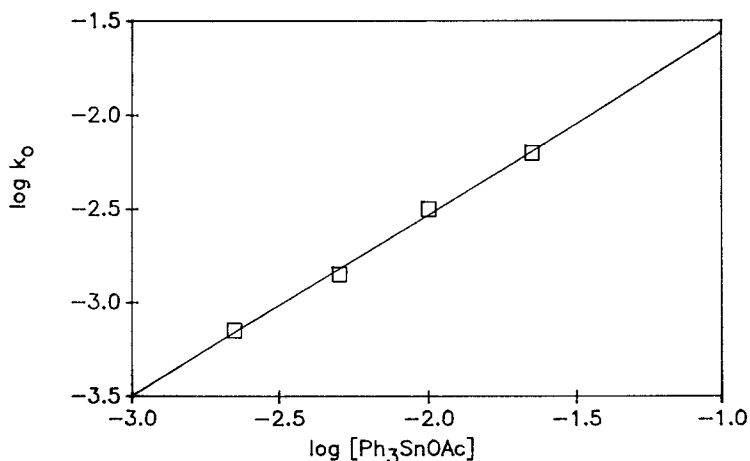straight line with a slope of 1.06 (Figure 2).

Figure 2. Log-log plot zero order rate constants k$_o$ versus catalyst
concentration

The molecular weight of the poly (CL) depends only on the conversion and
is independent of the concentration of triphenyltin acetate (Figure 3).

All polymers showed very broad molecular weight distributions.
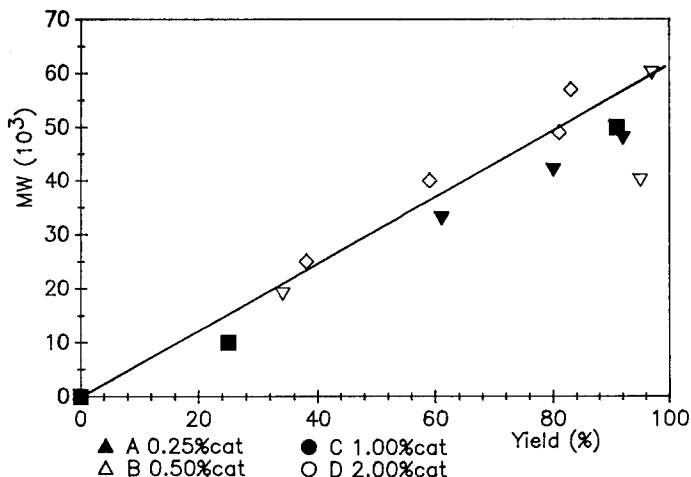

Figure 3. Molecular weight of poly (CL) as a function of conversion at different catalyst concentrations.

   The polymer after purification does not contain any tin. From all these facts we can conclude that triphenyltin acetate is a <u>catalyst</u>, not an initiator.

<u>Effect of Water</u> - Schindler et al.(2) reported that they were unable to remove the final traces of water from the monomer before polymerization despite careful efforts. The presence of trace water in our monomer was also suspected. If water acts as an initiator, we can calculate the water content in our original monomer. The molecular weight of the polymers obtained without added water is about 50,000 (DP=500). If each water molecule initiates one polymer chain, our monomer CL contains 0.2 mole% of water (0.03 wt% or 300 ppm).
   Accordingly, Series E was run with 0.50 mole percent triphenyltin acetate and 0.25 mole percent deliberately added water. The presence of 0.25 mole percent water increased the induction period. Following the induction period, the linear rate of polymerization became slightly slower than without added water (Table 1). The presence of 0.25 mole percent water in Series E resulted in somewhat lower molecular weights with respect to percent conversion. As shown in Run F, the presence of 0.50 mole percent added water produced only the same effect with respect to the length of the induction period, the rate of polymerization, and the molecular weight decrease. Accordingly, water acts as a (rather ineffective) <u>initiator</u>.

<u>Effect of Acetic Acid</u> - If water initiates the polymerization, a carboxylic acid end group is formed in the initiation step by ring-opening of CL. Accordingly, Series G polymerizations were performed with 0.25 mole percent acetic acid present in the reaction mixture. Added acetic acid causes the induction period to increase significantly in length (25 minutes versus 10

minutes for the blank). When the induction period is over, polymerization proceeds in a linear fashion at a slower rate (k_o = 0.78 x 10^{-3} mole L^{-1} s^{-1} versus k_o = 1.47 x 10^{-3} mole L^{-1} s^{-1} for the blank). Accordingly, carboxylic acid is a mild _retarder_. The molecular weight of the polymer obtained is not affected by the acid present.

Mechanism- We propose the following mechanism for the tin-catalyzed alcoholysis reaction.

First CL is a cis-lactone, and, like its familiar relative γ-butyrolactone, is a dipolar aprotic solvent. We assume that triphenyltin acetate dissolves in it with coordination of two CL molecules to form a hexacoordinate tin-IV species. This coordination makes the carbonyl group of CL more electrophilic.
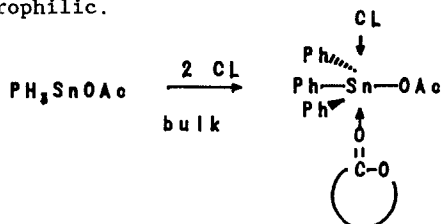
In the slow rate-determining step, the nucleophilic hydroxyl end group of the growing polymer reacts at the C=O→Sn group. Significantly in our proposed mechanism, the new ester bond forms in the s-trans conformation and the carbonyl loses its donating power. Therefore the tin becomes coordinatively unsaturated (shaded orbital). Rapid combination of a new CL molecule to this vacant orbital restores the original hexacoordinate tin species. This sequence reasonably explains the lack of dependence of polymerization rate on CL concentration.
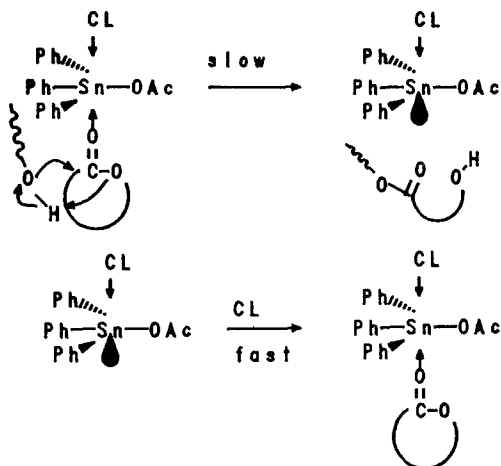
The induction periods we observe are ascribed to the intermediacy of ε-hydroxycaproic acid. Here chelation holds the carboxyl function near the tin, interfering with its catalytic activity. We showed that external carboxyl groups act as retarders. Only when the chain grows past this "bottle-neck" size can the growth rate reach its maximum linear value. Broad MWD's find their explanation in terms of these several propagating sites.

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