THE POLYMERIZATION OF ε–CAPROLACTUM—III.

INITIATION BY TIN COMPOUNDS

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Abstract—The polymerization of ε-caprolactam initiated by weak acids and bases has been reported previously.[1,2] To extend these observations to Lewis acids, a variety of compounds of tin (II) and (IV) have been examined as possible initiates. The following compounds have been found to be effective: stannic chloride, stannous chloride, stannous octate. Other compounds including stannic fluoride, bromide and iodide are unstable under the reaction conditions. All tin compounds appear to decompose in molten caprolactam and to cause marked discoloration of the resulting polymer. In general, they are unsuitable as initiators.

INTRODUCTION

THE MECHANISM of the polymerization of caprolactam initiated by amines[1] and acids[2] has been reported previously. The general process of initiation was interpreted as that of protonation of the amino group,

$$\text{i.e. (I)} \quad \text{Amine.} \quad RNH_2 + \underset{|\quad|}{NHCO} \rightleftharpoons R\overset{+}{N}H_3 \ \overset{-}{N} \underset{|\quad|}{CO}$$

$$\text{(II)} \quad \text{Acid.} \quad HA + \underset{|\quad|}{NHCO} \rightleftharpoons \overset{+}{N}H_2 - \underset{|\quad|}{CO} \ A^-$$

followed in both cases by propagation involving addition of the protonated species to the CL unit with subsequent ring opening and regeneration of the propagating species,

$$\text{i.e.,} \quad -\overset{+}{N}H_2 + NH\!-\!\underset{\diagdown\diagup}{CO} \rightarrow -N\!-\!CO\,(CH_2)_5\!-\!\overset{+}{N}H_3$$
$$\qquad\qquad\qquad (CH_2)_5$$

In the present work strong non-protonating Lewis acids of the metal halide type are used as the initiating species in order to develop a more general mechanism of acid-base initiation.

EXPERIMENTAL

Polymerization procedure has been described elsewhere.[1] Stannic chloride was purified by vacuum distillation. Stannous chloride, stannous octoate, stannic fluoride, stannic bromide and stannic iodide were used as purified research samples under anhydrous conditions.

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RESULTS

(1) *Stannic chloride initiation*

The dilatometric polymerization rate curves at 230° are shown in Fig. 1 for various concentrations of stannic chloride. There is an apparent induction period in which the rate increases to a maximum value, but this period is short compared with that found with weak acids[2] and bases.[1] Allowing for a heating time correction for the dilatometers, the induction period varies inversely with the concentration of stannic chloride, see Fig. 2. After the initial period of increasing rate, the rate of polymerization is constant with conversion. This final rate (max. rate) is directly proportional to the initial concentration of stannic chloride, Table 1.
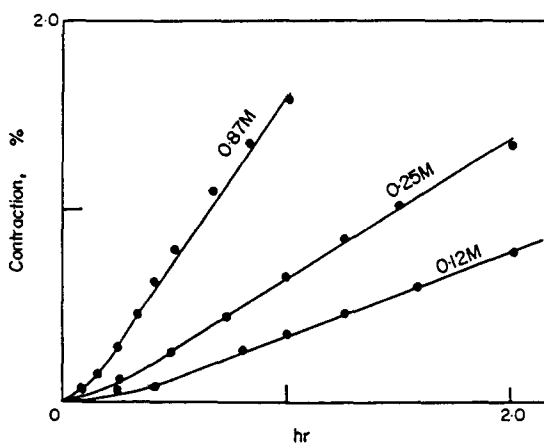
FIG. 1. Stannic chloride initiated polymerizations.
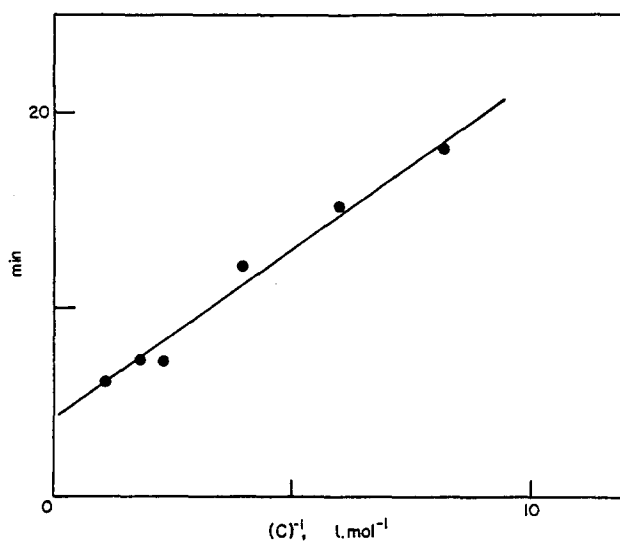
FIG. 2. Induction periods for stannic chloride initiation.

TABLE 1. STANNIC CHLORIDE INITIATION

(a) Initiator dependence at 230°
   Bulk polymerization   Monomer concn. $= 7\cdot89$ mol. $1.^{-1}$

Initiator concn. (mol. $1.^{-1}$)	Induction period (min)	Max. rate (% contr. hr^{-1})
0·122	18	0·424
0·166	15	0·591
0·251	12	0·803
0·432	7	1·55
0·540	7	1·62
0·870	6	1·98

(b) Monomer dependence (Dekalin as diluent) at 200°
   Initiator conc. $= 0\cdot305$ mol. $1.^{-1}$

Monomer concn. [M] (mol. $1.^{-1}$)	Max. rate Rp (% contr. $hr.^{-1}$)	$\dfrac{Rp}{[M]}$ ($\times 10^2$)
7·82	0·147	1·87
6·87	0·125	1·82
5·93	0·113	1·96
5·71	0·111	1·94
4·96	0·098	1·95

(c) Activation energy
   Initiator concn. $= 0\cdot325$ mol. $1.^{-1}$
   Monomer concn. $= 7\cdot8$ mol. $1.^{-1}$

Temp. (°C)	Max. rate (% contr. $hr.^{-1}$)	Activation energy (kcal $mol.^{-1}$)
170	0·050	23 ± 2
200	0·163	
230	1·173	

The dependence of the rate on monomer concentration was also studied using dekalin as a diluent at 200° (below the boiling point). At this temperature dekalin was found to be a satisfactory solvent for the polymer, provided the reaction was restricted to less than 10 per cent conversion. The polymerization was first order with respect to monomer.

The overall activation energy for the maximum polymerization rates over the range 170–230° was $23\cdot0 \pm 2\cdot0$ kcal $mol.^{-1}$; the Arrhenius factor was 10^9 min^{-1}. This value compares with $18\cdot3$ kcal $mol.^{-1}$ and 10^6 min^{-1} previously found for the benzylamine hydrogen chloride initiated polymerization.[1]

The initiator showed obvious signs of decomposing with increasing polymerization as the polymer was stained light brown; the colour could not be removed by reprecipitation from trifluoroethanol.

(2) *Stannous chloride initiation*

Several polymerizations were carried out at 230° using stannous chloride as initiator in order to determine the mode of action of stannic chloride in initiation. However, the characteristics of the polymerizations were completely different. In general,

stannous chloride initiated polymerizations were considerably slower than those of stannic chloride. At low concentrations there were very lengthy induction periods which rapidly decreased with increasing concentration. No induction period was present at all at the higher concentration of initiator, but the initial high rate of conversion decreased with conversion to a constant value independent of the initial concentration of stannous chloride. This limiting value almost corresponded in value with the maximum rate attained in the slower polymerizations, see Fig. 3 and Table 2.
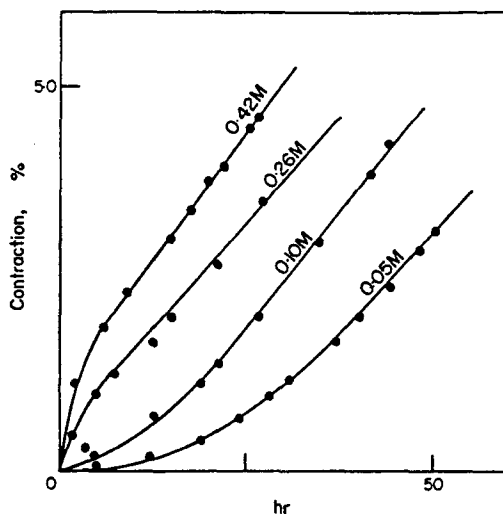
FIG. 3. Stannous chloride initiated polymerizations.

TABLE 2. STANNOUS CHLORIDE INITIATION

Initiator dependence at 230°
Bulk polymerization   Monomer concn. = 7·89 mol. l.$^{-1}$

Initiator concn. (mol. l.$^{-1}$)	Max. rate (% contr. hr^{-1})	Final rate (% contr. hr^{-1})	Induction period (hr)
0·052	0·099	0·099	21·5
0·103	0·125	0·125	14·5
0·120	0·134	0·134	12·0
0·263	0·268	0·123	0·0
0·398	0·355	0·132	0·0
0·423	0·374	0·128	0·0

There seem to be two distinct concentration regions. At low concentration there is an apparent induction period, which varies with the reciprocal concentration of the initiator. The final maximum rate of conversion exhibited a half order dependence on initiator concentration; at concentrations higher than 0·1 M, a linear dependence was observed between maximum rate and initiator concentration—see Fig. 4.

It is unlikely that the zero-order dependence of the limiting final rate of conversion can be attributed to initiation by a SnCl$_2$/co-catalyst complex in which the co-catalyst is a trace impurity in the Cl. Instead, it must reflect on the nature of the termination process in the polymerization.
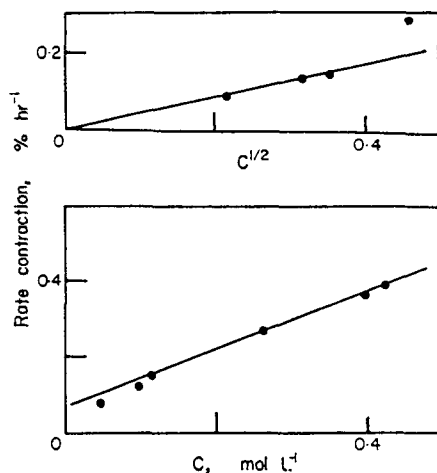
FIG. 4. Initiator-reaction order.

The polymerization media darkened progressively and the polymer isolated was discoloured. The stannous chloride was obviously decomposing.[3]

(3) Stannous octoate initiation

The stannous octoate initated polymerizations studied at 230° are listed in Table 3. The conversion–time curves are similar to those for stannic chloride initiated polymerization in that they exhibit rather short induction periods and the maximum rate

TABLE 3. STANNOUS OCTOATE INITIATION

Bulk polymerization at 230° Monomer concn. = 7·89 mol. l.⁻¹			
Initiator concn. [I] (mol. l.⁻¹)	Max. rate R_p (% contr. hr⁻¹)	$\frac{R_p}{[I]}$	Induction period (hr)
0·105	0·182	1·73	1·0
0·115	0·187	1·63	1·0
0·162	0·246	1·52	0·3
0·215	0·371	1·72	0·0
0·230	0·403	1·75	0·0

is linearly dependent on concentration. The conversion rate per unit mass of initiator is less than that for stannic chloride. There is no fall in rate with conversion, and in general stannous octoate is more analogous to stannic chloride polymerizations than stannous chloride—see Fig. 5.

Stannous octoate, despite the low rates of conversion, has a distinct advantage over all the other compounds of tin in that the resulting polymer was less discoloured and there were less signs of decomposition of the tin compound.

The octoate ion alone could not be the initiating species, and give these rates of polymerization. Carboxylic acids are slow to initiate the polymerization of CL² and their salts are ineffective.
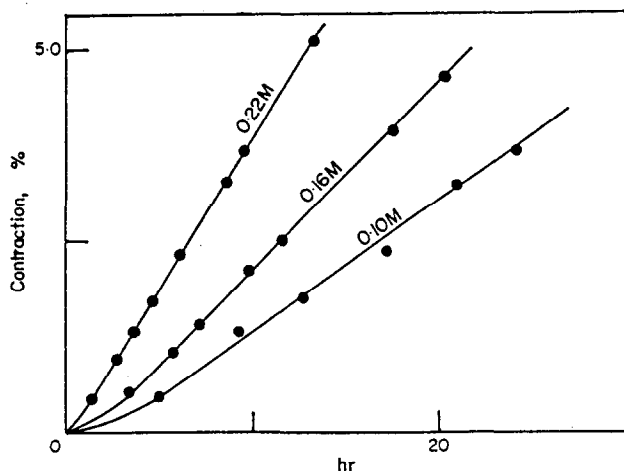
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FIG. 5. Stannous octoate initiated polymerizations.

(4) *Other tin compounds*

Stannous thiocyanate, stannous sulphate, stannic fluoride, stannic bromide and stannic iodide were also studied as effective initiators. The strong reducing environment of CL rapidly decomposed them.

Stannous thiocyanate proved to be insoluble in CL, and no polymerization was observed.

Stannous sulphate was partly soluble, and polymerized CL to a dark brown product. Kinetic studies were not attempted due to the heterogeneity of the system. Stannic fluoride decomposed with the evolution of a gas. Stannic bromide and stannic iodide rapidly turned the molten CL black. Volume contraction did occur but no polymer was isolated.

DISCUSSION

The polymers obtained from the tin chloride initiators were discoloured. Repeated extraction with methanol, and reprecipitation from trifluoroethanol did not remove the discolouration. These initiators are obviously unstable and this clearly limits the usefulness of these compounds as CL initiators. It also makes interpretation of the kinetics impossible.

End group analysis and molecular weight analysis cannot have any significance in the presence of a decomposition reaction.

Recently[4] it has been shown that CL does form a solid complex with stannic chloride, with the formula $SnCl_4(CL)_2$. Infra-red analysis showed that the carbonyl band of the lactam ring shifted from 1665 cm^{-1} to 1600 cm^{-1}. The amide N—H stretching frequency was unaltered. Accordingly, it was suggested that the adduct has the formula

$$\left(\begin{array}{c} (CH_2)_5{-}C{=}O \\ \diagdown \diagup \\ NH \end{array}\right)_2 \rightarrow SnCl_4$$
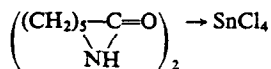
This formula was substantiated by chemical analysis, and the decomposition pattern in the mass spectrometer. It is also analogous to that proposed for the complexes produced with carboxylic acid and stannic chloride.[5]

This solid complex is not acidic. It would not protonate *p*-nitro diphenylamine, and it decomposed at temperatures approaching its melting point with the evolution of 2 moles of HCl per mole complex, producing a black tarry substance. This black substance contained no N—H stretching frequency in its i.r. spectra and was obviously polymeric. A suggested structure was
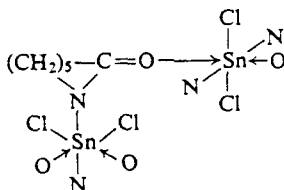
In the case of the tin chloride catalysed polymerizations, the true initiating species is hydrogen chloride. Silicon tetrachloride, which is incapable of forming complexes of the $SnCl_4$ type, was also found to be a very effective initiator. The product was a highly crossed-linked gel. The hydrogen chloride produced during decomposition of $SiCl_4$ initiated the polymerization, and Si—O or Si—N cross-links were formed.

Further consideration of the mechanism does not seem justified because the limited stability of tin compounds restricts their applications.

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Résumé—On a déjà décrit précédemment[1,2] la polymérisation du ε-caprolactame sous l'action d'acides et de bases faibles. Pour étendre cette étude à des acides de Lewis on a examiné une série de dérivés de l'étain (II) et (IV) comme agents d'amorçage possibles. Les composés suivants se sont révélés actifs: chlorure stannique, chlorure stanneux, octoate stanneux. D'autres dérivés comme les fluorure, bromure et iodure stanneux sont instables dans les conditions réactionnelles. Tous les composés de l'étain semblent se décomposer dans le caprolactame fondu et conduisent à une coloration importante du polymère formé. D'une manière générale, ils sont inutilisables comme agents d'amorçage.

Sommario—È stato già riportato precedentemente[1,2] lo studio sulla polimerizzazione dell' ε-caprolattame iniziarto da acidi e basi deboli. Per estendere le osservazioni agli acidi di Lewis, sono stati esaminati come possibili iniziatori una serie di composti della Stagno (II) e (IV). Composti efficaci sono risultati il cloruro stannico, il cloruro stannoso e l'ottoato di calcio. Altri composti tra i quali fluoruro, bromuro e ioduro stannico, si sono dimostrati instabili nelle condizioni di reazione. Tutti i composti dello Stagno agiscono decomponendo parzialmente in caprolattame fuso e causando una decolorazione marcata del polimero risultante. In generale si possono considerare poco adatti come iniziatori.

Zusammenfassung—Über die Polymerisation von ϵCaprolactem unter Initiierung durch schwache Säuren und Basen ist schon berichtet worden.[1,2] Um diese Untersuchungen auf Lewissäuren auszudehnen, wurde eine Anzahl von Zinn IV Verbindungen als Initiatoren untersucht. Die folgenden Verbindungen wurden als wirksam gefunden: Zinn IV chlorid, Zinn II chlorid und Zinn II oktoat. Andere Verbindungen einschliesslich Zinn IV fluorid bromid und -jodid waren unter den Reaktionsbedingungen instabil. Alle Zinnverbindungen scheinen sich in geschmolzenem Caprolactam zu zersetzen und eine ausgeprägte Verfärbung des entstehenden Polymeren zu verursachen. Im allgemeinen sind sie als Initiatoren ungeeignet.