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Soluble Bimetallic Oxoalkoxide Catalysts. IV. Ring-Opening Polymerization of β-Propiolactone

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Soluble Bimetallic Oxoalkoxide Catalysts. IV.* Ring-Opening Polymerization of β-Propiolactone

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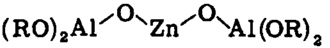
ABSTRACT

The polymerization of β-propiolactone by aluminum-zinc oxoalkoxides corresponding to the structure  $(RO)_2Al{\diagup}\overset{O}{}{\diagdown}Zn{\diagup}\overset{O}{}{\diagdown}Al(OR)_2$ has been studied. The overall kinetics of the reaction follow a first current order in monomer and a first order in catalyst. Mechanistic studies also indicate that these initiators operate through selective acyl-oxygen cleavage of the lactone ring with insertion in the aluminum-oxygen bond. Moreover, the polymerization proceeds by a perfectly "living" process.

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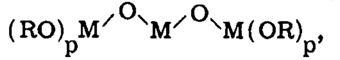
*For the preceding papers in this series, see N. Kohler, M. Osgan, and Ph. Teyssie, J. Polym. Sci., B, 6, 559 (1968); and M. Osgan, J. J. Pasero, and Ph. Teyssie, J. Polym. Sci., B, 8, 319 (1970).

INTRODUCTION

It has been known for a long time that β-propiolactone polymerizes to form a liquid or solid polyester by heating to 130 to 150°C in the presence of ferric chloride or to 60 to 80°C in the presence of sulfuric acid [1]. This polymerization has received further considerable attention following the discovery that certain organometallic catalysts are effective in promoting the formation of polylactones having extremely high molecular weights [2, 3].

We have recently reported the preparation of a new family of polynuclear compounds [4] containing several metal atoms (eventually different), linked together by oxygen bridges. These compounds have a well-defined structure, characterized by M—O—M' groupings, and corresponding to the general formula  $(RO)_pM\overset{O}{\diagup\diagdown}M\overset{O}{\diagup\diagdown}M(OR)_p$, where R is usually an hydrocarbon group. The presence of M—O—M' groupings in their structure makes these compounds excellent stereospecific catalysts for the polymerization of methyloxirane (and thiirane) to high molecular weight polyethers [5, 6].

In addition, as reported elsewhere [7], these new catalysts proved to be excellent initiators for ε-caprolactone polymerization. In fact, they rank among the best ones for the homogeneous polymerization of this monomer, and a particularly interesting feature of the reaction is its perfectly "living" character.

In this paper we present the results of our investigations of β-propiolactone polymerization initiated by this new family of soluble bimetallic oxoalkoxides.

EXPERIMENTAL

Reagents

β-Propiolactone. The commercial reagent (pure grade, Fluka) was dried over CaH_2 at room temperature, and distilled under reduced pressure (10^{-3} Torr).

Dichloromethane (pure grade) was dried by refluxing over CaH_2 and distilled under argon atmosphere.

Polymerization Procedure

The polymerizations were carried out under magnetic stirring in a flask previously dried and flushed with argon, which was kept at constant temperature (±1°C) in a thermostated bath for the necessary period of time. The reactions were stopped by addition of about 50 ml of a 2-N HCl solution.

The catalyst residues were extracted four times with dilute aqueous HCl, and the dichloromethane solution was washed with distilled water up to neutral PH. The polymeric product was further purified by precipitation of this solution in an excess of heptane (after elimination of about 2/3 of the dichloromethane under reduced pressure), and dried for 24 hr at room temperature under vacuum.

Separation of the Product Resulting from the First Step of the Polymerization

Using β-propiolactone/catalyst molar ratios from 0.5 to 1, the main product obtained corresponds to the fixation of one molecule of monomer per active catalytic center. After hydrolysis of the reaction products and extraction (four times) of the catalyst residues by a dilute HCl aqueous solution, the product of this first insertion step was isolated by distillation under reduced pressure (T = 60 to 70°C under 10^{-3} Torr), and purified by preparative GLC (on a Varian 2800 Chromatograph, equipped with a silicone column maintained at 280°C).

Molecular Weight Determination

The number-average molecular weights were measured by vapor pressure osmometry in chloroform at 32°C (with a precision of about ±5% on a Knauer apparatus).

Spectra

Infrared spectra were recorded on liquid films, using a Perkin-Elmer model 21 infrared spectrometer. NMR spectra were obtained from carbon tetrachloride solutions on a Varian HA-100 spectrometer; T.M.S. was used as an internal reference.

RESULTS AND DISCUSSION

Activity Test

High molecular weight polyesters can be prepared from lactones in the presence of anionic or cationic catalysts, and numerous examples of such systems have been described in the literature [2]. More recently, in the course of a systematic investigation of heterocyclic monomer polymerizations by this new family of soluble bimetallic oxoalkoxides catalysts [4, 7], we have been led to test their activity in β-propiolactone polymerization. As indicated by the results gathered in Table 1, aluminum-zinc oxoalkoxides rank among the best catalysts discovered in this field.

Their high activity has consequently prompted a detailed study of the characteristic features and mechanism of the corresponding polymerization reaction, the more as these compounds promote, in the limits of the experimental error (less than 1%), a practically quantitative conversion of β-propiolactone to the corresponding polyester (in other words, the equilibrium is shifted toward the open chains to an extent of more than 99%).

"Living" Character of the Polymerization

A perfect "living" behavior has been observed during the polymerization of β-propiolactone in the presence of aluminum-zinc oxoalkoxides. This has been ascertained, besides certain polymerization resumption experiments, by the straight-line relationship between the $\overline{DP}$ of the polymer obtained and the monomer/catalyst molar ratio presented in Fig. 1.

Thanks to this living character of the process, an accurate control of the polymers molecular weight and nature of end-groups is easily performed. Furthermore, by withdrawing of the product as soon as the polymerization comes to completion, a narrow molecular weight distribution may be expected as indicated by the $\overline{M}_w/\overline{M}_n$ values of 1.05 to 1.10 obtained in the case of ϵ-caprolactone polymerization [5].

Kinetics

As shown in Fig. 2, the β-propiolactone polymerization is first current order in monomer in the presence of $Zn[OAl(O\text{-}i\text{-}C_3H_7)_2]_2$ in dichloromethane at 40 °C.

Under the same conditions, this polymerization is first order in catalyst as shown in Fig. 3.

In conclusion, the polymerization proceeds regularly, following a simple overall kinetics of the form $R_p = k[M][C]$, which could fit in very well with a coordination-type mechanism.

TABLE 1. Polymerization of β-Propiolactone

Catalyst	[M]/[C] molar ratio	Temperature (°C)	Solvent	Time (hr)	Extent of polymerization (%)
$Zn[OAl(O\text{-}i\text{-}C_3H_7)_2]_2$	142	40	CH_2Cl_2 ([M] = 1 mole/liter)	10	51.0
$Zn[OAl(O\text{-}i\text{-}C_3H_7)_2]_2$	140	0	None	15	84.0
$Al(O\text{-}i\text{-}C_3H_7)_3$ [2]	100	0	None	21	62.2
$Zn(C_2H_5)_2$ [2]	100	15	None	24	1.3
Li_2-benzophenone [2]	100	15	None	72	6.8

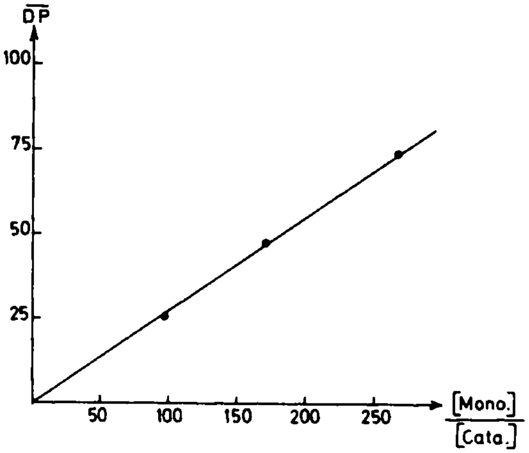


FIG. 1. Dependence of $\overline{DP}$ on [monomer]/[catalyst] ratio in the polymerization by Zn[OAl(O-n-C_4H_9)$_2$]$_2$. Conditions: T = 40°C; solvent, CH_2Cl_2; [M] = 1 mole/liter.

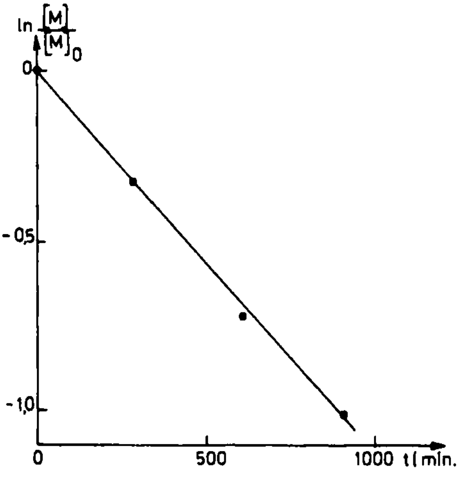


FIG. 2. Monomer consumption as a function of time. Conditions: T = 40°C; solvent, CH_2Cl_2; [M] = 1 mole/liter; [M]/[C] = 142; catalyst, Zn[OAl(O-i-C_3H_7)$_2$]$_2$. Under these conditions, K' = K[C] = 1.12×10^{-3}/min.

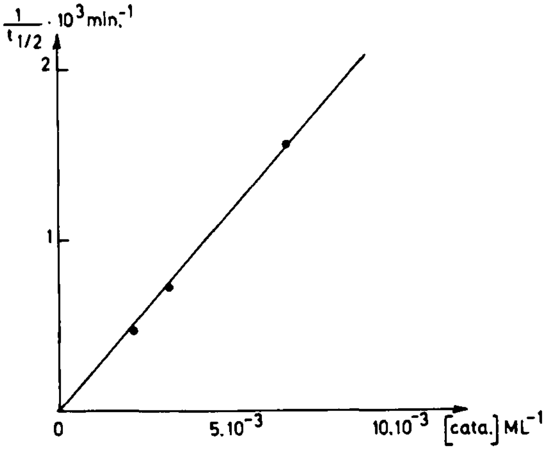
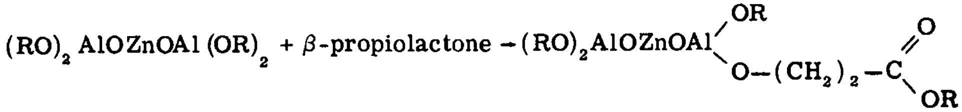


FIG. 3. Dependence of the half-reaction time on catalyst concentration. Conditions: T = 40°C; solvent, CH_2Cl_2; $[M] = 1$ mole/liter; catalyst, $Zn[OAl(O\text{-}i\text{-}C_3H_7)_2]_2$.

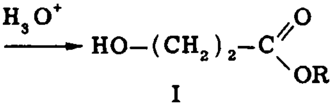
Mechanism of the Chain Growth

Thanks to the "living" character of the propagation reaction, it is possible to perform a polymerization where the extent of the growing chain is limited to one (or two) monomeric units. This has been realized with β-propiolactone/catalyst molar ratios from 0.5 to 1. After completion of the polymerization and hydrolysis of the mixture, the main product of this first step was isolated (see Experimental section), and characterized by its IR (Table 2) and NMR (Table 3) spectra, together with molecular weight determination and elementary analysis (Table 4).

All of the data obtained fit in very well with a process involving successive insertions of the lactone molecules into an Al—OR bond of the catalyst by a selective acyl-oxygen cleavage of the lactone ring in a way which maintains the chain bound to the catalyst (by an Al—O link) throughout the polymerization reaction:



$$(RO)_2AlOZnOAl(OR)_2 + \beta\text{-propiolactone} \rightarrow (RO)_2AlOZnOAl\begin{matrix} OR \\ O-(CH_2)_2-C\begin{matrix} {}^{\nearrow}O \\ {}_{\searrow}OR \end{matrix}\end{matrix}$$



$$\xrightarrow{H_3O^+} HO{-}(CH_2)_2{-}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown OR\end{smallmatrix} \quad + \text{Al and Zn salts} \qquad (OR = O{-}n{-}C_4H_9)$$

I

The Number of Active Centers

As reported elsewhere for the lactones polymerizations initiated by both bimetallic oxoalkoxides [5, 8] and aluminum alkoxides [9], the number of the active OR groups may depend closely on the composition of the reaction medium (nature of solvent, presence of ligands).

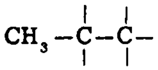
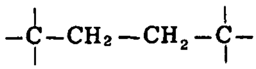
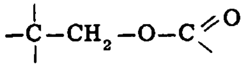
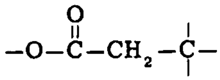
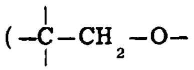
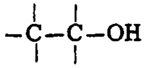
In the β-propiolactone polymerization initiated by a bimetallic oxoalkoxide in dichloromethane as solvent, the slope (0.27) of the straight-line relationship between the degree of polymerization and monomer/catalyst ratios (Fig. 1) allows us to conclude that, in the limit of experimental error (less than 8%), one catalytic unit initiates four polyester chains; in other words, thanks to a complete dynamic dissociation of the catalyst, all four OR groups are indeed precursors for a growing chain, following the mechanism demonstrated previously.

TABLE 2. IR Spectrum of the First-Step Product in β-Propiolactone Polymerization Initiated by $Zn[OAl(O{-}n{-}C_4H_9)_2]_2$

Assignments	Model absorption frequency[a] (cm^{-1})	Observed absorption frequency (cm^{-1})
O–H stretching	3450	3500
C=O stretching	1725	1737
C–O stretching (in $O{=}C\begin{smallmatrix}/\\ \diagdown O-\end{smallmatrix}$)	1175	1175
C–O stretching (in $-\overset{\vert}{\underset{\vert}{C}}-OH$)	1050	1050

[a] Data corresponding to the model compound $HO(CH_2)_5COO{-}n{-}C_4H_9$.

TABLE 3. NMR Spectrum of the First-Step Product in β-Propiolactone Polymerization Initiated by $Zn[OAl(O-n-C_4H_9)_2]_2$

	Model compounds		Observed	
Assignments	δ (ppm)	Relative peak areas	δ^b (ppm)	Relative peak areas
 $CH_3-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$	0.90	3	0.86	2.9
 $-\overset{\vert}{\underset{\vert}{C}}-CH_2-CH_2-\overset{\vert}{\underset{\vert}{C}}-$	1.45	4	1.41	4.1
 $-\overset{\vert}{\underset{\vert}{C}}-CH_2-O-C\overset{\nearrow O}{\searrow}$	3.98	2	3.99	2.0
 $-O-\overset{O}{\overset{\Vert}{C}}-CH_2-\overset{\vert}{\underset{\vert}{C}}-$	2.21	2	2.30	1.9
 $(-\overset{\vert}{\underset{\vert}{C}}-CH_2-O-$	3.45	2	3.71	2.0
 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-OH$	(3-4) variable	1	3.46	1.0

[a] Data corresponding to the model compound $HO(CH_2)_5COO-n-C_4H_9$.
[b] Downfield from TMS internal standard in carbon tetrachloride.

TABLE 4. Molecular Weight and Elementary Analysis of the First-Step Product in β-Propiolactone Polymerization Initiated by $Zn[OAl(O-n-C_4H_9)_2]_2$

Characterization type	Calculated[a]	Found
Molecular weight	146	149
C (%)	57.53	58.60
H (%)	9.58	9.32
O (%)	32.89	32.08

[a] Data corresponding to Compound I.

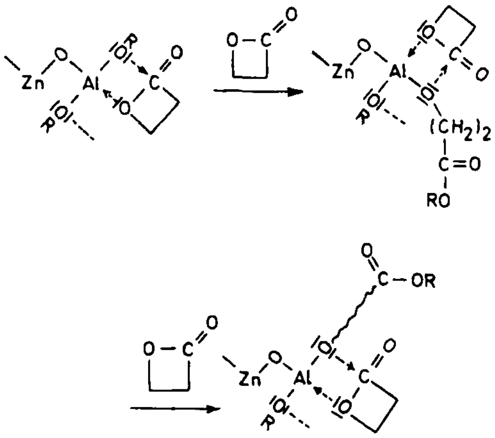


FIG. 4. β-Propiolactone polymerization mechanism in the presence of aluminum-zinc oxoalkoxides.

CONCLUSION

This type of polymerization basically obeys a simple insertion mechanism of the monomer into the Al—OR bond, a mechanism which is most probably of a coordinative-anionic nature. Kinetic and structure data indicate that the chain growth is a "living" process.

Accordingly, the reaction scheme shown in Fig. 4 can be proposed. As could be anticipated, there is a close similarity between this scheme and that one reported elsewhere [5, 7] for the polymerization of ϵ-caprolactone by these bimetallic oxoalkoxides. It must be remembered, however, that β-propiolactones are able to undergo a different type of ring-opening, yielding the corresponding α,β-unsaturated acids through alkyl-oxygen bond cleavage, when reacted under different conditions (same catalyst under drastic temperature condition or in the presence of different catalysts). These systems obviously offer interesting potentialities toward the formation of high molecular weight polyesters, the control of their molecular weights and molecular weight distributions, and the synthesis of new block copolymers.

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REFERENCES

[1] T. L. Gresham, J. E. Jansen, and F. W. Shaver, J. Amer. Chem. Soc., 70, 998 (1948).
[2] S. Inoue, Y. Tomoi, T. Tsuruta, and J. Furukawa, Makromol. Chem., 43, 229 (1961).
[3] R. D. Lundberg and E. F. Cox, Ring-Opening Polymerization, Vol. 2 (K. C. Frisch, ed.), Dekker, New York, 1969, pp. 247-302.
[4] T. Ouhadi, J. P. Bioul, and Ph. Teyssie, "Synthesis of a New Family of Soluble Bimetallic Oxoalkoxides," In Preparation.
[5] T. Ouhadi, Ph.D. Thesis, University of Liège, 1973.
[6] J. P. Bioul, Ph.D. Thesis, University of Liège, 1973.
[7] A. Hamitou, R. Jerome, A. J. Hubert, and Ph. Teyssie, Macromolecules, 6, 651 (1973).
[8] T. Ouhadi, A. Hamitou, R. Jerome, and Ph. Teyssie, "Soluble Bimetallic Oxoalkoxide Catalysts. V. Lactones polymerization," In Preparation.
[9] T. Ouhadi, C. Stevens, and Ph. Teyssie, "Mechanism of ϵ-Caprolactone Polymerization by Aluminum Alkoxides," Makromol. Chem., In Press.

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