

NOTES

**Asymmetric Selective Polymerization of β -Butyrolactone
Catalyzed by Optically Active Cobalt Complex/
Triethylaluminum System**

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(Received July 28, 1987)

KEY WORDS Asymmetric Selective Polymerization / β -Butyrolactone /
Chiral Catalyst System / Optically Active Cobalt(salen) Type Complex /
Triethylaluminum / Chiral Recognition / Optically Active Polyester /

In the chemistry of coenzyme B₁₂, the Co^I species has attracted much attention for its high nucleophilicity.^{1,2} As models of coenzyme B₁₂, various kinds of square planar quadridentate complexes including cobaloxime² and Co(salen)³ have been investigated. Optically active cobalt(salen) type complex, *N,N'*-disalicylidene-(1*R*,2*R*)-1,2-cyclohexanediaminocobalt(II), Co*,⁴ was prepared, and monovalent species of Co* have also been investigated⁴ in relation to asymmetric isomerization of oxirane to ketone. It was found that many kinds of metals or organometals, such as Na, LiBu, ZnEt₂, MgEt₂, AlEt₃, reduce the Co* to monovalent species.

Here we wish to report a new aspect of Co^I chemistry, catalyst as an asymmetric selective polymerization, taking the polymerization of β -butyrolactone as an example by the combination of Co* and AlEt₃. The optically active polyester obtained here by the catalysis of Co*/AlEt₃ is essentially the same material as the naturally occurring optically active poly- β -hydroxybutyrate, which has been attracting much attention⁵ recently as large-scale biotechnological production, because of its biodegradability and high tensile strength as thermoplastic.

EXPERIMENTAL

Reagents

The optically active cobalt(salen) type complex, Co*, was prepared according to procedure.⁴ Triethylaluminum was purified by distillation and stored under dry nitrogen.

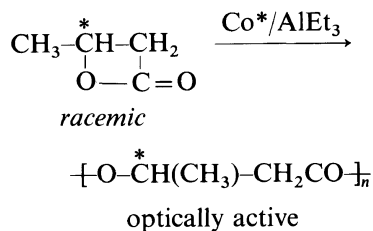
Polymerization of β -Butyrolactone

Into a flask were added Co* (0.5 mmol, 0.1895 g) and 10 ml of solvent under dry nitrogen. The red suspension became a clear blue-green solution on adding AlEt₃ (0.5 mmol). β -Butyrolactone (50 mmol, 4.2 ml) was then added and the solution was kept stirred at room temperature under N₂. After an appropriate reaction time, the volatile part was collected, and optical rotation of the unreacted monomer and conversion of monomer were determined by polarimetry and GLC, respectively. The nonvolatile part was dissolved in chloroform and precipitated into ether. The crude polymer was purified by column chromatography on silica gel (acetone) and freeze-dried from benzene. The polymer was characterized by IR, ¹H and ¹³C NMR, GPC, and optical rotation. Monomer conversion was determined either by GLC analysis of the

volatile part or by ^1H NMR of the reaction mixture.

RESULTS AND DISCUSSION

The asymmetric selective polymerization of β -butyrolactone was attempted by the catalyst system of $\text{Co}^*/\text{AlEt}_3$ in benzene, dioxane or without solvent. The results are summarized in Table I. Both the recovered monomer and



produced polymer showed optical activity, indicating asymmetric selective polymerization had occurred. The signs of optical rotation of the recovered monomer and produced polymer were the same in the reaction with benzene or dioxane solvent or without solvent; $\text{D}(+)$ -monomer reacted selectively and polymer having $(-)$ optical rotation was obtained. As the polymerization proceeded, the optical rotation of the recovered monomer increased, and both yield and molecular weight of the polymer increased.

The polymer was identified by IR, ^1H , and ^{13}C NMR. IR spectra of the polymer is shown in Figure 1. Carbonyl ($\text{C}=\text{O}$) of the ester group is identified as a large absorption at 1740 cm^{-1} , and together with the ^1H and ^{13}C NMR spectra of the polymer, which agreed

Table I. Asymmetric selective polymerization of β -butyrolactone^a

Co*	AlEt ₃	Solv	Temp °C	Time day	Monomer		Polymer		
					Conv %	$[\alpha]_D$ °	Yield %	$10^{-3} \bar{M}_w / 10^{-3} \bar{M}_n^e$	$[\alpha]_D$ °
0.5	0.5	— ^b	33	8	36.7	-0.143 (neat)	34.7	9.2/7.7 = 1.2	-29.6 (c, 1.00 Bz)
0	0.5	—	33	8	52.2	0	49.7	10.8 ^f	0
0.5	0	—	33	8	0	0	0	—	0
0.5	0.5	Bz ^c	23	11	40.5	-0.82 (c, 25.6 Bz)	18.5	6.5/4.6 = 1.4	—
0.5	0.5	Bz	25	12	60.5	-2.04 (c, 15.9 Bz)	26.9	15.2/9.2 = 1.7	—
0.5	1.0	Bz	30	14	72.3	-0.74 (c, 13.0 Bz)	45.8	15.0 ^f	-84.4 (c, 0.64 Bz)
0.5	0.5	Bz	30	14	51.1	-1.65 (c, 16.2 Bz)	41.4	9.4 ^f	-46.1 (c, 1.00 Bz)
1.0	0.5	Bz	30	14	64.8	-2.80 (c, 11.0 Bz)	58.7	—	—
0.5	0.5	Diox ^d	27	8	64.0	-0.78 (c, 13.2 Diox)	57.2	9.4 ^f	-55.0 (c, 0.10 Bz)
0.5	0.5	Diox	27	12	68.0	-0.89 (c, 15.2 Diox)	64.0	13.0 ^f	-46.2 (c, 0.10 Bz)

^a β -Butyrolactone 50 mmol.

^b Without solvent.

^c Benzene.

^d Dioxane.

^e By gel permeation chromatography (polystyrene standard).

^f Peak on GPC.

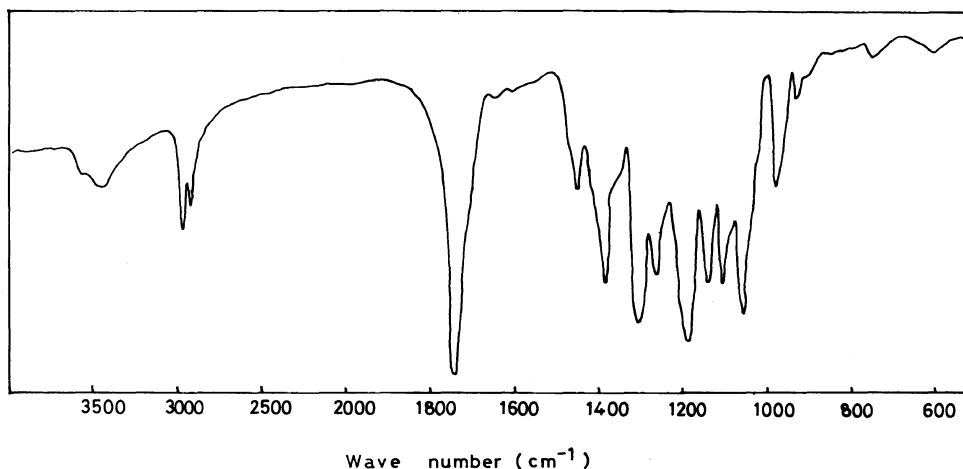


Figure 1. IR spectrum (KBr) of poly(β -butyrolactone) prepared by the $\text{Co}^*/\text{AlEt}_3$ catalyst system.

with those of the previous report,^{6b} the formation of poly- β -hydroxybutyrate was identified. IR spectra of polymers from various four-membered lactones were studied in detail,⁶ and it was made clear that fine structure of the IR spectra is due to the crystalline state rather than tacticity. The chiral polymer obtained here by the $\text{Co}^*/\text{AlEt}_3$ system does not seem to have high crystallinity, when judged by the fine structure of the IR spectra.

AlEt_3 alone catalyzes polymerization of β -butyrolactone, in which case conversion of monomer and yield of the polymer are higher than those in the polymerization with the $\text{Co}^*/\text{AlEt}_3$ system. But the molecular weight distribution was multimodal and very wide, in contrast with the $\text{Co}^*/\text{AlEt}_3$ system, in which case molecular weight distribution was unimodal and much narrower ($\bar{M}_w/\bar{M}_n = 1.2$ — 1.6). This indicates that the molecular weight distribution is also controlled by the presence of Co^* . This also suggests homogeneity of the active species in the $\text{Co}^*/\text{AlEt}_3$ system. In the AlEt_3 catalyst system, on the other hand, various kinds of active species are considered to account for the multimodal distribution of molecular weight. The effect of trace amounts of water or the interaction of solvent with AlEt_3 are considered to be the some possible

reasons. Co^* alone could not cause polymerization.

Catalyst efficiency of this asymmetric polymerization was found to be 25—52% with the ether-insoluble part of the polymer, when calculated from polymer yield, number average molecular weight (\bar{M}_n) of the polymer, and moles of catalyst.

In the $\text{Co}^*/\text{AlEt}_3$ catalyst system, Co^* is considered to be reduced to the monovalent state⁴ and stabilized by the delocalization of electrons over the highly conjugated ligand. Aluminum is coordinated with the phenolic oxygen of Co^* , to form the $\text{Co}^*/\text{AlEt}_3$ complex as shown in Figure 2. It is considered that monomers are coordinated with aluminum and D(+)-monomers react preferentially under the influence of the chiral moiety of the $\text{Co}^*/\text{AlEt}_3$ complex, thus giving rise to asymmetric selective polymerization. It is unlikely that cobalt functions as the active catalyst site

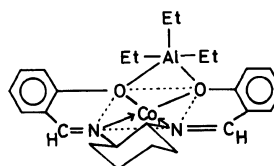


Figure 2. Proposed structure of the $\text{Co}^*/\text{AlEt}_3$ complex.

for this polymerization, because Co^{I} species are very strong nucleophiles and if monomers are coordinated with cobalt, the cobalt-alkyl bond will be formed, which is not likely to induce polymerization.

Acknowledgements. We deeply appreciate professor Teiji Tsuruta of Science University of Tokyo and Dr. Michihiro Ishimori of Central Research Institute of Electric Power Industry for their helpful comments.

REFERENCES

1. R. H. Abeles and D. Dolphin, *Acc. Chem. Res.*, **9**, 114 (1976).
2. G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968).
3. a) G. Costa, G. Mestroni, and L. Stefani, *J. Organometal. Chem.*, **7**, 493 (1967).
b) W. P. Schaefer, R. Waltzman, and B. T. Huie, *J. Am. Chem. Soc.*, **100**, 5063 (1978).
4. a) H. Aoi, M. Ishimori, S. Yoshikawa, and T. Tsuruta, *J. Organometal. Chem.*, **85**, 241 (1975).
b) H. Aoi, M. Ishimori, and T. Tsuruta, *Bull. Chem. Soc. Jpn.*, **48**, 1897 (1975).
5. a) P. P. King, *J. Chem. Technol. Biotechnol.*, **32**, 2 (1982).
b) E. R. Howells, *Chem. Ind. (London)*, **7**, 508 (1982).
c) P. A. Holmes, *Phys. Technol.*, **16**, 32 (1985).
6. a) K. Teranishi, M. Iida, T. Araki, S. Yamashita, and H. Tani, *Macromolecules*, **7**, 421 (1974).
b) M. Iida, T. Araki, K. Teranishi, and H. Tani, *Macromolecules*, **10**, 275 (1977).