Stereospecific Polymerization of β-Alkyl-β-propiolactone

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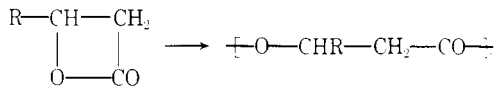
ABSTRACT: Crystalline isotactic poly(β-alkyl-β-propiolactones) were obtained by the fractionation of the raw polymers obtained from D,L-β-alkyl-β-propiolactones (alkyl: methyl, ethyl, and isopropyl) with $AlEt_3$–H_2O and $AlEt_3$–H_2O–epichlorohydrin catalyst system. The latter catalyst especially gave high enough molecular weight polymers to elongate the samples for taking X-ray fiber diagrams. It was assumed that the real active species on this type of the stereospecific polymerization could be $Et_2Al(OAlEt)_nOAlEt_2$ ($n \geq 1$) and the polymerization proceeds through a coordinated cationic mechanism.

The stereospecific polymerizations of β-methyl-, β-ethyl-, and β-isopropyl-β-propiolactones have been studied as those of a new series of monomer. These stereoregular poly-β-esters should be formed by ring-opening reaction of four-membered β-lactones, and composed of identical main-chain atoms (-O—CHR—CH_2—CO-) but of different side chains (R = Me, Et, or *i-Pr*).[2-8]



The main object of this work was to establish the nature and preparation of catalyst and/or the reaction condition which can give a stereoregular polymer having a sufficiently high molecular weight to give an oriented sample in high yield, and to extend our knowledge on the stereospecific polymerization. A research group at Cleveland, independently, synthesized the lowest member of this series in order to compare it with the naturally occurring product.[9,10] But unfortunately, the molecular weight of polymer was relatively low and the survey of polymerization conditions was not extensive.

This paper deals with the essence of the preparation, fractionation, structure, and some properties of a novel series of these isotactic polymers as briefly and systematically as possible.

Experimental Section

All of the manipulations, except for the treatments of polymers, were done under a dry inert gas (nitrogen or argon) atmosphere.

Reagents. Toluene. Commercial toluene was purified by the usual method, and distilled after refluxing over Na-K alloy.

Epichlorohydrin. Commercial product was distilled after drying over molecular sieve 5A. **Triethylaluminum.** Commercial product (Ethyl Corp.) was used without further purification.

Catalysts. a. $[Et_2AlOCPhNPh]_2$. This catalyst was prepared according to the method of Yasuda *et al.*[11] and recrystallized from *n*-hexane-toluene. **b. $AlEt_3$–H_2O Catalyst.** Toluene solution of $AlEt_3$ was prepared by dissolving $AlEt_3$ (0.66 g) in toluene (20.0 ml). After adding a specified amount of H_2O to the toluene solution (2.0 ml) at −78°, the solution was allowed to reach room temperature with stirring, and maintained at that temperature until no gas evolution was observed. **c. $AlEt_3$–H_2O–Additive Catalyst.** A specified amount of an additive (*e.g.*, epichlorohydrin) was added to the above $AlEt_3$–H_2O catalyst solution at −78°. The mixture was allowed to reach room temperature, and then allowed to stand at that temperature for 10 min. **d. High-Vacuum Treatment of $AlEt_3$–H_2O Catalyst.** $AlEt_3$–H_2O catalyst was made by heating the toluene solution at 60° for 2 hr, allowed to stand overnight at room temperature, and then adjusted to the concentration of the solution. This solution was concentrated *in vacuo*, heated under high vacuum (about 1×10^{-3} mm) up to 170° until almost no distillate was detected, and then diluted with toluene to the required volume. A specified amount of epichlorohydrin was added dropwise to this solution under stirring for 1.5 hr.

β-Alkyl-β-propiolactone. The methyl, ethyl, or isopropyl derivatives were synthesized from ketene and a corresponding aldehyde. The purity of methyl and isopropyl derivatives was determined with analytical glpc after drying the sample over CaH_2 for 3 days. The purified samples distilled after drying them with molecular sieve 5A, and then with dried $CaCl_2$. The determination with analytical glpc (Silicone DC 550) indicated that the ethyl derivative contained about 10% of by-product. This by-product could not be removed by the spinning-band-type rectifier under reduced pressure, but it was removed by using a preparative glpc (Varian aerograph Model 700, Silicon DC 550). This by-product was determined to be 1,1-propanediol diacetate by elemental analyses, ir, nmr, and mass spectroscopy. Some properties of these β-propiolactones are shown in Table I.

Polymerization. A specified amount of monomer (2.0 or 1.0 ml) was added to the toluene solution of catalyst (0.02 mol of catalyst/1.0 monomer) in the polymerization ampoule at −78°. This ampoule was allowed to stand at a specified temperature for a specified period. The polymerization was terminated by adding either diethyl ether-water (100:1.0) (for methyl derivative) or petroleum ether-water (100:1.0) (for ethyl or isopropyl derivative) to the polymerization system. The crude polymer was obtained after removing solvents under reduced pressure. The raw (or total) polymer was obtained after drying the precipitates which were obtained by adding diethyl ether (for methyl derivative) or petroleum ether (for ethyl or isopropyl derivative) to the filtered and concentrated chloroform solution of the crude polymer. These polymers were identified by elemental analyses. The percentage ratio of the raw polymer to the monomer is the total yield (%) of polymer.

Fractionation of Polymer. The raw polymers were dissolved in 100 ml of chloroform. The solution was concentrated to 2.0 ml after filtration, and then fractionated into two parts by adding 100 ml of acetone (for methyl derivative) or diethyl ether (for ethyl or isopropyl derivative). The insoluble fraction was crystalline and the soluble fraction was amorphous polymer. The percentage ratio of crystalline to raw polymer is a measure of stereoregulating capacity of the catalyst, and represented as an IS (index of stereospecificity) value.

Instruments. For analytical glpc, a gas chromatograph (Yanagimoto Model GCG 550) packed with Silicone DC 550 (2.0 m) was used, and hydrogen was used as a carrier gas. For preparative glpc, a gas chromatograph (Varian aerograph Model 700) packed with Silicone DC 550 (3.0 m) was used, and helium (60 cm^3/min) was used as a carrier gas. The nmr spectrum was taken at room temperature with a spectrometer (Varian T60), and Me_4Si was used as an external standard. Ir spectrum was measured with a spectrometer (Hitachi Model EPI2) by using a KBr disk. For an oriented film, the same spectrometer equipped with a microscopic accessory was used with an AgCl disk. The intrinsic viscosity of a polymer was used as a measure of molecular weight. This value (units; dl/g) was determined in chloroform at 30.0 ± 0.05° in an Ubbelohde-type viscometer.

Results and Discussion

I. Fractionation and Structure Determination. i. Fractionation into Structurally Different Polymer. The fractionation of raw polymer into the crystalline and amorphous fractions was an important problem in present work, so a rather long time was spent on this work. A difference in solubility behavior was used for this purpose,

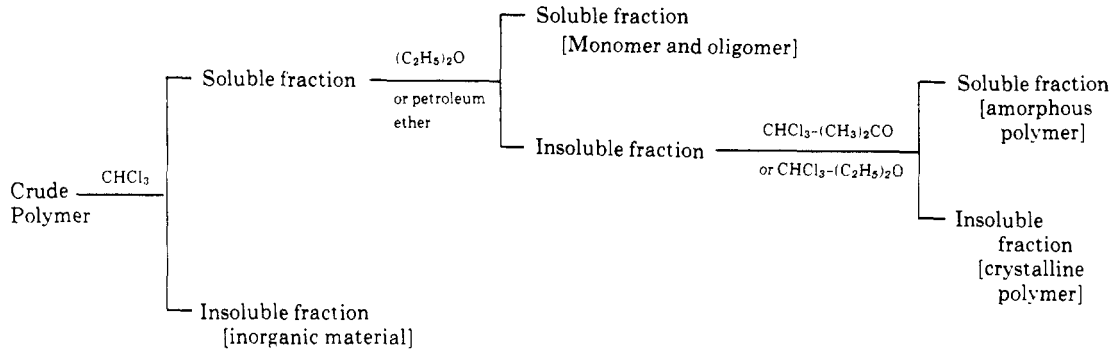


Figure 1. Fractionation of poly(β-alkyl-β-propiolactone).

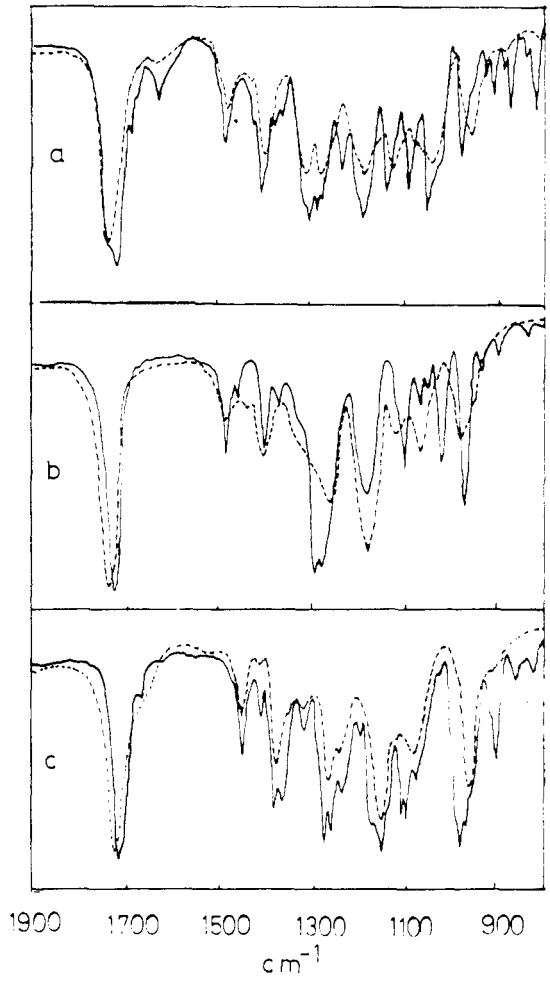


Figure 2. Ir spectra of crystalline (——) and amorphous (----) poly(DL-β-alkyl-β-propiolactones): (a) poly(DL-β-methyl-β-propiolactone), (b) poly(DL-β-ethyl-β-propiolactone), (c) poly(DL-β-isopropyl-β-propiolactone).

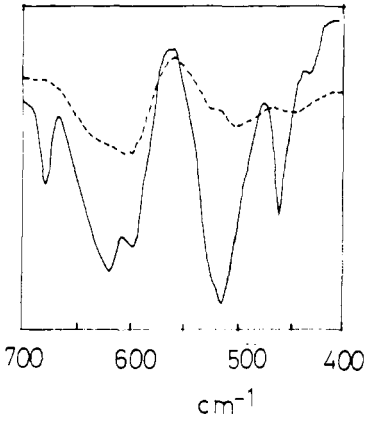


Figure 3. Ir spectra (700-400 cm^{-1}) of crystalline (——) and amorphous (----) poly(DL-β-methyl-β-propiolactone).

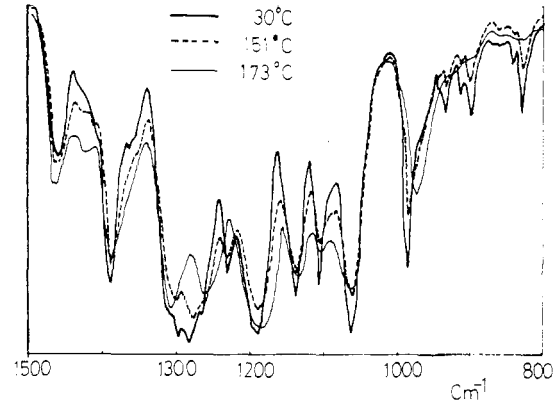


Figure 4. Ir spectra of crystalline poly(DL-β-methyl-β-propiolactone) at various temperature.

but unfortunately, the ^1H nmr method (100 MHz) for measuring the degree of tacticity was unsuccessful at the present stage. Therefore, the solid-state ir and X-ray spectra were applied to judge the efficiencies of fractionation. The fractionation methods varied depending on the nature of alkyl groups (Figure 1). These methods gave percentage values of crystalline to total (or raw) polymers, *i.e.*, IS values, for each member.

ii. Origin of Ir Spectra of Crystalline Polymer. Fractionated crystalline and amorphous polymers were found to differ clearly in their ir spectra (Figures 2 and 3). Therefore, the solid-state ir spectra were used for the characterization of fractionated polymers.

In order to establish whether the fine structure in the ir spectra originated from tacticity or crystallinity, the temperature dependences of the ir bands were studied. The ir spectra of three crystalline polymers changed reversibly to those of amorphous ones at temperatures just above their melting points (Figure 4). Therefore, we can conclude that the fine structures observed in the ir spectra of these crystalline polymers are due to their crystallinity, not to their tacticity.

iii. Structure Determination of Crystalline Polymer. Fractionation of the raw polymer into crystalline and amorphous polymers is an indispensable prerequisite, and the assignment of the structure (isotactic or syndiotactic) to the crystalline polymer is a problem. Although the former problem was solved as mentioned before, the latter one is the object of this paragraph.

X-Ray fiber diagrams and polarized ir spectra were obtained for the oriented samples of three homologous poly-

Table I
Physical Constants and Elemental Analysis of β-Alkyl-β-propiolactone

Alkyl	Bp, °C (mm)	$d^{20}4$	$n^{20}D$	Anal. Obsd (%) C	Anal. Obsd (%) H	Anal. Calcd (%) C	Anal. Calcd (%) H
Methyl	46–47 (7)	1.0471	1.4098	55.61	6.92	55.80	7.02
Ethyl	95–96 (36)	1.0106	1.4190	59.95	8.07	59.98	8.05
Isopropyl	49–50 (2)	0.9813	1.4219	62.99	8.73	63.13	8.83

Table II
Polymerizations of β-Alkyl-β-propiolactones with Various Types of Catalysts

Catalyst	Alkyl Groups of Monomer: Methyl	Ethyl	Isopropyl
n-BuLi	*a*	*a*	*a*
Et_3N	*a*	*a*	*a*
$BF_3 \cdot OEt_2$	*b*	*b*	*b*
$AlEt_2Cl$	*b*	*b*	*b*
$AlEt_2Cl$–dioxane	*c*	*c*	*c*
$ZnEt_2$	*a*	*a*	*a*
$ZnEt_2$–H_2O	*c*	*c*	*c*
$AlEt_3$–H_2O	*d*	*d*	*d*
$[Et_2AlOCPhNPh]_2$	*d*	*d*	*d*

[a] No polymer. [b] Oily polymer. [c] Amorphous high polymer. [d] Crystalline and amorphous high polymers. For a to d, polymerization condition: temperature, 60°; time, 7 days (methyl derivative), 14 days (ethyl derivative), 35 days (isopropyl derivative); catalyst, 2 mol % of monomer; monomer, 2.0 ml; solvent, toluene 2.0 ml.

Table III
Polymerizatons of β-Alkyl-β-propiolactone with $AlEt_3$–H_2O Catalyst System in the Presence or Absence of Epichlorohydrin[a]

Alkyl	H_2O–$AlEt_3$–ECH (mol:mol:mol)	Polymerization Time (days)	Total Yield (%)	IS (%)	Crystalline Polymer [η]
Methyl	0.9:1:0	7	91	32	2.20
	0.9:1:1	7	42	43	3.24
Ethyl	1:1:0	13	94	37	0.82
	1:1:1	13	61	64	1.10
Isopropyl	1:1:0	30	49	28	1.26
	1:1:1	30	32	51	1.38

[a] Polymerization condition: temperature, 60° catalyst, 2 mol % of monomer; monomer, 2.0 ml; solvent, toluene 2.0 ml.

mers, when the molecular weights exceeded certain values. These properties are the essential requirement for exact structure determination. We applied the following logical arguments to these homologous derivatives.

For a methyl derivative, the X-ray fiber diagram and polarized ir spectrum of the oriented films were recorded for the polymer derived from our racemic monomer. Both spectra were identical with the patterns for the natural isotactic poly(β-hydroxybutyric acid).[12,13] These facts showed that our crystalline polymer is an isotactic polymer having a 2_1 helix and building the crystallites by independent aggregation of D and L chain.[3] This conclusion was later definitely confirmed by Yokouchi *et al.*[6]

For an ethyl derivative, quite similar results were obtained by X-ray and polarized ir methods (Figure 5). We assigned an isotactic configuration to this crystalline polymer based on a preparation method which was quite similar to the corresponding methyl derivative. Recently, the isotactic configuration assigned to this polymer was completely supported by Yokouchi *et al.*[7]

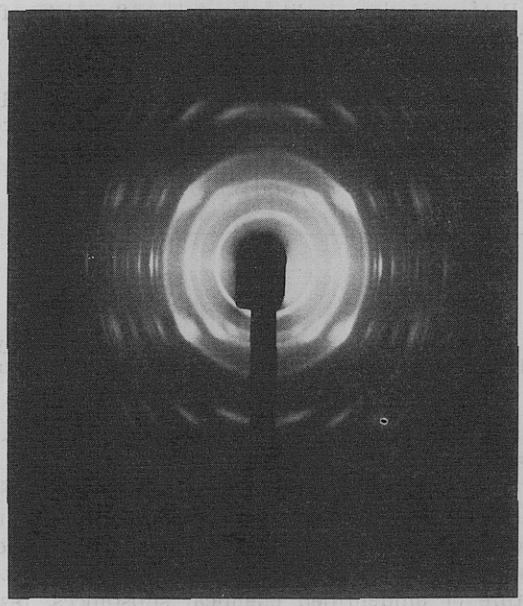


Figure 5. X-Ray fiber photograph of the crystalline poly(DL-β-ethyl-β-propiolactone).

For an isopropyl derivative, X-ray fiber diagram and polarized ir spectra of the oriented films were recorded for the polymer derived from racemic monomer. The high crystallinity of the crystalline polymer indicated that the main-chain configuration is either regular, isotactic, or syndiotactic. Polymerization variables such as the temperature, the nature of catalyst, and the solvent required for preparing the crystalline polymer are almost identical with corresponding methyl and ethyl derivatives. Therefore, it is reasonable to assign an identical main-chain configuration, that is, isotactic, for three kinds of crystalline polymers.[4] Detailed studies for this polymer, including fiber repeat distance, chain symmetry, and so on, are being done by Tadokoro's group in our Department.

In conclusion, the isotactic configuration was assigned to three members of crystalline poly(β-alkyl-β-propiolactones). This conclusion indicates the correctness of our logical argument.

II. Polymerization Reaction. Preliminary experiments on the polymerization with typical types of catalysts covered a wide range such as anionic, cationic, and coordinated active species. The experimental results obtained for these three homologous racemic monomers (R = Me, Et, or *i*-Pr) showed that only a very limited type of organoaluminum catalyst, not organozinc catalyst, gave an isotactic polymer to a varying degree of stereospecificity. Typical anionic catalyst gave no polymer, and typical cationic and some coordinated catalysts gave only amorphous polymers. Some typical results picked up from our experiments were shown schematically in Table II.

In general, the $AlEt_3$–H_2O system was found to give the isotactic polymer in a faster rate and in a higher IS value than a $[R_2AlOCR'NPh]_2$ type catalyst in various condi-

Table IV
Polymerization of β-Alkyl-β-propiolactone with Some Typical Cationic Catalysts[a]

Alkyl	Catalyst	Temp (°C)	Time (days)	Polymer Yield (%)	IS (%)
Methyl	$BF_3 \cdot OEt_2$	60	2	30	0
Ethyl	$BF_3 \cdot OEt_2$	60	14	16	0
Isopropyl	$BF_3 \cdot OEt_2$	70	21	Trace	
Isopropyl	$AlEt_2Cl$	65	31	18	0

[a] Polymerization condition: catalyst, 2 mol % of monomer; monomer, 2.0 ml; solvent, toluene 2.0 ml.

Table V
Dependence of Polymerization of β-Methyl-β-propiolactone on Polymerization Temperature with $AlEt_3$–H_2O (mol ratio, 1:1) Catalyst[a]

Temp (°C)	Total Yield (%)	IS (%)
60	26	50
80	95	42
100	92	35

[a] Polymerization condition: time, 7 days; catalyst, 2.0 mol % of monomer; monomer, 2.0 ml; solvent, toluene 2.0 ml.

tions. Therefore, we wish to describe only the former type of catalyst.

i. Polymerization with $AlEt_3$–H_2O Catalyst System. The $AlEt_3$–H_2O catalyst system was found to give isotactic polymers starting from three homologous racemic members. Although these systems were well known to be a mixture of unidentified chemical substances, results of polymerizations exhibited a relative order of polymerizability (Me > Et > *i*-Pr) judged from polymer yield (Table III). This relative order is similar to that of typical cationic catalysts (Table IV). Therefore, catalytic behavior of this catalyst system was studied in some detail for a methyl derivative.

Catalytic behavior of this catalyst system is known to depend profoundly on the ratio of H_2O to $AlEt_3$, catalyst preparation conditions, and other polymerization variables. Unexpected results were found by varying the ratio (Figure 6). Total yield of polymer had two maxima separated by a minimum. An amorphous polymer yield first reduced and then reached to a second maximum, and an isotactic polymer began to appear from a point corresponding to this minimum (about H_2O–$AlEt_3$ = 0.36) and followed a bell-shaped curve having a maximum point. IS values fell on a single straight line starting from about 0.36.

Temperature dependence of polymerization with a fixed ratio of $AlEt_3$ to H_2O (*i.e.*, H_2O–$AlEt_3$ = 1:1) (Table V) revealed that the IS value was most favorable at 60° in a range of 60–100°. At lower temperatures, the rate of polymerization was low. At 60°, rates of polymerization followed a straight line, while $[\eta]$ values remained almost constant (Figure 7). The latter behavior means that the propagation reaction is fast.

ii. Polymerization with Modified $AlEt_3$–H_2O Catalyst System. The $AlEt_3$–H_2O catalyst system is known to be a superior one for the stereospecific polymerization of some polar monomers, but unfortunately the nature and the number of catalytically active sites have been unknown exactly because its chemical nature is too complex to be analyzed adequately. The catalytic behavior of this system toward the polymerization of β-alkyl-β-propiolactone led us to modify it in order to increase the IS value and/or molecular weight. Three different methods were conceivable for this purpose.

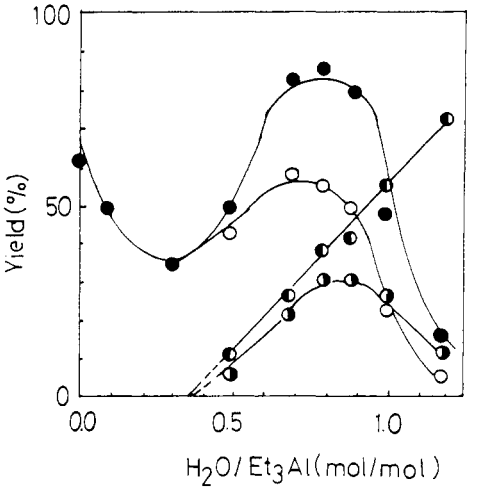


Figure 6. Polymerization of β-methyl-β-propiolactone by $AlEt_3$–H_2O catalyst. Polymerization conditions: monomer, 2.0 ml; solvent, toluene 2.0 ml; catalyst, 2.0 mol % of monomer; time, 7 days; temperature, 60°: (●) total yield; (◑) crystalline polymer yield; (○) amorphous polymer yield; (◐) index of stereospecificity.

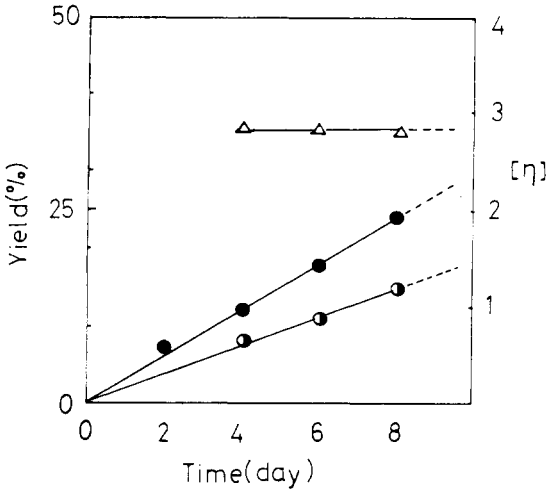


Figure 7. Time dependence of polymer yield (●), crystalline polymer yield (◑), and intrinsic viscosity of crystalline polymer (△) on the polymerization of β-methyl-β-propiolactone with $AlEt_3$–H_2O (mol ratio, 1:1) catalyst. Polymerization conditions: monomer, 1.0 ml; solvent, toluene 1.0 ml; catalyst, 1 mol % of monomer; temperature, 60°.

a. Effect of an Additive Compound. The first method was the examination of the effect of an additive substance. Addition of a substance which is known to have a so-called promoter character or its relatives was expected to increase the rate of polymerization very significantly.[14] But unexpectedly, addition of such a compound tended to decrease the rate of polymerization and increased the molecular weight of isotactic polymer (Table VI). This type of behavior was observed especially for epichlorohydrin (Table III). The equimolar amount of epichlorohydrin to $AlEt_3$ was found most favorable for the stereospecificity of the polymer produced (Figure 8). These phenomena led us to conclude that a polymerizable compound with this catalyst (*e.g.*, epichlorohydrin or oxetane) had such effects, while a compound contributing solely to the coordination (*e.g.*, triethylamine) only slowed down the rate of polymerization without changing the molecular weight.

b. Effect of Catalyst Aging. The second method was the prolongation of the aging time in order to change the chemical composition of this catalyst system in relation to its catalytic activity. An effect of an aging time was ex-

Table VI
Effect of an Additive on the Polymerization of β-Methyl-β-propiolactone[a]

Catalyst (mol ratio)	Total Yield (%)	IS (%)
$AlEt_3$–H_2O–ECH (1:1:1)	36	43
$AlEt_3$–H_2O–oxetane (1:1:1)	48	34
$AlEt_3$–H_2O–PO (1:1:1)	26	33
$AlEt_3$–H_2O (1:1)	53	25
$AlEt_3$–H_2O–THF (1:1:1)	17	20
$AlEt_3$–H_2O–NEt_3 (1:0.9:0.2)	41	16
$AlEt_3$–H_2O–piperidine (1:1:1)	30	15
$AlEt_3$–H_2O–Et_2O (1:1:1)	13	12

[a] Polymerization conditions: catalyst, 2 mol % of monomer; time, 7 days; temperature, 60°; monomer, 1.0 ml; solvent, toluene 1.0 ml.

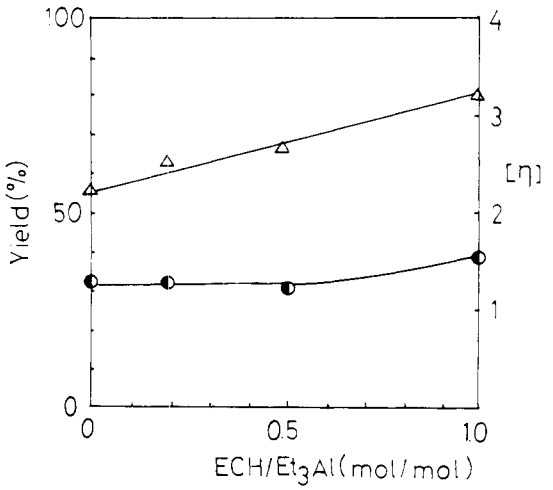


Figure 8. Effect of addition of epichlorohydrin on the polymerization of β-methyl-β-propiolactone with $AlEt_3$–H_2O (mol ratio, 1:0.9). Polymerization conditions: monomer, 1.0 ml; solvent, toluene 1.0 ml; catalyst, 1 mol % of monomer; time, 7 days; temperature, 60°: (△) intrinsic viscosity of crystalline polymer; (◐) index of stereospecificity.

amined for the catalyst of low activity (H_2O-$AlEt_3$ = 0.6:1.0), because this system is not so suitable for giving an isotactic-rich raw polymer (Figure 9). Aging of the catalyst was found to have a role in increasing the IS value and the molecular weight, but has almost no effect on the total conversion (Figure 9). The degree of isotacticity reached an almost constant value after about 5 hr, while the molecular weight continued to increase steadily even after 24 hr. In contrast, a similar effect was observed after a very short aging time (about 10 min) for an H_2O-$AlEt_3$ = 1:1 system. Thus, the prolongation of aging time affects the IS value more for a lower ratio of H_2O-$AlEt_3$ than for a higher one. This fact is very important for speculating about the active sites of this catalyst system.

c. Effect of High-Vacuum Treatment of Catalyst. The third method was based on our speculation on the stereospecifically active sites of this catalyst system. This speculation was applied positively in designing the catalyst system.

A curve observed for the dependence of total yield on the H_2O-$AlEt_3$ ratio is quite similar to that reported by Cherdron *et al.*[15] (Figure 10). The former was prepared from a β-methyl-substituted monomer (R = Me) and the latter from an β-unsubstituted one (R = H). The former monomer has an asymmetric carbon atom and the latter one has not. These two curves should originate from identical catalytically active sites. At two maxima, the monomer without an asymmetric carbon gave a configurationally identical polymer, and the monomer with an asymmetric carbon atom gave two polymers configurationally different, *i.e.*, isotactic and atactic polymers.

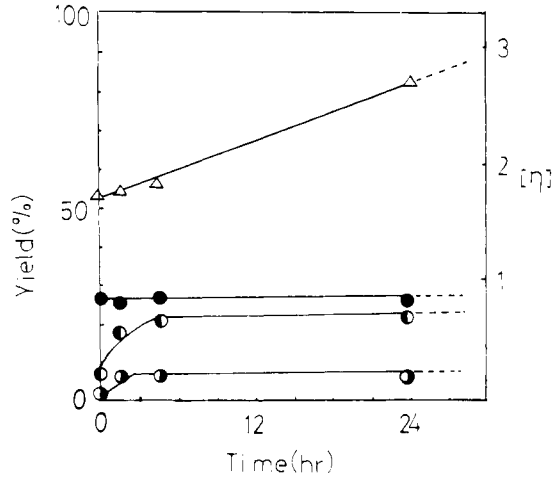


Figure 9. Effect of aging time of the catalyst system ($AlEt_3$–H_2O–epichlorohydrin, mol ratio 1:0.6:1) on the polymerization of β-methyl-β-propiolactone: (●) total yield; (◐) index of stereospecificity; (◑) crystalline polymer yield; (△) intrinsic viscosity of crystalline polymer.

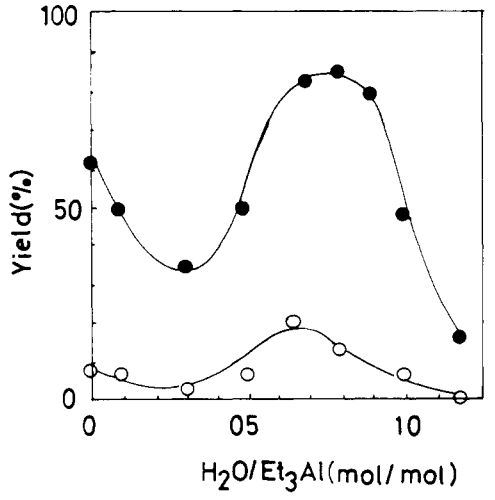


Figure 10. Comparison of polymerization results of β-methyl-β-propiolactone (●) and β-propiolactone (○) with $AlEt_3$–H_2O catalyst. The latter was cited from the report by Cherdron *et al.*[15]

In our case (Figure 6), the isotactic polymer began to appear at a molar ratio of about H_2O-$AlEt_3$ = 0.36, and the IS value increased rather steeply by following a single straight line, instead of complicated curves, corresponding to total, isotactic, and amorphous polymers. These experimental curves were analyzed by assuming that $AlEt_3$ gave an atactic low molecular weight polymer: $Et_2AlOAlEt_2$, an atactic polymer with less reactivity; and $Et_2AlOAlEtOAlEt_2$, and/or its higher homologs, an isotactic polymer. Assuming this interpretation is correct, $AlEt_3$ which was unreacted and formed in disproportionation should be removed from the catalyst system prior to the polymerization to increase the isotactic polymer content (IS value). In the case of the polymerization of propylene oxide with the diethylzinc-water catalyst system, the isotacticity of polymer was increased by freeze-drying treatment, perhaps by the evaporation of unreacted diethylzinc, and lowered again by adding diethylzinc to this freeze-dried system.[16] These results now were extended to the triethylaluminum-water catalyst system. Bis(diethylaluminum)

Table VII
Polymerization of β-Methyl-β-propiolactone with the Pretreated Catalyst System of $AlEt_3$–H_2O under High-Vacuum Condition[a]

H_2O–$AlEt_3$ (mol ratio)	Catalyst Treatment	Polymerization Time (days)	Total Yield (%)	IS (%)	Crystalline Polymer [η]
0.6[c]	None	7	64	23	0.48
	HV[a]	10	85	51	1.48
	HV[a] + ECH[b]	13	53	62	2.46
0.8[d]	None	7	87	38	1.42
	HV[a]	10	68	69	1.94
	HV[a] + ECH[b]	10	52	72	2.33

[a] HV, high vacuum (1×10^{-3} mm) for 2 hr at 170°. [b] ECH epichlorohydrin. Removal of $AlEt_3$ seems to be not complete. [d] Removal of $AlEt_3$ was promoted by the coexistence of decaline. Polymerization condition: temperature, 60°; catalyst, 2 mol % of monomer; epichlorohydrin, 2 mol % of monomer; monomer, 2.0 ml; solvent, toluene 2.0 ml.

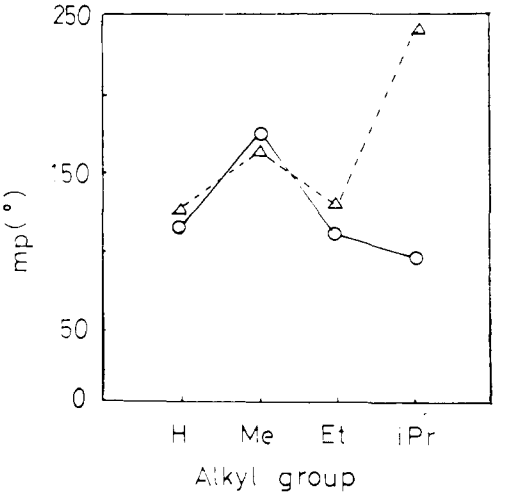


Figure 11. Melting points of crystalline poly(DL-β-alkyl-β-propiolactones) (○) and isotactic poly(α-alkyl-ethylenes) (△).

oxide, $Et_2AlOAlEt_2$, is known to be able to disproportionate easily to give a mixture of $AlEt_3$ and $Et_2Al[OAlEt]_nO$-$AlEt_2$.[17] Therefore, $AlEt_3$ is possibly removed under a high-vacuum condition.

$$(n+1)Et_2AlOAlEt_2 \rightarrow nAlEt_3 + Et_2Al[OAlEt]_nOAlEt_2$$

According to this speculation, the $AlEt_3$–H_2O catalyst system was evacuated under a high-vacuum condition prior to the addition of monomer. Actually, the polymerization carried out with this technique gave just such the results we expected (Table VII). IS values increased sharply and the molecular weight remained almost constant. In addition, the presence of epichlorohydrin sharply increased the molecular weight (Table VII).

iii. Stereospecific Polymerization Mechanism. Amorphous polymer was prepared only with a typical cationic, not an typical anionic, catalyst. Isotactic polymer always accompanied amorphous polymer with a varying amount and both types of polymers could be fractionated cleanly. Removal of $AlEt_3$ under high vacuum condition from the $AlEt_3$–H_2O catalyst system enhanced the formation of the isotactic polymer, and addition of an additive compound, *e.g.*, epichlorohydrin, increased the molecular weight of isotactic polymer. In addition, rates of polymerization of β-alkyl-β-propiolactone followed qualitatively the order of Me > Et > *i*-Pr, in both free cationic and organoaluminum catalysts. This order parallels with the bulkiness of β substituent in the side chain, and also corresponds to the values of electronegativity of the ring oxygen atom calculated from internal chemical shift and vicinal coupling constant observed for ^1H nmr spectra (Table VIII). The latter values seem to be consistent with the idea that the ring oxygen atom is an electron accepting center. According to this interpretation, the relative ease of polymerization of three homologous monomers parallels with the electron density of ring atom.

Table VIII
Electronegativity Calculated from Internal Chemical Shift and Vicinial Coupling Constants[a]

Alkyl	$-(\nu_a + \nu_b)/2$ (ppm (δ))[b]	χ_{o-c}	J_{vic}	ΔE_χ
Methyl	1.38	2.72	5.0	4.14
Ethyl	1.18	2.58	5.2	3.85
Isopropyl	0.82	2.34	5.3	3.72

[a] Calculation: $\chi = 0.684\Delta\nu + 1.78$ (B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, **77**, 3977 (1955)) $J_{vic} = 7.9 - 0.7\Delta E$. [b] Tetramethylsilane was used as the external standard.

These experimental results, when combined with our previous interpretation on the nature of the catalyst, seem to lead us to propose a coordinate cationic mechanism for the isotactic polymer formation.

III. Melting Point of Isotactic Polymer. One of the interesting phenomena of synthetic polymers is the variation of melting point depending on the nature of their β substituents. The observed melting point is plotted in Figure 11 as solid lines in comparison to the corresponding β-alkyl-substituted ethylene derivatives represented by dotted lines. These two series belong to an isotactic configuration. Both curves follow similarly for the first three members, but in a different manner for the isopropyl derivatives. It is pertinent to point out here the similarity and the difference observed between these two homologous series. The comparison may reflect the inter- and/or intrachain interactions, and will be solved completely by analyzing the three-dimensional crystal lattice of an isopropyl derivative.

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α-(4)-Nitrocyclohexyl)-ω-nitropoly(azo-1,4-cyclohexylene *N,N'*-dioxide), an Oligomeric Nitrosoalkane, Exemplifying a Novel Potential Catenation System

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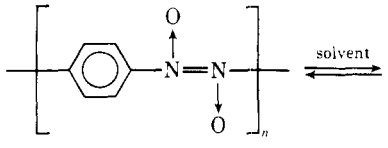
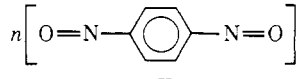
ABSTRACT: Investigations describing the preparation of an oligomeric nitrosoalkane derived from 1,4-dinitrosocyclohexane are reported. The characterization of the oligomer is described. Also, the degradation of this low molecular weight polymer is discussed.

New methods of catenation are of great general interest to polymer chemists, and we wish to report that we have recently completed some initial investigations concerning the use of the nitrosoalkane dimer function to achieve catenation.[1]

It has long been surmised that *p*-dinitrosobenzene and related compounds are polymeric, or at least, oligomeric.[2] However, even though *p*-dinitrosobenzenes may be polymeric (I) in the solid state, in solution they dissociate to form the usual blue or green monomeric species (II) typi-



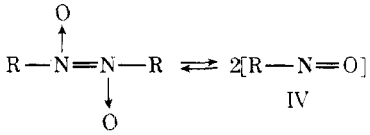
I



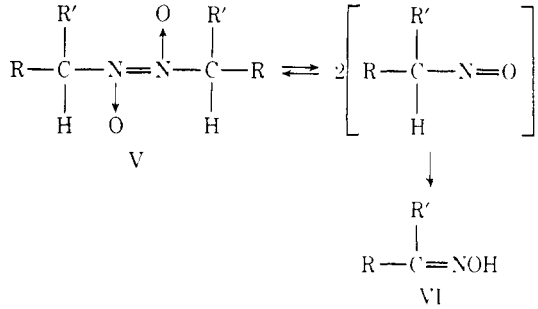
II

cal of nitrosoalkane or nitrosoaromatic compounds.[3] Molecular weight measurements made on solutions of *p*-dinitrosobenzene indicate that only monomeric species exist in solution. At present, to our knowledge, no one has reported the preparation of oligomeric or polymeric nitrosoalkanes.

When we began these investigations our goal was to prepare a bifunctional nitrosoalkane and to ascertain *via* suitable characterization studies whether or not it was polymeric. To this end, we made use of the available literature to define the stability of the simple nitrosodimer function (III). In the normal solid crystalline state, nitrosodimers (III) tend to be colorless or almost colorless. Upon melting or dissolution in a suitable solvent, blue to green monomeric species (IV) are formed.[3] If the carbon atom bonded to the nitroso group also bears additional substituents which are electronegative, dissociation to IV is more facile[4] and in some cases, only the monomer exists.[5] Steric crowding on or about the nitroso bearing carbon atom also decreases the stability of the dimer.[6] The ability of primary and secondary nitrosoalkanes (V) to isomerize irreversibly to oximes (VI) also is a factor in the stability of both the monomer and the dimer.[7] The isomerization occurs when such nitroso compounds are melted[7] or heated in suitable neutral solvents[7] with varying degrees of facility depending on the structural characteris-



III IV



V

VI

tics of the molecule involved. Also, the isomerization is catalyzed by acids and bases.[7] In addition, polar solvents seem to facilitate the isomerization,[7] and primary nitroso compounds isomerize more readily than secondary nitroso compounds.[7]

Only a very few stable bifunctional nitrosoalkanes are known,[8] and in these cases, the nitroso groups are bonded to the rest of the molecule such that dimerization may yield six-membered rings.[8]

Thus, it appeared that in order to prepare a stable polymeric dinitrosoalkane, the following criteria might be important: (1) the nitroso groups should not be directly attached to an aromatic nucleus; (2) electronegative substituents should not be present on the nitroso bearing carbon atoms; (3) the nitroso bearing carbon atoms should not be