Effect of Substituents on Stereospecific Polymerization of β-Alkyl- and β-Chloroalkyl-β-propiolactones

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ABSTRACT: By the use of the polymeric catalyst $(EtAlO)_n$ it has been possible to compare the polymerization behavior of seven different β-substituted propiolactones. The substituents are methyl, ethyl, isopropyl, *tert*-butyl, chloromethyl, dichloromethyl, and trichloromethyl groups. This study disclosed an empirical generalization concerning the polymerizability and the stereospecificity in the polymerization reaction with respect to the substituent group in the monomer. The electron-withdrawing groups (Cl series) cause a significant rate-increasing effect surpassing their steric inhibition. The electron-releasing groups (alkyl series), decrease the rate by a cooperative effect of electronic and steric factors. A limitation of stereospecific polymerization by this catalyst was observed when spatial crowding at the α carbon in the substituent group is present. Newly formed crystalline poly-β-esters are poly(β-chloromethyl-β-propiolactone) and poly(β-dichloromethyl-β-propiolactone). The spectroscopic characteristics are shown for certain of the stereoregular polymers and atactic polymers (obtained from the EtZnOZnOZnEt catalyst).

The polymerization of β-substituted-β-propiolactones is known[2] to give β-polyesters. Recently more attention has been paid to the synthesis of this series of polymers,[3] especially with regard to the stereoregular polymerization[4] of this type of lactone.

The present work covers the fundamental aspects of the polymerizability of β-lactones carrying β-substituents, e.g., alkyl and chloroalkyl, which are varied systematically to change their electronic and steric contributions. Comparison between the monomer reactivities was made satisfactorily by using a new polymeric catalyst $(EtAlO)_n$. This catalyst has been used by the authors for the stereoregular polymerizations of acetaldehyde,[5] epoxides,[5] and β-methyl-β-propiolactone.[6]

For the synthesis of high molecular weight atactic polymers of lactones, the EtZnOZnOZnEt catalyst (derived from the $Et_2Zn–H_2O$ catalyst) was found to be effective. Thus, a comparison of stereoregular polymers with the corresponding atactic polymers became possible especially their spectroscopic properties. Some of these are included in this article.

The catalyst system, $AlEt_3–H_2O$, has been used in previous work[4c,d,6] concerning the polymerization of β-alkyl-β-propiolactones. Several catalyst improvements have been investigated and it has been found that the $AlEt_3–H_2O$–epichlorohydrin system is superior to $AlEt_3–H_2O$.[4d,6] The highest catalytic activity with respect to stereospecific polymerization was obtained at a ratio of $AlEt_3$ to water of 1:1. For the role of epichlorohydrin we have suggested that it is not essential for the stereoregulation or catalytic activity but plays some part in suppressing side reactions caused by the presence of unreacted or free $AlEt_3$, $Et_2AlOAlEt_2$, and hydroxylated organoaluminum compounds included in the $AlEt_3–H_2O$ (1:1) system. The adverse effect of aluminum trialkyls, which has been reported for the stereospecific polymerization of propylene oxide,[7] is also found for β-substituted propiolactones. In a previous paper we have stated that high vacuum treatment of the reaction product of $AlEt_3$ and water gave a polymeric soluble compound formulated as $-(EtAlO)_n-$[5] and that the latter compound showed better catalytic activity for β-methyl-β-propiolactone than the $AlEt_3–H_2O$–epichlorohydrin catalyst.[6]

Results and Discussions

Polymerization Catalyst $(EtAlO)_n$. The most successful method for obtaining the soluble $(EtAlO)_n$ compound for the stereoregular polymerization of lactone monomers involves distillation of $AlEt_3$ from the reaction product of $AlEt_3$ and water under high vacuum in the presence of decalin. Decalin helps elimination of $AlEt_3$ from the system because of the similarity of their boiling temperatures. At the end of the distillation the bath temperature was kept at 180–190 °C for half an hour to allow disproportionation to the resultant viscous compound. More decalin was added and the distillation was repeated. In this way we obtained a hexane-soluble polymeric catalyst which showed improved reproducibility in catalytic action and was stable after storage in an argon atmosphere for about 1 year.

Since we have already shown that the $Et_2AlOAlEt_2$ compound can be converted into $(EtAlO)_n$ compound by a disproportionation reaction which eliminates $AlEt_3$ under a high vacuum condition,[5] this treatment is appropriate for the simultaneous removal of $AlEt_3$ and $Et_2AlOAlEt_2$ both of which have a severe adverse effect on the stereoregular polymerization of lactones. Another merit of this treatment is that such hydroxylated organoaluminum compounds as $Et(EtAlO)_m–Al(OH)Et$, if present, can be converted into Al–O type compounds through thermal condensation reaction with $AlEt_3$, $Et_2AlOAlEt_2$, and their higher homologues during this treatment.

Polymerization Results of β-Substituted-β-propiolactones by the Use of $(EtAlO)_n$ Catalyst. The polymerization behavior of seven kinds of β-substituted-β-propiolactones catalyzed by $(EtAlO)_n$ catalyst was compared in toluene at 60 °C with respect to apparent rate of polymerization and stereospecificity. The monomers used are: β-methyl- (MPL), β-ethyl- (EPL), β-isopropyl- (IPPL), and β-*tert*-butyl- (TBPL) substituted lactones with electron-releasing substituents and β-chloromethyl (MCPL), β-dichloromethyl (DCPL), and β-trichloromethyl (TCPL) derivatives with electron-attracting substituents. Typical results are summarized in Table I.

The total yield and index of stereospecificity (IS), described in the experimental section, were obtained by extraction techniques. The apparent rate of polymerization (R_P) was estimated from the time–conversion plot determined by the amount of isolated polymer. Although these values are somewhat variable (±ca. 5%) because of the extraction techniques used, the figures obtained are useful for understanding the major features of the polymerizability of the lactones examined and for deriving empirical rules for the syntheses of the stereoregular polymers.

The time dependence of polymer formation from MPL, EPL, and MCPL in Figure 1 exemplifies the similarity in their polymerization behaviors. The most obvious effect is the linear

Table I
Polymerization Results of β-R-β-propiolactones by $(EtAlO)_n$ Catalyst[a]

R	Polymerization time, days	Total yield, %	Stereoregular polymer yield, %	IS,[b] %	Melting temp,[c] °C	$\overline{M}_v$ of stereoregular polym,[d]	$R_p \times 10^3$, mol L^{-1} min^{-1}
CH_3	7	78	52	66	160–170	400 000	9.0
C_2H_5	7	26	19	73	102–110	100 000	3.1
i-C_3H_7	22	49	22	44	72–79	100 000	1.8
t-C_4H_9	32	21	0	0	69–73 (T_s)[g]	10 000	0.5
CH_2Cl	7	32	22	70	140–146	20 000[e]	3.7
$CHCl_2$	12	71	34	48	138–146	20 000[f]	4.8
CCl_3	7	92	0	0	135–141 (T_s)[g]	20 000	10.5

[a] Polymerization conditions: monomer, 1.16×10^{-2} mol; catalyst/monomer ratio, 0.04 (mol/mol); solvent, toluene (1 mL); temp, 60 °C. [b] Index of stereospecificity: (stereoregular polymer yield)/(total polymer yield) × 100. [c] Determined by DSC. [d] Most probable average molecular weight estimated from GPC eluted with $CHCl_3$. [e] Chloroform-soluble (atactic) fraction. [f] Ether–acetone-soluble (atactic) fraction. [g] Softening temperature determined by a microscopic apparatus under polarized light.

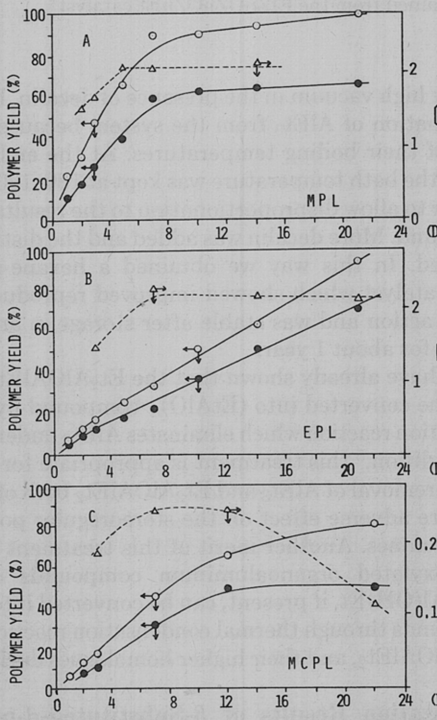


Figure 1. Time dependence of polymerization of MPL (A), EPL (B), and MCPL (C): (○) total polymer yield, (●) stereoregular polymer yield, and (△) [η] of the stereoregular polymer in $CHCl_3$ at 30 °C (A and B), and $\eta_{sp/C}$ of the stereoregular polymer in DMSO at 30 °C (C = 1 g/dL). Polymerization conditions: catalyst, $(EtAlO)_n$; monomer, 1.16×10^{-2} mol; catalyst/monomer ratio, 0.04 (mol/mol); solvent, toluene 1 mL; polymerization temperature, 60 °C.

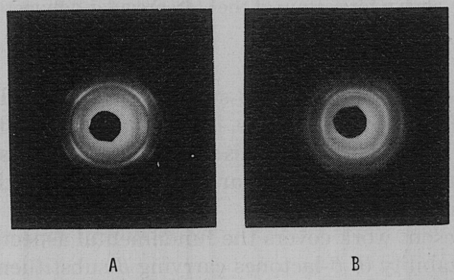


Figure 2. X-ray fiber photographs of crystalline poly(MCPL) (A) and poly(DCPL) (B): fiber period, c = 6.19 ± 0.1 Å for poly(MCPL) and c = 5.77 ± 0.1 Å for poly(DCPL).[23]

increase of stereoregular and nonstereoregular polymers in constant proportions, as was the case for $AlEt_3$–H_2O (1:1) and $AlEt_3$–H_2O–epichlorohydrin (1:1:1) catalysts.[6] The polymerization of MCPL involves some chain degradation at longer polymerization times; this behavior will be discussed in a later section.

From the results of Table I several important features can be derived. First, stereoregular polymers of MCPL and DCPL were newly obtained in addition to previously reported poly(MPL), poly(EPL), and poly(IPPL). The x-ray diagrams and IR spectra of the new polymers are shown in Figures 2 and 3. In Figure 3 the change in IR spectra from crystalline to amorphous states with temperature is illustrated. IR dichroism of the poly(MCPL) is shown in Figure 4 in which the variation of electronic vectors caused significant changes in the crystalline IR bands. Crystalline melting temperatures of poly(MCPL) and poly(DCPL) (ca. 146 °C) were higher than those of corresponding monomethyl and dimethyl derivatives, i.e., T_m(poly(EPL)) = ca. 110 °C and T_m(poly(IPPL)) = ca. 79 °C, indicating that the chlorine atom disturbs the chain movement of the polymers to some extent. The poly(MCPL) and poly(DCPL) of the stereoregular type are not cross-linked, because these are soluble in DMF and DMSO. The poly(DCPL) is soluble in diethyl ether as well.

Second, the rate of polymerization was slower with increasing alkyl substitution at the α carbon in the side chain but was faster when the carbon atom was substituted by an increasing number of chlorine atoms. This behavior of the monomers was analyzed by plotting ln (R_p) vs. electronic factor σ^* (Figure 5) and steric factor E_S (Figure 6) for the substituent groups, where σ^* is a substituent constant defined by Taft,[8] and E_S is a steric factor defined by the same author. In the case of the electron-releasing alkyl series, the σ^* and E_S factors participate cooperatively to result in a significant lowering of rate with an increased number of methyl groups. For the electron-attracting chlorine series, on the other hand, the electronic factor σ^* dominates the steric factor E_S to give increased rates with successive introduction of chlorine atoms.

The contribution of the steric factors for the alkyl series and for the chlorine series must be almost identical when the van der Walls radii of the methyl group (2.0 Å) and the chlorine atom (1.8 Å) are considered. The upward curvature in the plot of the chlorine series in Figure 6 compared to the alkyl series clearly indicates that the rate-increasing electronic effect of one chlorine atom is larger than its rate-decreasing steric effect.

Spectroscopic Properties of Lactone Monomers in Relation to Their Polymerizability. Spectroscopic investigations by ^1H NMR, ^{13}C NMR, and IR for the monomers

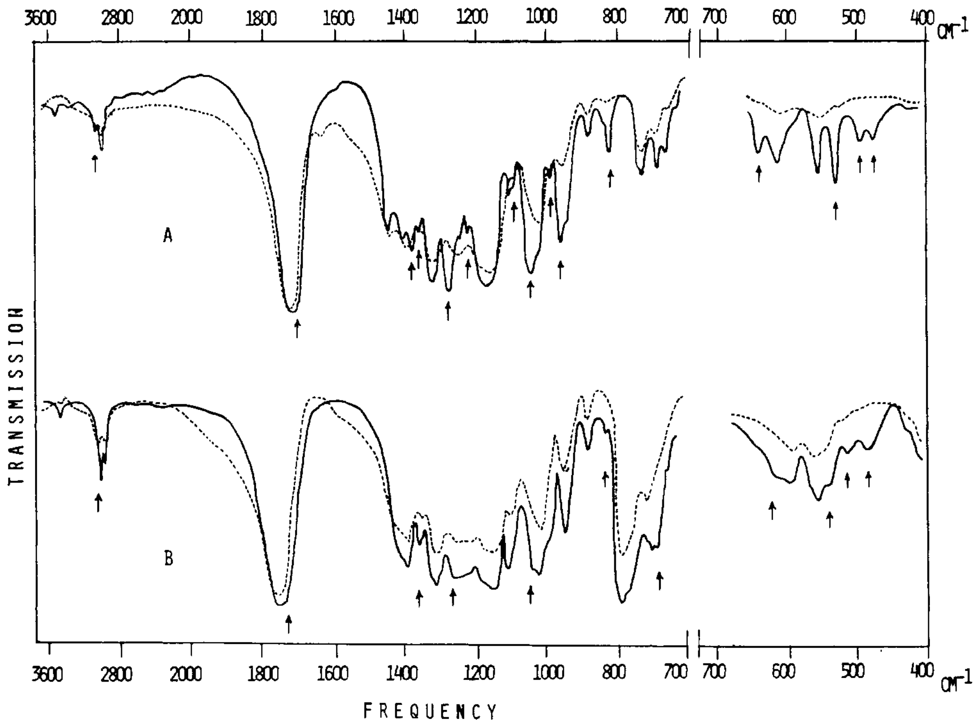


Figure 3. IR spectra of stereoregular poly(MCPL) (A) and poly(DCPL) (B): (—) spectra of crystalline state at room temperature, and (· · ·) spectra of molten state at 150 °C. Crystalline bands are shown by arrows.

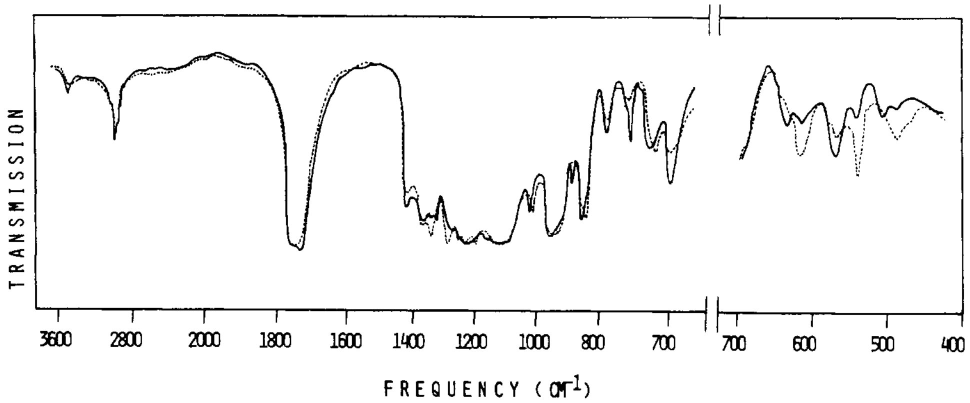


Figure 4. IR spectra of crystalline poly(MCPL) under polarized lights: (—) spectrum taken with electron vector perpendicular to the direction of elongation, and (· · ·) spectrum taken with electron vector parallel to the direction of elongation.

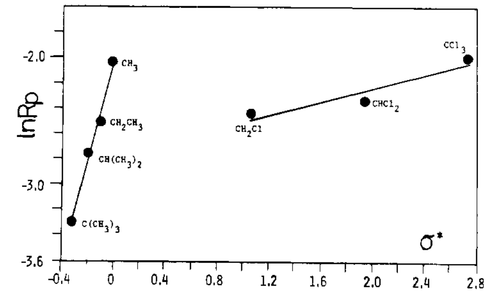


Figure 5. Relation between ln R_p and σ^* for polymerization of lactones: catalyst, $(EtAlO)_n$, at 60 °C. Polymerization conditions should be referred to Table I.

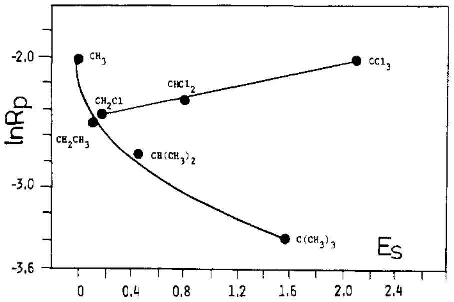


Figure 6. Relation between ln R_p and E_s for polymerization of lactones.[21]

revealed the positions in the molecule at which electronic effects predominated. The results are tabulated in Tables II, III, and IV, respectively. For the substituents of the alkyl series, large contributions are restricted to the C^2 and C^3 carbons, while only small changes are observed at the carbonyl carbon (C^1) and extremely slight effects are at C–O–C and C=O bonds. In contrast, the considerable substituent effects in the chlorine series clearly cover all the atoms in the molecule to cause a significant decrease in the strength of the C–O–C bond and an increase in the strength of C=O bond in addition to changing the electronic state of the carbonyl carbon.

On combining the spectroscopic results and rate data, it can

Table II
Values of Chemical Shift and Spin Coupling Constant for ^1H NMR Spectra of β-R-β-propiolactones[a]

	Chemical shift, ppm (δ)[b]				Coupling constant, Hz		
R	*a*	*b*	(*a* + *b*)/2	*c*	J_{ab}	J_{ac} (cis)	J_{bc} (trans)
CCl_3	3.38 q	3.58 q	3.70	5.07 q	−17.1	5.6	3.9
$CHCl_2$	3.69 q	3.49 q	3.59	4.84 m	−16.9	5.6	4.2
CH_2Cl	3.57 q	3.35 q	3.48	4.80 m	−16.8	5.7	4.3
CH_3	3.53 q	3.05 q	3.27	4.67 m	−16.5	5.7	4.3
C_2H_5	3.47 q	3.05 q	3.26	4.43 m	−16.4	5.7	4.3
i-C_3H_7	3.40 q	3.08 q	3.24	4.18 m	−16.5	5.7	4.6
t-C_4H_9	3.28 q	3.14 q	3.21	4.24 q	−16.5	5.8	4.8

[a] Neat, at 37–40 °C. Notations of protons should be referred to the formula below. [b] Standardized from TMS (0.00 ppm (δ)).

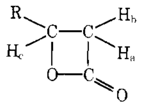


Table III
Values of Chemical Shift in ^{13}C NMR Spectra of β-R-β-propiolactones[a]

	Chemical shift, ppm (δ)[b]			
R	C_1	C_2	C_3	C_4
CCl_3	163.3	42.0	75.8	96.8
$CHCl_2$	165.2	41.3	71.1	71.3
CH_2Cl	166.5	41.3	68.8	44.8
CH_3	167.5	44.1	67.6	20.2
C_2H_5	167.5	42.3	71.8	27.7
i-C_3H_7	167.3	40.8	75.3	32.4
t-C_4H_9	167.0	38.1	77.3	32.7

[a] All spectra C_1–C_4 were singlets. 25.16 Hz. 50% solution in benzene-d_6. Notations of Carbons should be referred to the formula below. [b] Standardized from TMS (0.00 ppm (δ)).

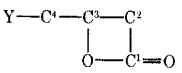


Table IV
IR Frequencies $\nu_{C=O}$ and ν_{C-O-C} of β-R-β-propiolactones[a]

R	$\nu_{C=O}$, cm^{-1}	ν_{C-O-C}, cm^{-1}
CCl_3	1855	1095
$CHCl_2$	1840	1100
CH_2Cl	1830	1110
CH_3	1825	1125
C_2H_5	1825	1125
i-C_3H_7	1825	1125
t-C_4H_9	1825	1130

[a] Neat.

Table V
Polymerization Results of β-R-β-propiolactones Catalyzed by EtZnOZnOZnEt Catalyst[a]

R	Polymerization time, days	Polymer yield, %	$\eta_{sp/C}$,[b] dL/g	T_s, °C
CH_3	14	89	0.52[c]	*d*
C_2H_5	14	41	0.33	*d*
i-C_3H_7	14	77	0.51	*d*
t-C_4H_9	14	25	0.26	67–73
CH_2Cl	6	100	0.20	29–33
$CHCl_2$	4	96	0.18	72–76
CCl_3	14	52	0.09	135–141

[a] Polymerization conditions: monomer, 1.16×10^{-2} mol; catalyst/monomer ratio, 0.02 (mol/mol); solvent, toluene (1 ml); temp, 30 °C. [b] Determined in $CHCl_3$ (*C*, 1 g/dL) at 30 °C. [c] $\overline{M}_v$ ca. 50 000 by GPC. [d] The polymers are softened at room temperature.

Table VI
Reaction of β-R-β-Propiolactones with Typical Anionic Catalysts[a]

R	Catalyst	Time, days	Conversion of monomer,[b] %	Polymer yield, %
H	CH_3ONa	5		24
H	*n*-BuLi	5		62
H	$PhCOONEt_4$[c]	5		81
CH_3	CH_3ONa	15	0–5	0
CH_3	*n*-BuLi	12	0–5	0
CH_3	$PhCOONEt_4$[d]	5	ca. 100	0
i-C_3H_7	CH_3ONa	15	0	0
i-C_3H_7	*n*-BuLi	12	0	0
t-C_4H_9	CH_3ONa	15	0	0
t-C_4H_9	*n*-BuLi	12	0	0
CH_2Cl	CH_3ONa	15	0–5	0
CH_2Cl	*n*-BuLi	12	ca. 40	0
$CHCl_2$	CH_3ONa	15	0–5	0
$CHCl_2$	*n*-BuLi	12	ca. 30	0
CCl_3	CH_3ONa	15	ca. 50	0
CCl_3	*n*-BuLi	12	ca. 20	0
CCl_3	$PhCOONEt_4$[e]	5	ca. 60	0

[a] Reaction conditions: monomer, 0.58×10^{-2} mol; catalyst/monomer ratio, 0.01 (mol/mol); solvent, THF (1 mL); temp, 30 °C. [b] Determined from IR spectra of the reaction products. [c] In THF: monomer, 0.58×10^{-5} mol. [d] Similar results were obtained in THF and in CH_3CN. [e] In CH_3CN: monomer, 0.58×10^{-5} mol.

be deduced that cleavage at the O–CO linkage is the most probable mode of the ring opening of the lactone molecules by $(EtAlO)_n$ catalyst. This conclusion agrees with the observation by Shelton et al.[4a] that optically active β-butyrolactone (β-BL) polymerizes without changing the configuration of the asymmetric carbon atom. In addition, there is no contradiction with the observation made by Yamashita et al.[9] on the copolymerization of propiolactone with styrene.

Other Catalytic Systems. The zinc–water system was found to produce exclusively atactic high polymers from the seven lactones studied. We prefer to use a notation "EtZnOZnOZnEt catalyst" for the zinc–water system according to the characterization of Colclough et al.,[10] since it was freeze dried.[10,11] This catalyst seems to promote polymerization (Table V) by a different mechanism, which is probably not anionic inasmuch as use of conventional anionic catalysts either caused no ring opening or else terminated propagation at a very early stage (Table VI).

The inability of the zinc system to give stereoregular polymers can be explained in terms of its noncoordination-accepting property with the lactone monomers. This is exemplified by a comparison of NMR spectra of IPPL and Et_2Zn in benzene-d_6 at 30 °C (Figure 7). The NMR patterns shown by IPPL alone were retained for quite a long period even in the presence of an equimolar amount of Et_2Zn. In addition, there was no significant change in the chemical shift of the ethyl protons attached to the Zn atom.

All of the seven monomers studied behave similarly with the EtZnOZnOZnEt catalyst, i.e., atactic high polymers are

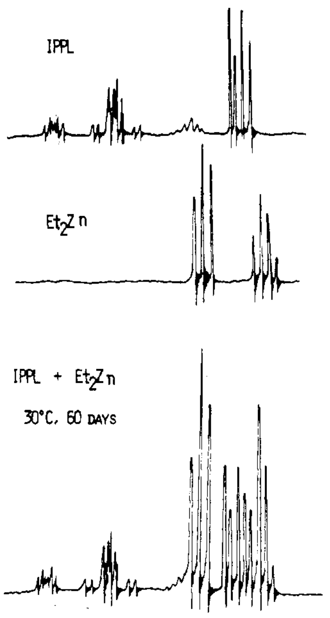


Figure 7. 60 MHz ^{1}H NMR spectra of IPPL, Et_2Zn, and their equimolar mixture in benzene-d_6.

formed at relatively high rate. With cationic catalysts, e.g., $BF_3 \cdot OEt_2$ and $SnCl_4$, all of these monomers gave atactic polymers of relatively low molecular weight in high yields in short reaction times. Similarity of the behavior of the monomers was also observed with anionic catalysts. These results suggest that the substituent group in the monomer has little effect on the ring-opening mechanism for a given type of catalyst.

Boundary of Stereoregular Polymerization by $(EtAlO)_n$ Catalyst. Our observations appear to be useful for predicting the synthesis of stereoregular polymers by $(EtAlO)_n$ catalyst from other lactones. The results in Table I show a critical boundary at which the stereoregular polymer formation becomes difficult. This is the case when the α carbon in the substituent is highly crowded as the cases of $C(CH_3)_3$ and CCl_3. In contrast, when the carbon atom is less hindered as in the case of $CH(CH_3)_2$, CH_2CH_3, CH_3, CH_2Cl, and $CHCl_2$, the formation of stereoregular polymer is possible. The polymers from TBPL and TCPL contained no detectable amounts of stereoregular fractions as determined by extraction techniques. They resisted any crystallizing attempts and showed amorphous x-ray diagrams. They were readily soluble in most organic solvents such as ether, benzene, acetone, chloroform, ethyl acetate, etc. Variation of polymerization conditions such as polymerization temperature, catalyst concentration, monomer concentration, and the polymerization solvent did not give any indication of the formation of stereoregular polymers from these two monomers. Further, stereoregular polymerization of these monomers was not observed with any of the organoaluminum catalysts listed in Table VII.

The possibility that the poly(TBPL) and poly(TCPL) obtained by $(EtAlO)_n$ catalyst were noncrystallizable stereoregular polymers was excluded by the following observations. First, the poly(TBPL) and poly(TCPL) were fractionated carefully and the fractions were investigated by DSC under extremely slow temperature elevation. No exothermal peaks due to crystallization were observed for any fractions. Second, attempts were made to crystallize the polymers, both in bulk state and by precipitation from various solvents. When these samples were examined by x-ray and under polarized light, no indication of crystallization was observed for any of these treatments. Third, the IR spectrum of the poly(TCPL) of this study was compared with that of isotactic insoluble poly(TCPL) obtained by solid state radiation polymerization by Yokouchi et al.[12] Details of the IR spectra were different in some respects in which crystalline bands were involved. Melting and solubility behaviors also differ for the two types of poly(TCPL). Fourth, IR spectra of poly(TBPL) and poly(TCPL) obtained by $(EtAlO)_n$ and EtZnOZnOZnEt catalysis, which are shown in Figure 8, indicate that the polymers obtained by $(EtAlO)_n$ catalysis have almost the same spectra as the atactic polymers obtained by EtZnOZnOZnEt catalysis.

Table VII
Catalysts used for Polymerization of TCPL and TBPL[a]

$AlEt_3$–H_2O (1:0.5)[b,c]
$AlEt_3$–H_2O (1:0.9)[b,c]
$AlMe_3$–H_2O (1:0.5)[b]
$AlMe_3$–H_2O (1:0.9)[b]
Ali–Bu_3–H_2O (1:0.5)[b]
Ali–Bu_3–H_2O (1:0.9)[b]
$AlEt_3$–H_2O–ECH (1:0.9:0.5)[b,c]
$AlEt_3$–CH_3OH (1:2)[b]
Et_2AlCl[b]
Et_2AlCl–H_2O (1:0.5)[b]
$EtAlCl_2$[b]
$EtAlCl_2$–H_2O (1:0.3)[b]
Et_2AlCl–$EtAlCl_2$ (1:1)[b]
$AlEt_3$–H_2O–acac (1:0.5:0.5)[b]

[a] Most of the catalysts were active for polymerization of these two monomers at 30 and 60 °C. Polymers were obtained in ca. 100% for TCPL ([η] 0.06–0.14, in $CHCl_3$, 30 °C) and 15–30% for TBPL ($\eta_{sp/C}$ 0.2 in $CHCl_3$ at 30 °C). However, no polymers contained any stereoregular fraction. [b] Used for TCPL. [c] Used for TBPL.

X-ray analyses of poly(MPL) and poly(EPL) obtained by $AlEt_3$–H_2O–epichlorohydrin catalysis have indicated these polymers to be isotactic.[13] It is reasonable to assume that the $(EtAlO)_n$ catalyst also favors isotactic placement, since poly(MPL) and poly(EPL) obtained by these catalysts showed

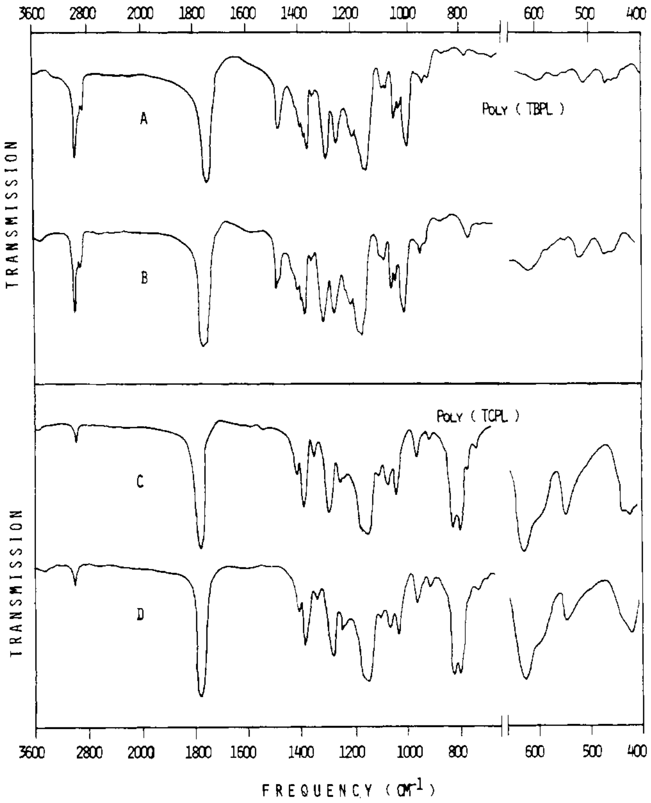


Figure 8. IR spectra of poly(TBPL) and poly(TCPL): (A) poly(TBPL) prepared by $(EtAlO)_n$ catalyst at 60 °C; (B) poly(TBPL) prepared by EtZnOZnOZnEt catalyst at 30 °C; (C) poly(TCPL) prepared by $(EtAlO)_n$ catalyst at 60 °C; (D) poly(TCPL) prepared by EtZnOZnOZnEt catalyst at 30 °C.

Table VIII
Temperature Dependence of NMR Chemical Shift for the Ring Protons of Monomers in the Presence and Absence of $(EtAlO)_n$ Catalyst[a]

R in monomer		H_c proton, δ ppm[h]					H_a and H_b proton $((H_a + H_b)/2)$, δ ppm[h]				
		−50 °C	−25 °C	0 °C	35 °C	Δδ[b]	−50 °C	−25 °C	0 °C	35 °C	Δδ[b]
CH_3	Alone	1.97	1.98	1.99	2.00	0.03					
	(Cat.)[f]	1.71	1.76	1.78	1.80	0.09					
C_2H_5	Alone	1.75	1.76	1.77	1.79	0.04	0.57	0.60	0.61	0.62	0.05
	(Cat.)[f]	1.63	1.65	1.67	1.69	0.07	0.45	0.49	0.50	0.51	0.06
$i-C_3H_7$	Alone	1.35		1.42	1.46	0.11	0.50	0.55	0.57	0.59	0.09
					(1.40)[c]					(0.46)[c]	
	(Cat.)[f]		1.47	1.50	(1.44)[c]	(0.03)[d]		0.54	0.58	(0.50)[c]	(0.04)[d]
$t-C_4H_9$	Alone	1.90	1.92	1.93	1.94	0.04	0.62	0.64	0.64	0.65	0.03
	(Cat.)[f]	1.70	1.74	1.76	1.78	0.08	0.49	0.51	0.53	0.55	0.06
CH_2Cl	Alone	1.61	1.63	1.64	1.65	0.04	0.64	0.66	0.69	0.71	0.07
	(Cat.)[f]	1.46	1.50	1.52	1.54	0.08	0.49	0.53	0.57	0.59	0.10
$CHCl_2$	Alone	1.68	1.74	1.80	1.83	0.12	0.50	0.55	0.63	0.65	0.13
	(Cat.)[f]	1.77	1.81	1.84	(1.77)[c]	(0.07)[e]	0.59	0.63	0.66	(0.59)[c]	(0.07)[e]
CCl_3	Alone		1.87	1:95	2.00	0.13		0.56	0.63	0.67	0.11
	(Cat.)[f]		1.92	1.96	2.01	(0.09)[g]		0.62	0.65	.0.69	(0.07)[g]

[a] Determined in 20% toluene-d_8 solution. Chemical shift values are internally standardized from toluene–CH_3 proton (δ = 0.00 ppm). [b] $\Delta\delta = \delta_{35\,°C} - \delta_{-50\,°C}$. [c] In 10% solution. [d] $\delta_{0\,°C} - \delta_{-25\,°C}$. [e] $\delta_{0\,°C} - \delta_{-50\,°C}$. [f] The catalyst $(EtAlO)_n$ was added in a ratio of Al atom/monomer mol = 1.0. [g] $\delta_{35\,°C} - \delta_{-25\,°C}$. [H] Notations of H_a, H_b, and H_c should be referred to the formula in Table II.

the same melting points, respectively. In these cases the polymerization seems to occur through coordination. Investigation of the NMR chemical shift of monomer protons by ^1H NMR in toluene-d_8 (Table VIII) revealed that most of the monomers used, including TBPL, showed a significant change in chemical shift due to coordination with the catalyst. The change depended significantly both upon temperature (−50 to +35 °C, where no detectable polymerization was initiated during the measurement) and upon monomer concentration in the presence of the catalyst, as compared with their free states. Coordination of the $(EtAlO)_n$ catalyst with the monomers was thus elucidated.

From the NMR experiment of Table VIII it was found that the atactic polymerization of TBPL was not due to the lack of coordination ability of this monomer. In the case of TCPL, however, its weakened coordination ability may explain partly its atactic polymerization. Since weak coordination was also observed for IPPL which gave stereoregular polymer, some other factor in the propagation stage must be considered to interpret the lack of stereoregularity in the cases of TBPL and TCPL. The crowding at the α carbon of the substituent group possibly increases the arrangement opposed to the normal stereoregular placement on the $(EtAlO)_n$ catalyst.

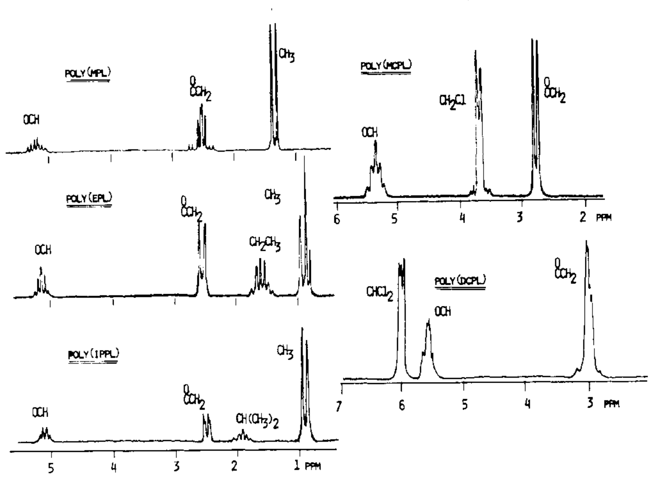


Figure 9. 100 MHz ^1H NMR spectra of atactic poly(MPL), poly(EPL), poly(IPPL), poly(MCPL), and poly(DCPL) obtained with $(EtAlO)_n$ catalyst; measured in $CDCl_3$. The stereoregular polymers showed correspondingly the same spectra. The spectra were internally standardized from TMS (0.0 ppm).

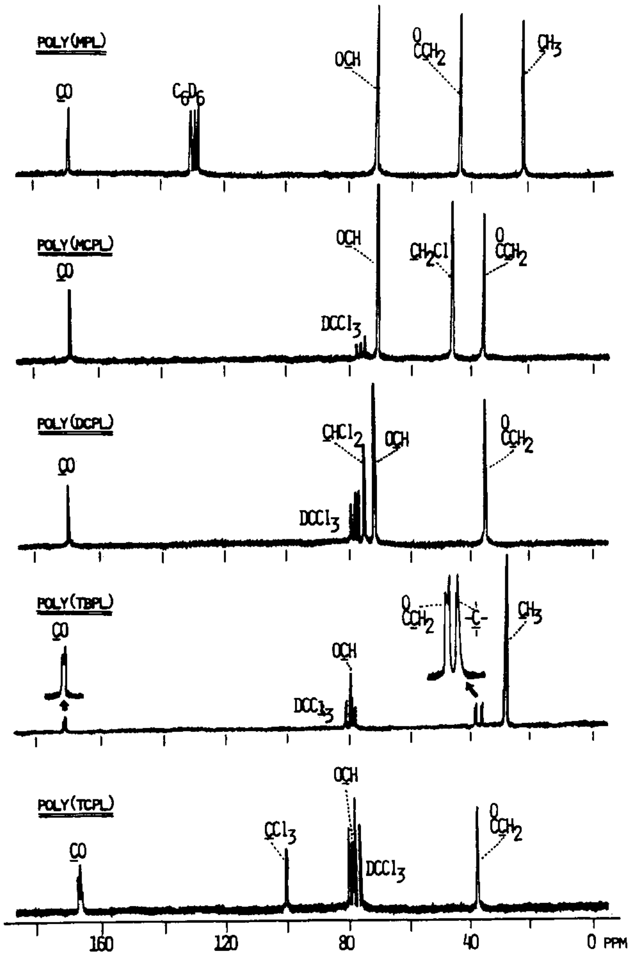
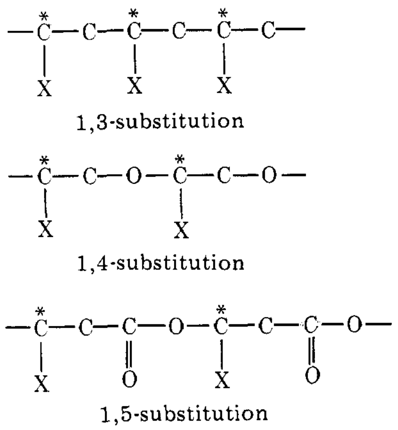


Figure 10. ^{13}C NMR spectra of atactic poly(MPL), poly(MCPL), poly(DCPL), poly(TBPL), and poly(TCPL) obtained with $(EtAlO)_n$ catalyst. The spectra were recorded at 25.16 MHz, decoupled at the frequency of TMS and FT accumulated. Poly(MPL) was measured in benzene-d_6 and others were in $CDCl_3$. Assignments of the signals were carried out by comparing with their undecoupled signals. The CH_2Cl carbon and $COCH_2$ carbon in the poly(MCPL) were assigned by considering the shielding effects of the Cl and CO groups based on reference tables. Chemical shift values were internally standardized from TMS (0.0 ppm). Poly(MPL), poly(MCPL), poly(DCPL) of stereoregular type showed correspondingly the same spectra as illustrated in these figures.

Scheme I
Rough Guideline of Tacticity Separation in NMR Spectroscopy[a]



1,3-substitution: triad tacticity is observable in 60 MHz ^{1}H NMR

1,4-substitution: dyad tacticity is observable in 100 MHz ^{1}H NMR
triad tacticity is observable in ^{13}C NMR

1,5-substitution: dyad and triad tacticities are difficult to observe in 100 MHz ^{1}H NMR; indication of dyad separation is found to be observable in ^{13}C NMR

[a] Some deviations come from the nature of the X group and the chain conformation in the solvent used.

NMR Spectra of Polyesters from Lactones. ^{1}H NMR spectra of poly(MPL), poly(EPL), poly(IPPL), poly(MCPL), and poly(DCPL) and ^{13}C NMR spectra of poly(MPL), poly(MCPL), poly(DCPL), poly(TCPL), and poly(TBPL) are shown in Figures 9 and 10, respectively. The spectra corresponded well to polyester type structures, and the assignments of the signals are represented in the figures. We found that the stereoregular and atactic polymers from individual monomers give identical NMR patterns in 100 MHz ^{1}H NMR spectra.

Principally, the separation of the NMR signals due to polymer tacticity depends on the distance of the adjacent asymmetric carbon atoms interacting with each other. This appears to be the case when a vinyl polymer (1,3-substitution) is compared with a polyoxirane (1,4-substitution). Extension of the principle to the poly-β-ester (1,5-substitution) studied indicated that the asymmetric centers are too far apart to observe tacticity separation in the NMR spectra as found in the case of 1,4-substitution systems (see Scheme I).

Slight separations of the carbonyl and methylene carbons of noncrystallizable poly(TBPL) and poly(TCPL) in ^{13}C NMR were observed. Two other examples may be atactic poly(EPL) and atactic poly(IPPL). In addition, atactic poly(MPL) was found to show slight separation in the ^{13}C NMR spectrum by the aid of a shift reagent. These findings on the tacticity separation in 1,5-substitution systems are based on an extensive study which will be published later.

Molecular Weight Distribution. Gel permeation chromatograms of the acetone-insoluble (isotactic) fractions of poly(MPL), poly(EPL), and poly(IPPL) (Figures 11a,d,e) and the acetone-soluble (atactic) fraction of poly(MPL) (Figure 11b) show that the polymers have wide molecular weight distributions. The isotactic fraction of poly(MPL) (Figure 11a) is located at a relatively higher molecular weight region and its nonstereoregular fraction at a relatively lower region (Figure 11b). The atactic polymer of MPL obtained with EtZnOZnOZnEt catalyst, on the other, showed a simpler distribution pattern based on the GPC diagram (Figure 11c). The difference in the GPC patterns between the polymers obtained with Al and Zn catalysts indicates that the difference of polymerization mechanism mentioned in the former section is largely due to termination and/or chain transfer reactions. These observations show that the so called "atactic polymers" obtained with the Al catalyst and with the Zn catalyst differ in their molecular weight distribution.

Gel permeation chromatograms of "atactic" fractions of poly(MCPL) and poly(DCPL) together with poly(TBPL) and poly(TCPL) obtained by the $(EtAlO)_n$ catalyst are illustrated in Figure 12. By calibration with standard polystyrene, the following values were obtained: $\overline{M}_v$(poly(MCPL)) = ca. 15 000, $\overline{DP}$ = ca. 125; $\overline{M}_v$(poly(DCPL)) = ca. 15 000, $\overline{DP}$ = ca. 100; $\overline{M}_v$(poly(TBPL)) = ca. 10 000, $\overline{DP}$ = ca. 80; $\overline{M}_v$(poly(TCPL)) = ca. 20 000, $\overline{DP}$ = ca. 105. The atactic fractions of poly(MCPL) and poly(DCPL) show some indication of a wide molecular weight distribution. Comparison with corresponding stereoregular polymers in GPC was not carried out because of the insoluble nature of the stereoregular polymers in the eluent used for the GPC. However, it is clear from viscosity measurements that the stereoregular polymers have

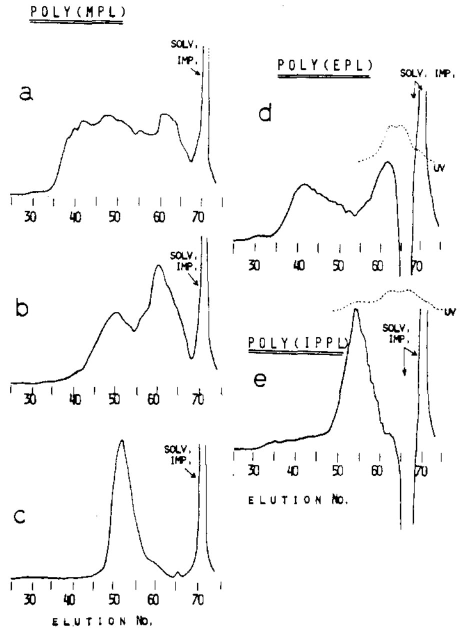


Figure 11. GPC patterns of polymers: (a) stereoregular fraction of poly(MPL) obtained with $(EtAlO)_n$ catalyst; (b) atactic poly(MPL) obtained with $(EtAlO)_n$ catalyst; (c) atactic poly(MPL) obtained with EtZnOZnOZnEt catalyst; (d) stereoregular poly(EPL) obtained with $(EtAlO)_n$ catalyst; (e) stereoregular poly(IPPL) obtained with $(EtAlO)_n$ catalyst. Chromatography was carried out by eluting with $CHCl_3$ and detecting with a refractometer. In the cases of poly(EPL) and poly(IPPL) in which negative peaks were observed, a UV photometer was also used (shown by dashed lines).

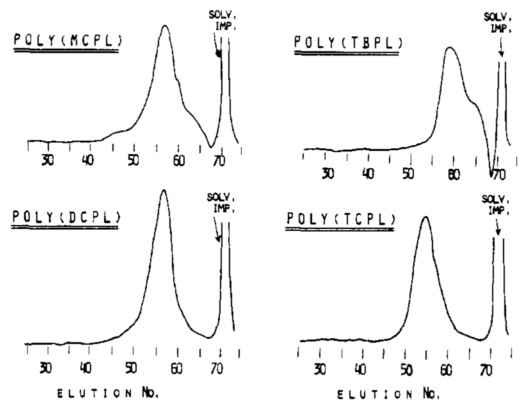
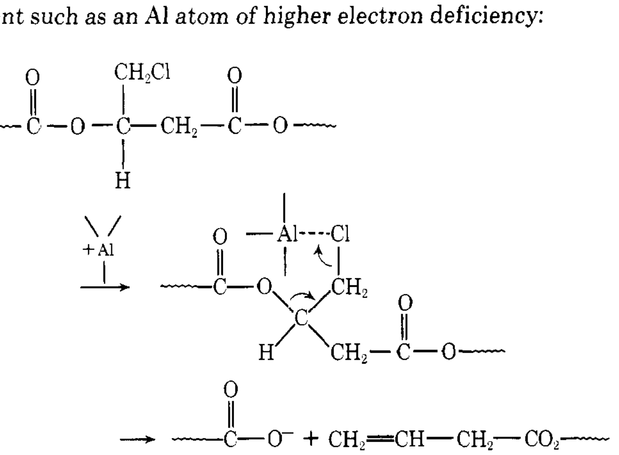


Figure 12. GPC patterns of atactic fractions of poly(MCPL), poly(DCPL), poly(TBPL), and poly(TCPL) obtained with $(EtAlO)_n$ catalyst.

molecular weight higher than the atactic polymer fractions. This result is usual in stereoregular polymerization, as we observed in the case of polymerization of propylene oxide by $R_2AlOAlR_2$ catalysts (the lowest homologue of $(RAlO)_n$ compound).[7]

The question of why the nonstereoregular chain growth terminates at lower DP than the stereoregular system is of interest. This phenomenon suggests a certain protecting effect of the stereoregular polymer chain from termination reaction. However, we have no clear evidence on this problem at present, and all we can say is that the absolute rate of stereoregular propagation is much higher than the apparent rate of polymerization, i.e., the time dependence of the molecular weight of the stereoregular fraction in Figure 1 shows that the high molecular weight polymer is formed at relatively low conversion.

Suppression of Side Reaction. When the Al catalyst or the monomer contains adverse components as in the case of $AlEt_3$–H_2O (1:1) in situ or an impure monomer, additional difficulty occurs, e.g., chain degradation. This is particularly important in the case of polymerization of MCPL.[14] The product subjected to chain degradation showed new IR bands at 1610, 1580, and 1480 cm^{-1} corresponding to COO^- and C=C groups, along with the lowering of Cl content (from 29.36% down to 28.77%) in elemental analysis. A possible mechanism for chain degradation of the polymer appears to involve abstraction of chlorine atoms by an electrophilic reagent such as an Al atom of higher electron deficiency:



This process does not occur very frequently (since NMR spectra showed little detectable change), but it does cause a significant decrease in molecular weight (η_{sp}/c from 0.2 down to 0.1). This chain degradation is suppressed satisfactorily at least for 12 days by the use of $(EtAlO)_n$ catalyst and extensively purified monomer.

Experimental Section

Synthesis and Purification of Monomers. β-Methyl-β-propiolactone (MPL), β-ethyl-β-propiolactone (EPL), and β-isopropyl-β-propiolactone (IPPL) were synthesized from corresponding aldehydes by cycloaddition with ketene, as described in the preceding paper.[6]

β-Chloromethyl-β-propiolactone (MCPL). Chlorination of acetaldehyde by Cl_2 at 10–15 °C followed by distillation gave monochloroacetaldehyde hydrate $ClCH_2CHO\cdot\frac{1}{2}H_2O$.[15] The hydrate was dehydrated by azeotropic distillation at room temperature under reduced pressure by using CH_2Cl_2. This technique was successful because of the low boiling point of the azeotropic mixture (bp 38.1 °C, H_2O 1.5%). After the distillation of the azeotropic mixture was completed, the remainder of the aldehyde solution was adjusted to a given concentration in CH_2Cl_2, then it was subjected to the cycloaddition with ketene at −60 °C catalyzed by $BF_3\cdot OEt_2$.[16] The reaction mixture was neutralized by aqueous 40% NaOH, filtered, extracted with Et_2O, and then distilled under reduced pressure. Purification of MCPL thus obtained was carried out by repeated (40–50 times) extraction with *n*-hexane until gas chromatographically pure MCPL was obtained. Then it was distilled twice after drying over CaH_2 and then $CaCl_2$. Bp 76–78 °C (3 mm), mp −11 °C, d^{4}_{20} 1.3346. Yield, 35% from aldehyde. Anal. Calcd from $C_4H_5O_2Cl$ (120.5): C, 39.83; H, 4.15; Cl, 29.46. Found: C, 39.47; H, 4.21; Cl, 29.51. NMR: see Tables II and III. IR: see Table IV. Purity: >99% by GLC and NMR.

β-Dichloromethyl-β-propiolactone (DCPL). Chlorination of monochloroacetaldehyde hydrate by chlorine at 40–50 °C followed by distillation then azeotropic distillation with CH_2Cl_2 gave a mixture of dichloro- and monochloroacetaldehydes.[17] The CH_2Cl_2 solution of the mixture was treated by P_2O_5 for 2 days to remove monochloroaldehyde then distilled bulb-to-bulb under reduced pressure. The resultant aldehyde was subjected to cycloaddition with ketene in ether at 0–10 °C. The reaction mixture was treated as for MCPL above, and the distillate was recrystallized from a mixed solution of Et_2O–*n*-hexane (1:1) at −78 °C four times. The recrystallized DCPL was distilled twice after drying over CaH_2 and then $CaCl_2$. Bp 71–75 °C (2 mm), mp 21 °C, d^{4}_{20} 1.4190. Yield, 70% from aldehyde. Anal. Calcd from $C_4H_4O_2Cl_2$ (155): C, 30.97; H, 2.58; Cl, 45.80. Found: C, 30.91; H, 2.83; Cl, 45.15. NMR: see Tables II and III. IR: see Table IV. Purity: >99% by GLC and NMR.

β-Trichloromethyl-β-propiolactone (TCPL). Commercial chloral was distilled and then subjected to cycloaddition[20] with ketene in CH_2Cl_2 at −60 to −40 °C. The reaction mixture was treated as for MCPL above, and the distillate obtained, which solidified at room temperature, was dissolved in Et_2O. The ether solution of TCPL was chilled at −20 °C to allow crystallization. After being recrystallized from ether three times, it was dried under reduced pressure for three days. Mp 37 °C, bp 78–80 °C (3 mm). Yield, 30% from aldehyde. Anal. Calcd from $C_4H_3O_2Cl_3$ (189.5): C, 25.24; H, 1.53; Cl, 56.02. Found: C, 25.33; H, 1.58; Cl, 56.04. NMR: see Tables II and III. IR: see Table IV. Purity: >99.9% by GLC and NMR.

β-*tert*-Butyl-β-propiolactone (TBPL). Pivalaldehyde (trimethylacetaldehyde) was prepared by the reaction of methyl formate with *t*-BuMgCl in ether at −40 to −50 °C,[18] followed by distillation. The distilled aldehyde was dried with CaH_2 under reflux of its ether solution in an argon atmosphere for 3 h. This solution was distilled bulb-to-bulb, and after the purity of the aldehyde was confirmed by GLC and NMR by taking an aliquot of the ether solution, the ether solution was subjected to cycloaddition with ketene at 0–10 °C. The reaction mixture was treated as for MCPL above, but the distillate obtained was only 95% pure and did not initiate polymerization. The material was therefore treated with the $(EtAlO)_n$ compound in toluene at room temperature for ca. 8 h under vigorous stirring, distilled bulb-to-bulb in vacuo after the toluene was removed, then distilled again. Bp 55–57 °C (3 mm), mp −9 °C, d^{4}_{20} 0.9596. Yield, 60% from aldehyde. Anal. Calcd from $C_7H_{12}O_2$ (128): C, 65.63; H, 9.38. Found: C, 65.13; H, 9.61. NMR: see Tables II and III. IR: see Table IV. Purity: >99% by GLC and NMR.

Preparation of Catalyst. All of the experiments were done under an argon atmosphere. Solvents used for catalyst preparation and polymerization were purified in the usual way.[22]

$(EtAlO)_n$ Catalyst.[5] Commercial $AlEt_3$ (Ethyl Corp.) and water were reacted in toluene at −78 °C as described in the preceding paper,[6] then the toluene solution was separated from the precipitate by hypodermic syringe. The toluene solution was mixed with a nearly equal amount of decalin, the mixture was distilled in vacuo (10^{-5} mm), and the residue was heated at 180–190 °C in vacuo for half an hour. After the residue was cooled, the same amount of decalin was added and the mixture was distilled out in vacuo. By this treatment, $AlEt_3$ formed during heating was distilled out simultaneously with the decalin. This procedure was repeated until there was no indication of the formation of $AlEt_3$ during the heat treatment (the presence of $AlEt_3$ is observable through the refluxing of liquid or the condensation of vapor on the inner wall of the distillation flask). The colorless, highly viscous product solidified into a white solid (or powder) on cooling. This white solid was dissolved in *n*-hexane, filtered, evaporated, dissolved in toluene, and then stored under an argon atmosphere.

$AlEt_3$–H_2O and $AlEt_3$–H_2O–Epichlorohydrin Catalysts. These catalysts were prepared as described in the preceding paper.[6]

Other Organoaluminum Catalysts. Organoaluminum compounds were obtained from Ethyl Corp. and used without further purification. The catalytic systems of Table VII were all in situ systems in which organoaluminum compounds were reacted in toluene with water, methanol, acetylacetone (acac), and epichlorohydrin (ECH) in the order shown. The molar ratio of the reactants is shown in parentheses. In all cases the reactions were completed by heating to ca. 60 °C until gas evolution ceased.

EtZnOZnOZnEt Catalyst.[10] This catalyst was prepared from Et_2Zn by reaction with water in a molar ratio of 1:0.6 in dioxane, followed by freeze drying the reaction mixture as described in the preceding paper.[6]

Tetraethylammonium Benzoate Catalyst.[19] Fully dried Et_4NCl was reacted with KOH in methanol (dried), then CH_3CN was added to precipitate KCl after the methanol was removed. Then a solution of benzoic acid in CH_3CN was added. After removal of CH_3CN, the product was recrystallized from ether–CH_3CN (2:1 v/v) three times and dried with P_2O_5 at 40 °C in vacuo. It was identified by NMR.

Polymerization. The polymerization experiments were done under an argon atmosphere. Except for the case of TCPL, 1.16×10^{-2} mol of monomer was added to a toluene solution (1 ml) of a given catalyst at −78 °C. The mixture was stirred for a few minutes to give a homogeneous solution, and then the polymerization tube was sealed. In the case of TCPL which is a solid, a toluene solution of the catalyst at −78 °C was added to a toluene solution of TCPL at −78 °C. The sealed tube was allowed to stand at a given temperature for a given period.

Termination and Fractionation. Quenching of the catalyst was carried out by the addition of water-containing solvents (100 ml/1 g initial monomer) to the polymerization mixture. The solvents used for this purpose varied with the nature of monomers because of the difference in solubilities of monomer and polymer. The following are the combination of monomers and solvents: MPL, ether;[6] EPL, petroleum ether;[6] IPPL, petroleum ether;[6] MCPL, ether; DCPL, ether–petroleum ether (1:1 v/v); TCPL, petroleum ether. For the case of TBPL where it was difficult to separate polymer from the monomer, the unreacted TBPL was removed at 30 °C from the mixture by distillation in vacuo (1 mm) after the addition of water-containing ether (2–3 ml). The polymers thus separated from the monomers were dried in vacuo (1 mm) at 30 °C. The total polymer yield is the percent of the total polymer formed from the monomer used.

The polymers were then fractionated by the following methods using 100 ml solvents per 1 g of polymer into soluble and insoluble fractions: MPL, $CHCl_3$–acetone (reprecipitation);[6] EPL, $CHCl_3$–ether (reprecipitation);[6] IPPL, $CHCl_3$–ether (reprecipitation);[6] MCPL, ether (extraction at room temperature); DCPL, $CHCl_3$–acetone (1:1 v/v) (extraction at room temperature). The insoluble polymers were dried in vacuo (3 mm) at 30 °C for 24 h. The insoluble polymer expressed as a percent of the unfractionated polymer is denoted as the index of stereospecificity (IS) of polymerization reactions.

Removal of the catalyst residue from all of the fractionated stereoregular polymers was achieved by immersing the polymers in 5 ml of acetylacetone per 1 g of the polymer for 48 h at room temperature, and after drying under reduced pressure, the polymers were examined by elemental analysis.

Characterization of Polymers. The polymers obtained were characterized by elemental analysis, IR, NMR, and x-ray diagram. Poly(MPL), poly(EPL), and poly(IPPL) were almost identical with those reported previously.[6]

Poly(MCPL). (1) Poly(MCPL) Obtained with $(EtAlO)_n$ Catalyst. The stereoregular fraction of poly(MCPL) was a white solid, melting at 140–146 °C, soluble in DMSO and DMF, slightly soluble in acetone and $CHCl_3$, and insoluble in *n*-hexane, benzene, and ether. Anal. Calcd from $C_4H_5O_2Cl$: C, 39.83; H, 4.15; Cl, 29.46. Found: C, 39.42; H, 4.30; Cl, 29.36. The $CHCl_3$-soluble fraction was almost identical with the polymer obtained with the Zn catalyst. **(2) Poly(MCPL) Obtained with EtZnOZnOZnEt Catalyst.** Colorless transparent film softens at ~31 °C, soluble in acetone and $CHCl_3$, slightly soluble in benzene, and insoluble in *n*-hexane and ether. Analytical data were similar to those of the stereoregular polymer described above.

Poly(DCPL). (1) Poly(DCPL) Obtained with $(EtAlO)_n$ Catalyst. The stereoregular fraction of poly(DCPL) was a white solid, melting at 138–146 °C, soluble in ether, DMSO, and DMF, slightly soluble in acetone and $CHCl_3$, and insoluble in *n*-hexane and benzene. Anal. Calcd from $C_4H_4O_2Cl_2$: C, 30.97; H, 2.58; Cl, 45.80. Found: C, 30.73; H, 2.76; Cl, 45.35. The ether–acetone-soluble fraction was almost identical with the polymer obtained with the Zn catalyst. **(2) Poly(DCPL) Obtained with EtZnOZnOZnEt Catalyst.** Colorless transparent film softens at ~76 °C, soluble in ether, benzene, acetone, and $CHCl_3$, insoluble in *n*-hexane. Analytical data were similar to those of the stereoregular polymer described above.

Poly(TCPL). The poly(TCPL) obtained with the Al and Zn catalysts were almost identical in nature. White powder, softens at 135–141 °C, soluble in ether, benzene, acetone, $CHCl_3$, and ethylacetate. Anal. Calcd from $C_4H_3O_2Cl_3$: C, 25.24; H, 1.53; Cl, 56.02. Found: C, 25.26; H, 1.85; Cl, 55.75.

Poly(TBPL). The poly(TBPL) obtained with the Al and Zn catalysts were almost identical in nature. Colorless solid, softens at 69–73 °C, soluble in ether, benzene, acetone, and $CHCl_3$, partially soluble in *n*-hexane. Anal. Calcd from $C_7H_{12}O_2$: C, 65.63; H, 9.38. Found: C, 65. 36; H, 9.67.

All of these polymers showed strong IR C═O stretching frequencies and the NMR spectra agreed well with the structure of β-polyester.

Instruments and Apparatus. NMR spectra were recorded with Varian-XL100, Varian-A-60D, and Varian-T-60 type spectrometers. For measurement of ^{13}C NMR FT computation was performed with the Varian-XL100 type apparatus. IR spectra were recorded with Nihon Bunko EPI-2 and DS-402G type spectrometers. X-ray (Cu Kα) diffraction experiments were carried out by the use of samples stretched more than ten times the length at a temperature below the melting point. Thermal behavior of polymers and monomers was measured by differential scanning calorimeter (Rigaku Denki) and a microscopic melting point apparatus under polarized light. An Ubbelohde type viscometer was used to measure the solution viscosities η of polymers. The molecular weight distribution of the polymers was measured by gel permeation chromatography with a Toyo Soda HLC-801A type apparatus (column constitution SG-6300 (50 cm) -SG-7000 (50 cm)) and a Shimadzu-Du Pont 830 type apparatus (column constitution HSG-60 (50 cm) -HSG-40 (50 cm) -HSG-20 (50 cm)). In both cases calibrations were carried out with standard polystyrene mixtures.

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Characterization of Polyether and Polyester Homo- and Copolymers Prepared by Ring Opening Polymerization with a New Catalytic System

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ABSTRACT: The ring-opening homopolymerization of tetrahydrofuran and ϵ-caprolactone and copolymerizations of tetrahydrofuran/ϵ-caprolactone and γ-butyrolactone respectively with a catalytic system consisting of phosphorus tricyanide and acetonitrile were studied. The homopolymers obtained were characterized by their molecular weights $\overline{M}_w$, infrared spectra, differential scanning calorimetry (DSC) behavior, and x-ray diffraction patterns. The poly(ether ester) copolymers contained approximately 3% γ-butyrolactone and 5% ϵ-caprolactone units, as determined by NMR. The copolymers were further characterized by their infrared spectra, DSC, and x-ray diffraction data.

The vigorous activities in the field of polyether and polyester ring opening polymerization are reflected in the considerable number of patents and papers published in this area.[2-11] Recently the results of tetrahydrofuran (THF) polymerization with a new catalytic system have been reported.[12] It was shown that in the presence of acetonitrile, phosphorus tricyanide, P(CN)$_3$, changes from off-white, when freshly prepared, through yellow to orange, on standing in a sealed vessel. This orange-yellow form of P(CN)$_3$ was shown to be an active catalyst in the bulk polymerization of THF to high molecular weight products.[12] Although the active species of this catalyst system is not yet fully understood owing to its complex nature, we have tested its applicability to other ring-opening polymerizations. Thus, the catalyst has been employed in polymerization reactions with ϵ-caprolactone and THF/ϵ-caprolactone as well as THF/γ-butyrolactone mixtures. The purpose of this paper is to report in some detail on the characterization of the products obtained.

Experimental Section

Viscosities were determined in Cannon Fenske viscometers at 303 K. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer and proton magnetic resonance spectra were obtained with a Jeol 4H 100S NMR spectrometer at 100 MHz on $CDCl_3$ solutions. Differential scanning calorimetry traces were obtained on a Perkin-Elmer DSC-2 calorimeter and the x-ray diffraction diagrams were recorded on a Philips goniometer PW 1050/25 (40 kV/20 mA; Cu Kα 1.54 Å).

For the sake of completeness the preparation of the catalyst and the THF homopolymer will be repeated here.

Preparation of the Catalyst. P(CN)$_3$ was prepared by adding 5 g of PCl_3 in 20 ml of CH_3CN (dried over P_2O_5 and distilled) to 15 g of AgCN vigorously stirred in 200 ml of CH_3CN under dry nitrogen. After 2 h at room temperature the product was filtered under nitrogen and the acetonitrile was removed on a rotary evaporator with a bath temperature of 318 K. When a solid residue was obtained, air was admitted and the flask was stoppered. On standing for 24 h the change from white to orange form occurred. This product was used in the polymerization studies.

Preparation of Polytetrahydrofuran. Previous to its use in the polymerization reaction THF (predried over KOH) was distilled from sodium and collected over molecular sieve. To 3.54 g (49.2 mmol) of THF 0.1 g of the above-mentioned catalyst was added and the mixture was shaken at room temperature. Within a few minutes the yellow color of the solution intensified and concomitantly the viscosity increased until the original solution solidified to a transparent yellow-brown solid after about 1 h. After standing for 2 days the reaction mixture was dissolved in 100 ml of THF and the polymer was precipitated as white rubbery solid by adding this solution dropwise to 1 L of ice water in a high-speed blender. Upon repetition of the dissolution and precipitation operations a white tough product, finally dried in the vacuum oven at 298 K for 48 h, was obtained with a yield of 49%. Anal. Calcd for C_4H_80: C, 66.7; H, 11.1; O, 22.2. Found: C, 66.3; H, 11.2; O, 22.3. Intrinsic viscosity [η] in chlorobenzene, 75 mL/g.

Preparation of Poly-(ϵ-caprolactone). Catalyst (52 mg) was added to 2.76 g (24.2 mmol) of ϵ-caprolactone. The reaction mixture immediately took up a red color. At room temperature the viscosity increased only slowly but heating to 333 K overnight produced a very viscous solution. After dilution with 40 ml of THF the solution was added dropwise under vigorous stirring to 400 ml of H_2O when the