benzenesulfonate. In each case a known weight (about 10 mg) of polymer derivative was dissolved in 100 ml of 0.1 *M* Veronal buffer (pH 8.5). This solution (1 ml) was mixed with 1 ml of a fresh solution of 30 mg of trinitrobenzenesulfonate in 50 ml of water. The resulting solution was incubated at 40° for 10 min and then diluted with 2 ml of glacial acetic acid. The absorbance of this mixture was measured at 340 nm. After correction for a blank, and on the basis of extinction coefficient of 12,000 for the picramide formed, we can calculate the amount of primary amine.

Nmr spectra were obtained on a Varian T-60 nmr spectrometer. To further confirm assignments, a few additional spectra were obtained on a 90-MHz Bruker nmr spectrometer.

Acknowledgment. This investigation was supported in part by a grant from the National Science Foundation. Assistance was also provided by a U. S. Public Health Service Training Grant (5Tl-GM-626) from the National Institute of General Medical Sciences. The authors also greatfully acknowledge the assistance of Mr. Charles Hoyle in several aspects of this work.

References and Notes

(1) L. E. Davis in "Water-Soluble Resins," R. L. Davidson and M. Sittig, Ed., Reinhold Publishing Corp., New York, N. Y., 1968, pp 216-226.
(2) O. C. Dermer and G. E. Ham, "Ethylenimine and Other Aziridines; Chemistry and Applications," Academic Press, New York, N. Y., 1969, Chapter 4.
(3) C. R. Dick and G. E. Ham, *J. Macromol. Sci. Chem.*, **A4**, 1301 (1970).
(4) I. M. Klotz and A. R. Sloniewsky, *Biochem. Biophys. Res. Commun.*, **31**, 421 (1968).
(5) I. M. Klotz, G. P. Royer, and A. R. Sloniewsky, *Biochemistry*, **8**, 4752 (1969).
(6) I. M. Klotz and V. H. Stryker, *J. Amer. Chem. Soc.*, **90**, 2717 (1968).
(7) G. P. Royer and I. M. Klotz, *J. Amer. Chem. Soc.*, **91**, 5885 (1969).
(8) I. M. Klotz, G. P. Royer, and I. S. Scarpa, *Proc. Nat. Acad. Sci. U. S.*, **68**, 263 (1971).
(9) S. L. Jung, J. G. Miller, and A. R. Day, *J. Amer. Chem. Soc.*, **75**, 4664 (1953).
(10) G. E. Means and R. E. Feeney, *Biochemistry*, **7**, 2192 (1968).
(11) (a) G. D. Jones, D. C. MacWilliams, and N. A. Braxter, *J. Org. Chem.*, **30**, 1994 (1965). (b) H. K. Hall, *ibid*, **29**, 3539 (1964).
(12) T. Okuyama and K. Satake, *J. Biochem.* (*Tokyo*), **47**, 454 (1960).
(13) K. Satake *et al.*, *J. Biochem.* (*Tokyo*), **47**, 654 (1960).
(14) G. E. Means, W. I. Congdon, and M. L. Bender, *Biochemistry*, **11**, 3564 (1972).
(15) Acetate ion was added to some solutions as an nmr marker. It gives a very sharp resonance about 0.1 ppm upfield from the secondary amides.
(16) T. W. Johnson and I. M. Klotz, *J. Phys. Chem.*, **75**, 4061 (1971).
(17) J. A. Yankeelov and C. J. Jolley, *Biochemistry*, **11**, 159 (1972).
(18) T. W. Johnson and I. M. Klotz, *Macromolecules*, **6**, 788 (1973).

Behavior of the $R_2AlOAlR_2$ Catalyst in the Polymerization of Propylene Oxide[1]

Norikazu Ueyama, Takeo Araki,* and Hisaya Tani

Department of Polymer Science, Faculty of Science, Osaka University,
Toyonaka, Osaka, 560, Japan. *Received August 4, 1973*

ABSTRACT: Polymerization of propylene oxide catalyzed by a type of $R_2AlOAlR_2$ (where R = CH_3, C_2H_5, and *i*-C_4H_9) compound derived from the reaction of R_2AlOLi with R_2AlCl gave three types of polymers; *i.e.*, a high molecular weight and highly isotactic polymer (M_v = 10^5-10^6), a low molecular weight and partially isotactic polymer (M_v = 600-1000), and an oligomer (~tetramer). Similar tri-dispersity was also observed in the polymers obtained with the corresponding AlR_3-H_2O (2:1) catalysts. The highest molecular weight and the most highly isotactic polymer was obtained with the $Me_2AlOAlMe_2$ catalyst. The isotacticity together with the molecular weight of the polymer varies with the nature of the alkyl groups in the catalyst: Me > *i*-Bu > Et. This decreasing order is not related to the bulkiness of the alkyl groups or to the polarizability of the Al-O-Al bond. In most experiments, a decrease in the isotacticity was coupled with a decrease in the molecular weight of the polymer. At low temperature, polymerization proceeded to form a high molecular weight and highly isotactic polymer, while the molecular weight and isotacticity were sharply decreased as temperature rose. One of the adverse factors for the stereoregular propagation reactions was the presence of AlR_3 or R_2AlCl which interacts with $R_2AlOAlR_2$ species. Since the polymerization at the final stage produces a polymer of a high stereospecificity (80%), one can conclude that the species $R_2AlOAlR_2$ gives mainly isotactic polymerization after the adverse species are consumed. A lower stereospecificity in the catalysis of AlR_3-H_2O (2:1) than in $R_2AlOAlR_2$ (R_2AlCl-R_2AlOLi) can be explained by the presence of a larger amount of AlR_3 and water unreacted in the catalyst preparation.

Bis(dialkylaluminum)oxide, $R_2AlOAlR_2$, is one of the key compounds for the study of the widely used catalyst systems derived from AlR_3 and water. We have discovered a new synthetic route to this series of compounds by reacting R_2AlOLi with R_2AlCl,[2a] and have shown that the $R_2AlOAlR_2$ compounds are actually formed.[2b] Also the catalytic behaviors of the systems Et_2AlOLi-Et_2AlCl (1:1) and $AlEt_3$-H_2O (2:1) are qualitatively identical for the polymerizations of acetaldehyde and epoxides.[3]

On reviewing the published works concerning the stereospecific polymerization of propylene oxide catalyzed by the AlR_3-water systems, one may find that two fundamental problems have remained unsolved. First, whether the species $R_2AlOAlR_2$ besides species $(\text{-RAlO-})_n$ affords a stereoregular polymer or not, and second, whether the stereoregular polymer obtained by the AlR_3-water catalytic systems is a polymer with high tacticity or a polymer having short isotactic sequences combined with structural disorderings. These problems appear highly important to the mechanism of the stereoregulating action of the AlR_3-water catalyst.

In the present paper we will report on the polymers from the polymerization of propylene oxide catalyzed by $R_2AlOAlR_2$ compounds derived from R_2AlOLi-R_2AlCl and from AlR_3-water. (For convenience, we denote hereafter as $R_2AlOAlR_2$ and AlR_3-H_2O (2:1) catalysts, respectively.) We conclude that the species $R_2AlOAlR_2$ can, though not exclusively, propagate the polymerization to a highly isotactic configuration, and that AlR_3 and R_2AlCl species included in the catalysts cause at least a part in sterically irregular propagation to give chain-terminated products.

Results and Discussion

Fundamental Aspect of R_2AlOLi-R_2AlCl Binary Catalyst Systems. Three kinds of $R_2AlOAlR_2$ compounds, *i.e.*, $Me_2AlOAlMe_2$, $Et_2AlOAlEt_2$, and *i*-Bu_2AlOAl*i*-Bu_2 prepared from the corresponding R_2AlOLi and R_2AlCl compounds,[2b] were used as the polymerization catalysts.

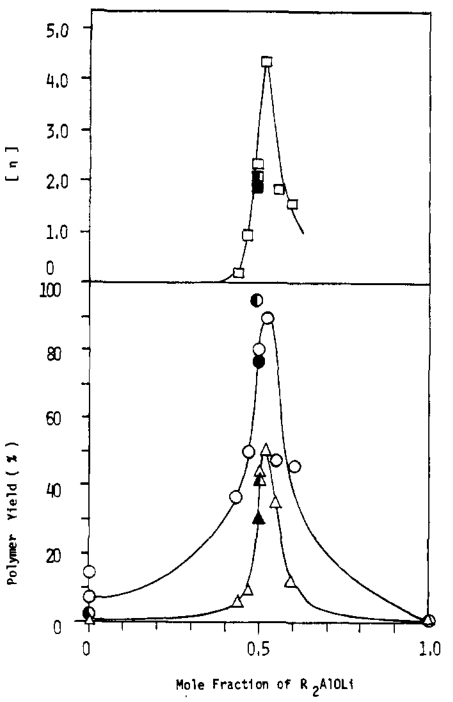


Figure 1. Polymerization of propylene oxide as a function of the mole fraction of R_2AlOM in the R_2AlOLi-R_2AlCl binary catalysts (R = *i*-Bu and Et; M = Li and Na). (i) *i*-Bu_2AlOLi-*i*-Bu_2AlCl catalyst: (○) total polymer yield; (△) *n*-hexane-insoluble polymer yield; (□) intrinsic viscosity of the *n*-hexane-insoluble polymer. (ii) Et_2AlOLi-Et_2AlCl catalyst: (◐) total polymer yield; (◭) acetone-insoluble polymer yield; (◧) intrinsic viscosity of the acetone-insoluble polymer. (iii) Et_2AlONa-Et_2AlCl catalyst: (●) total polymer yield; (▲) acetone-insoluble polymer yield; (■) intrinsic viscosity of the acetone-insoluble polymer. Polymerization conditions: monomer, propylene oxide, 2 ml; solvent, *n*-hexane, 2 ml; catalyst:monomer ratio, 0.01 mol/mol; temperature, −5°; time, 48 hr.

The polymerization of propylene oxide by these three catalysts was very sensitive to the molar ratio of R_2AlOLi to R_2AlCl as exemplified in Figure 1 for R = *i*-Bu, together with some results obtained for R = Et (Et_2AlOLi:Et_2AlCl = 1.0 and Et_2AlONa:Et_2AlCl = 1.0). The maximum yield of high molecular weight and stereoregular polymer was observed at a ratio of around 1:1.

The sharpness of the curve occasionally caused some fluctuation in the values of polymer yield and molecular weight and were minimized by adjusting the ratio of the two reagents to exactly 1:1 in the reaction of R_2AlOLi with R_2AlCl and by using aliquots from one batch of catalyst for a given series of experiments.

Polymerization Products. The polymerization products from propylene oxide with the $R_2AlOAlR_2$ catalysts contained at least three kinds of polymers, *i.e.*, high polymer with low solubility (I), highly soluble polymer (II), and oligomer (III). The relative yields of the three polymers varied considerably with the various polymerization conditions and the nature of catalyst.

The crude polymer was fractionated by three procedures: (i) extraction of the polymer by immersing in acetone at 0°; (ii) crystallization and precipitation from an acetone solution at 0°; (iii) crystallization and precipitation from a hexane solution at 0°. Procedure i was not useful because of its poor reproducibility while procedure iii was the most useful to estimate the relative yields of polymers studied. (For a description of the relative yield of isotactic polymers, index of stereospecificity (IS) is defined as a percentage value of the hexane-insoluble[4] fraction to total polymer yield.)

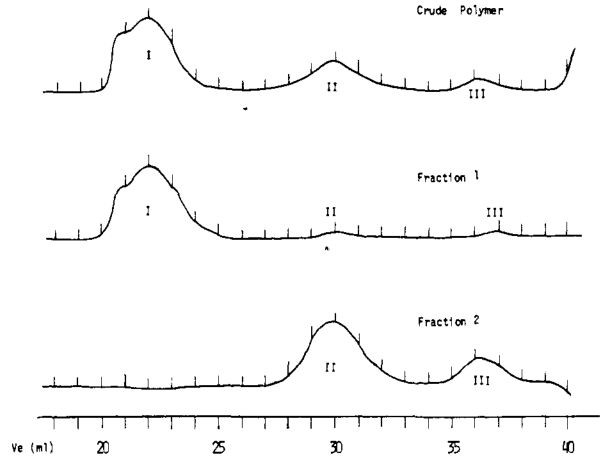


Figure 2. Gel permeation chromatograms of poly(propylene oxide) fractions prepared with *i*-Bu_2AlOAl-*i*-Bu_2 catalyst: (1) *n*-hexane-insoluble fraction; (2) *n*-hexane-soluble fraction. Chromatography; eluted with benzene at room temperature. Polymerization conditions: monomer, propylene oxide, 2 ml; solvent, *n*-hexane, 2 ml; catalyst:monomer ratio, 0.01 mol/mol; temperature, −5°; time, 48 hr.

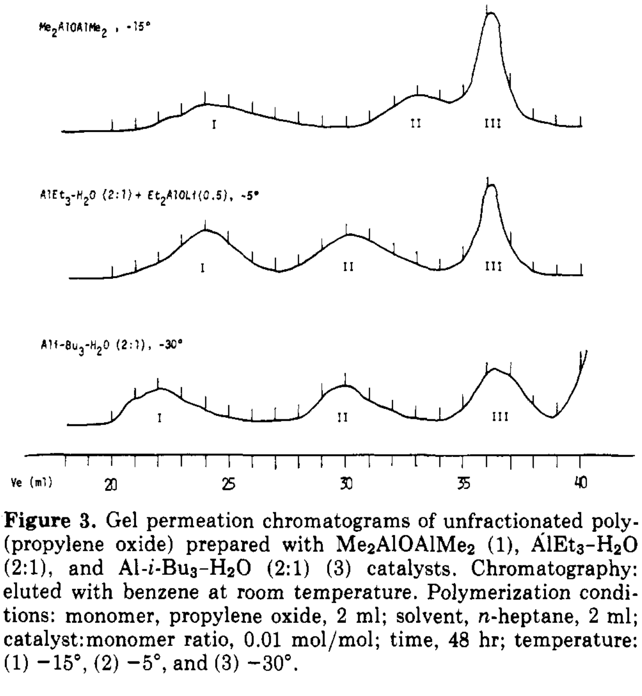


Figure 3. Gel permeation chromatograms of unfractionated poly(propylene oxide) prepared with $Me_2AlOAlMe_2$ (1), $AlEt_3$-H_2O (2:1), and Al-*i*-Bu_3-H_2O (2:1) (3) catalysts. Chromatography: eluted with benzene at room temperature. Polymerization conditions: monomer, propylene oxide, 2 ml; solvent, *n*-heptane, 2 ml; catalyst:monomer ratio, 0.01 mol/mol; time, 48 hr; temperature: (1) −15°, (2) −5°, and (3) −30°.

Table I shows a typical example of the relationship between the above fractionation procedures and polymer tacticities determined by nmr-dyad analysis of poly(propylene-α-*d* oxide[5] which was prepared in different diluents. The results of Table I combined with those of gel permeation chromatography (GPC) of the crude, hexane-insoluble and -soluble polymers (Figure 2) indicate that the hexane-insoluble fraction (mp 70°, highly crystalline X-ray fiber diagram) obtained with the *i*-Bu_2AlOAl*i*-Bu_2 catalyst is a high molecular weight isotactic polymer (I), and that the hexane-soluble fraction is a mixture of low molecular weight polymer (II) and oligomer (III).

Calibration with standard samples of polystyrene under given GPC conditions showed that the elution volume (V_e) of 22.6 counts corresponded to an M_v of 4.11×10^5 and 32.9 counts to an M_v of 600, respectively. Since Grubisic *et al.*[6] have indicated that the plots of log $[\eta]M_v$ *vs.* V_e are independent of the polymer regardless of its chemical nature, one can assume that peak I ($V_e \sim 22$) and peak II ($V_e \sim 30$) in Figure 2 correspond to polymers M_v

Table I
Nmr Analyses of Poly(propylene-α-d oxide) Fractions

Polymerization[a]		Polymer				
Catalyst	Solvent	Fraction[b]	i[c] (%)	s[c] (%)	H-T[d] (%)	T-T or H-H[e] (%)
i-Bu$_2$AlOAl-i-Bu$_2$	Et$_2$O	Crude	90–95	5–10	~90	~10
		I$_1$	~95	~5	~95	~5
		I$_2$	90–95	5–10	~95	~5
		II + III	60–65	35–40	~70	~30
	n-C$_6$H$_{14}$	Crude	90–95	5–10	90–95	5–10
		I$_1$	90–95	5–10	90–95	5–10
		I$_2$	~95	~5	90–95	5–10
		II + III	60–65	35–40	~70	~30
Et$_2$AlOAlEt$_2$	Toluene	I$_1$	~95	~5	~90	~10
		I$_2$ + II + III	~70	~30	~65	~35

[a] Polymerization conditions are: monomer, propylene-α-d oxide, 1 ml; solvent, 1 ml; catalyst:monomer ratio, 0.01 mol/mol; temperature, −15°; time, 48 hr. [b] I$_1$ acetone-insoluble fraction; I$_2$, acetone-soluble but n-hexane-insoluble fraction; II, n-hexane-soluble polymer; and III, oligomers. [c] Letters i and s denote isotactic and syndiotactic dyads, respectively, which were determined from the nmr methylene resonances with the aid of a curve resolver. [d] Head-to-tail structure. [e] Per cent of resonances due to the methylene protons other than of the head-to-tail structure. We denote them tentatively as tail-to-tail or head-to-head structures.

Table II
Temperature Dependence in the Polymerization of Propylene Oxide by $R_2AlOAlR_2$ Catalysts[a]

R$_2$AlOAlR$_2$[b]							AlR$_3$–H$_2$O (2:1)[c]						
			I[f]							I[f]			
Temp (°C)	Y[d] (%)	II + III[e] (%)	Yield	[η] (%)[h]	D_{1038}:D_{1016}[i]	IS[g] (%)	Temp (°C)	Y[d] (%)	II + III[e] (%)	Yield	[η] (%)[h]	D_{1038}:D_{1016}[i]	IS[g] (%)
			Me$_2$AlOAlMe$_2$[c]							AlMe$_3$–H$_2$O			
30	25	17	8			31							
−5	73	49	24	4.2	1.9 ± 0.1	33	−5	42	38	4	1.3		10
−15	61	38	23	5.5	2.1 ± 0.1	38	−15	42	36	6	1.9		14
−45	19	8	11	7.2	2.8 ± 0.1	58	−30	25	15	10	2.4		40
			Et$_2$AlOAlEt$_2$							AlEt$_3$–H$_2$O			
30	68	60.5	7.5	2.0		11	30	79	78	1	0.32		1
−5	64	46	18	2.5	0.24 ± 0.08	28	−5	59	55	4	0.71		7
−30	82	51	31	4.1		38	−30	62	48	14	3.0		23
			i-Bu$_2$AlOAl-i-Bu$_2$							Al-i-Bu$_3$–H$_2$O			
30	79	56	23	2.3		29	30[k]	46	45.7	0.3			0.8
−5	81	49	32	3.3–5.2	0.51–0.62	40	−5[k]	64	62	2	0.71	0.15 ± 0.08	3
−15[j]	85	11	74	5.6–6.2	0.66–0.71	87	−15	51	43	8	2.1	0.67 ± 0.08	16
−30	99	41	58	5.1		59	−30	47	33	14	4.7	0.85 ± 0.08	29

[a] Polymerization conditions are: monomer, propylene oxide, 2 ml; solvent, 2 ml; catalyst:monomer ratio, 0.01 mol/mol; time, 48 hr. [b] Solvent, n-hexane. [c] Solvent, n-heptane. [d] Total yield. [e] Hexane-soluble fraction. [f] Hexane-insoluble fraction. [g] Index of stereospecificity of the polymerization. [h] Intrinsic viscosity of the hexane-insoluble fraction. [i] Infrared crystallinity index of the hexane-insoluble fraction. [j] Polymerization time, 192 hr. [k] Polymerization time, 72 hr.

$> 10^5$ and of $1000 > M_v > 600$ ($17 > DP > 10$), respectively. Peak III ($V_e \sim 36$) is obviously within the range of low molecular weight compounds roughly corresponding to tetramers.[7,8]

The polymer I must have a molecular weight distribution of 10^5–10^6 as the front of the peak (V_e = 20 to *ca.* 24) was observed at the lower limit of the V_e of the GPC columns used. Considering the fact that the hexane-insoluble fraction contained small amounts of polymers II and III (as indicated by GPC), the isotacticity of the polymer I is suggested to be higher than estimated from the dyad analysis. It appears important that this fraction consists of polymers with a highly isotactic chain configuration.

Comparison of Catalyst Systems $R_2AlOAlR_2$ with AlR_3-H_2O. Essentially similar patterns as the above were observed for the polymers obtained with Et$_2$AlOAlEt$_2$ or Me$_2$AlOAlMe$_2$ and the corresponding AlR$_3$–H$_2$O (2:1) catalysts, though the quantitative details were different (some of related examples are shown in Figure 3). This fact clearly indicates that the reactions involved in the polymerization of propylene oxide by R$_2$AlOAlR$_2$ and AlR$_3$–H$_2$O (2:1) catalysts are qualitatively identical. This is in accord with the general trends of the polymerization results show in Table II including polymer yields, stereospecificity of polymerization, intrinsic viscosities, and infrared crystallinity indices of polymers.

However, three important differences in the catalyst behavior between R$_2$AlOAlR$_2$ and the corresponding AlR$_3$–H$_2$O (2:1) catalysts can be pointed out. First, the hexane-insoluble fraction obtained by the AlR$_3$–H$_2$O catalytic system has distribution at a lower molecular weight region than in the case of the corresponding R$_2$AlOAlR$_2$ catalyst. For example, when the GPC-I patterns of the polymers obtained by i-Bu$_2$AlOAl-i-Bu$_2$ at −5° (Figure 2) and Al-i-Bu$_3$–H$_2$O (2:1) at −30° (Figure 3) (−30° was the best condition to form high molecular weight polymer with Al-i-Bu$_3$–H$_2$O catalyst) are compared, the range in V_e for the former case is within 20–24 while that of the latter case is 20–25.5. Second, the proportions of the polymer II and the oligomer III are higher for the AlR$_3$–H$_2$O catalytic system than for the R$_2$AlOAlR$_2$ catalyst (compare the GPC diagrams for i-Bu$_2$AlOAl-i-Bu$_2$ and Al-i-Bu$_3$–H$_2$O catalyses shown in Figures 2 and 3). And third, the melting point (64°) and infrared crystallinity indices (Table II) for the n-hexane-insoluble polymers obtained at −5° are considerably lower for those with the water system.

The formation of the hexane-soluble polymers was almost terminated in 12 hr (at −30°) and in 6 hr (at −5°)

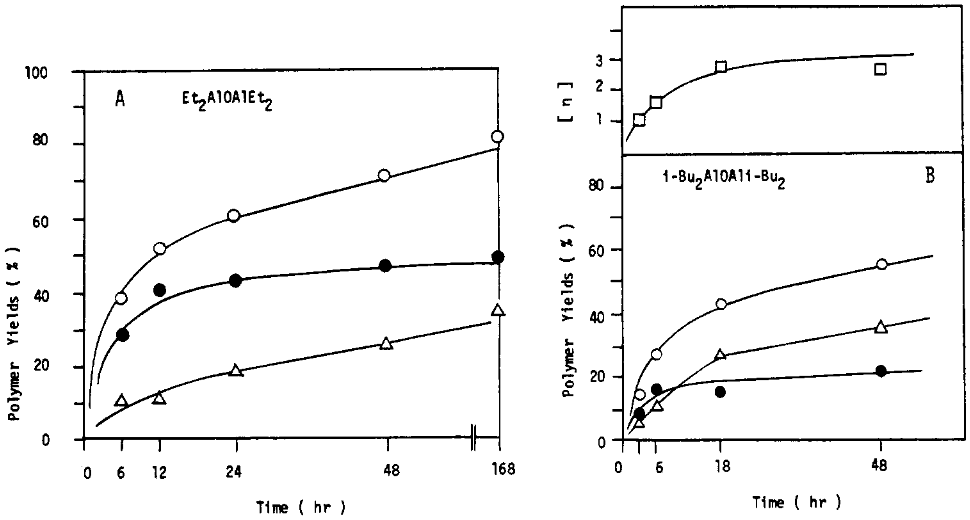


Figure 4. Time dependences of the polymerization of propylene oxide catalyzed by $Et_2AlOAlEt_2$ (A) and i-Bu_2AlOAl-i-Bu_2 (B): (○) total polymer yield; (△) n-hexane-insoluble polymer yield; (●) n-hexane-soluble polymer yield; (□) intrinsic viscosity of n-hexane-insoluble polymer. Polymerization conditions: (A) monomer, propylene oxide, 2 ml; solvent, toluene, 2 ml; catalyst:monomer ratio, 0.01 mol/mol; temperature, −30°. (B) Monomer, propylene oxide, 2 ml; solvent, n-heptane, 2 ml; catalyst:monomer ratio, 0.005 mol/mol; temperature, −5°.

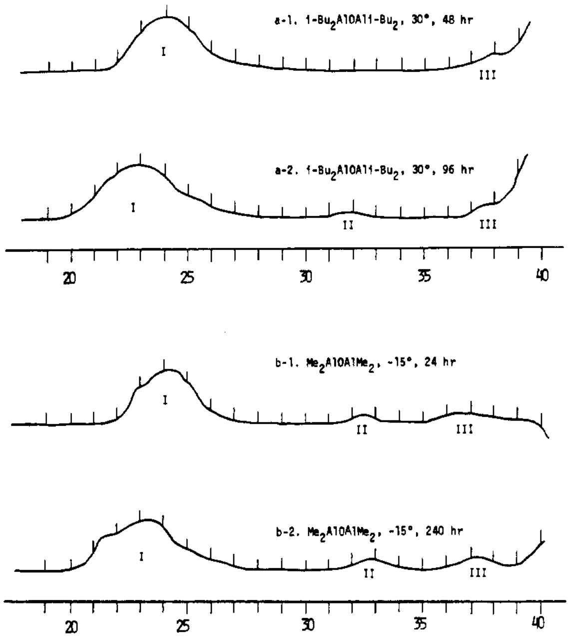


Figure 5. Gel permeation chromatograms of n-hexane-insoluble fractions of poly(propylene oxide) as a function of polymerization time: (a) catalyzed by i-Bu_2AlOAl-i-Bu_2 at 30° and (b) catalyzed by $Me_2AlOAlMe_2$ at −15°. Polymerization conditions: monomer, propylene oxide, 2 ml; solvent, n-heptane, 20 ml; catalyst:monomer ratio, 0.01 mol/mol; polymerization time, a-1, 48 hr; a-2, 2 ml of the monomer was newly added after 48 hr and then polymerized further 48 hr (*cf.* Table III); b-1, 24 hr; b-2, 240 hr.

for the $Et_2AlOAlEt_2$ (Figure 4A) and i-Bu_2AlOAl-i-Bu_2 (Figure 4B) catalysts, respectively. The time dependences of the polymerization observed were essentially identical with those observed by Colclough *et al.*[9] for the $AlMe_3$–H_2O catalytic system, where initial rapid formation of an atactic and low molecular weight polymer and slow propagation of a crystalline polymer have been elucidated.

Long-Lived Isotactic Polymerization. GPC diagrams of the hexane-insoluble fractions formed with i-Bu_2AlOAl-i-Bu_2 (at 30°) (Figure 5a) and $Me_2AlOAlMe_2$ (at −15°) (Figure 5b) catalysts clearly exhibit an increase in the molecular weight of the polymer fractions with time, suggesting the slow stage of the polymerization is mainly an isotactic propagation process of long life. Relevant to this, three of the polymerizations were carried out at low monomer concentration (Table III).

In run 3 in Table III, polymerization was undertaken for 48 hr as in run 1, then 2 ml of the monomer was added and then polymerized for an additional 48 hr. An increase in the total polymer yield during the additional 48 hr corresponded to 56% of the newly added monomer, and about 80% of the newly formed polymer was found to be hexane insoluble. The GPC diagram (Figure 5a-2) shows an increase in the molecular weight of the hexane-insoluble polymer in accord with a significant increase in the viscosity, indicating that the newly added monomer molecules were propagated isotactically onto the living end of the formerly produced polymer chain. This supports the presumption of the living nature of $AlMe_3$–H_2O catalysis for the propagation of crystalline polymer of propylene oxide,[9] and may be related to the observation that the polymerization of tetrahydrofuran catalyzed by $AlEt_3$–H_2O–epichlorohydrin system involves a living species.[10] Comparison of the figures of [η] in runs 1 and 2 in Table III revealed that a considerable extent of depolymerization occurred during prolonged contact of the polymer with the catalyst at low ratios of monomer to polymer. A decrease in the stereospecificity was also observed presumably due to the loss of hexane-insoluble polymer by the depolymerization resulting in hexane-soluble low molecular weight fractions. The existence of depolymerization indicates that the long life of $R_2AlOAlR_2$ catalyst does not mean a kinetically pure "living system."

Effects of Nature of $R_2AlOAlR_2$. The nature of the alkyl groups in $R_2AlOAlR_2$ catalysts exerts no important effect on the gross aspects of the polymerization reaction, in view of the facts that the polymerization products gave similar patterns of GPC diagram and nmr methylene resonances of the hexane-insoluble poly(propylene-α-d) oxide prepared by three kinds of $R_2AlOAlR_2$ catalyst at −5° (Figure 6) indicate these polymers to have isotactic dyad contents higher than 90%.

The detailed catalyst behaviors, however, vary with the nature of the alkyl group, *e.g.*, the peak widths together with the trough depths of the nmr resonances are different, indicating that the isotactic sequence lengths in the polymers decrease with the following order of catalysts used: $Me_2AlOAlMe_2$ > i-Bu_2AlOAl-i-Bu_2 > $Et_2AlOAlEt_2$.

Table III
Polymerization Results in Relation to Life of Catalyst[a]

			Polymer			
Run	Monomer (ml)	Time (hr)	Total Yield (%)	Hexane-Insoluble Polymer Yield (%)	[η] of Hexane-Insoluble Polymer	GPC
1	2	48	80	24	2.4	Figure 5a-1
2	2	240	72	16	1.5	
3	2 + 2	48 + 48	68	34.5	4.3	Figure 5a-2

[a] Solvent, *n*-heptane, 20 ml; *i*-Bu_2AlOAl-*i*-Bu_2:monomer ratio, 0.01 mol/mol; temperature, 30°.

This order is consistent with neither the increasing nor decreasing order of bulkiness of the alkyl groups. Variation in the infrared crystallinity indices (D_{1038}:D_{1016}) of the polymers (see Table II) shows the difference in the isotactic sequence lengths more clearly. Also the hexane-insoluble polymer has different physical forms. For example, the polymer obtained with $Me_2AlOAlMe_2$ catalyst could readily be cast into a highly crystallized film having low extensibility and high stiffness whereas that obtained with *i*-Bu_2AlOAl-*i*-Bu_2 catalyst was an opaque film with some elasticity and that obtained with $Et_2AlOAlEt_2$ was a fragile film.

Since the same decreasing order was observed for molecular weights of the hexane-insoluble polymers formed at a given temperature, and this was inverse of the apparent exotherm in the initial stage of the polymerizations ($Et_2AlOAlEt_2$ > *i*-Bu_2AlOAl-*i*-Bu_2 > $Me_2AlOAlMe_2$), we suggest that the disordering factor in the stereospecific chain propagation correlates with the chain-terminating factor. A similar correlation was definitely observed by varying the polymerization temperature (see Table II); *i.e.*, molecular weights and crystallinity indices of the hexane-insoluble polymer along with stereospecificities decreased as the temperature was raised.

Hypotheses for Activities of $R_2AlOAlR_2$ Catalyst. In order to interpret the observations above and the polydispersity in the molecular weight distribution of the polymer, we make the following assumptions. (a) The catalyst $R_2AlOAlR_2$ when contacted with the monomer at low temperature can principally *propagate* isotactic polymerization by a coordination mechanism. (For the coordinating properties of some kinds of donor molecules to $R_2AlOAlR_2$ compounds, the formation of some coordinated complexes with ethers and amines has been described in a preceding paper.[2b]) (b) Nonstereoregularity during the propagation reaction is not always due to an isotactic-syndiotactic configurational alteration in the attack of the incoming monomers but due to certain chemical reasons which cause chain termination (*e.g.*, alteration in the direction of ring opening, cyclization of the propagating chain, isomerization of the monomer, attack of compounds other than the monomer, and etc.). This means that the formation of the nonstereoregular sequences in the polymer chain is largely caused by certain chemical species which are stronger acids and, in most of the cases, chain termination predominates rather than propagation of an atactic chain. (c) The species which cause chain termination and/or nonstereoregularity are relatively short-lived, and are effectively consumed in the process.

Adverse Factors. According to the hypotheses above, the disturbances in the ideal isotactic propagation are caused, at least a part, by the existence of some highly reactive species (presumably more acidic compounds in this case) present in the vicinity of the propagating polymer end. This highly reactive species must be converted into an inactive species by the reaction with propylene oxide or its derivatives. A candidate for the reactive species in the $R_2AlOAlR_2$ catalyst derived from R_2AlOLi and R_2AlCl compounds are: unreacted R_2AlCl and AlR_3 formed by a disproportionation reaction of the $R_2AlOAlR_2$ compound.[2b,3,11] For the catalyst system AlR_3-H_2O (2:1), on the other hand, the presence of a higher amount of AlR_3 compound can be expected. In addition, the water molecule and a series of $R(RAlO)_nH$ ($n = 1, 2, \cdots$) compounds have to be taken into account as adverse reagents, since AlR_3-H_2O (2:1) system exhibited a weak and broad nmr resonance due to -OH protons and an ir absorption band at 1160 cm^{-1}.[2b] The following experimental findings show the effect of these candidates.

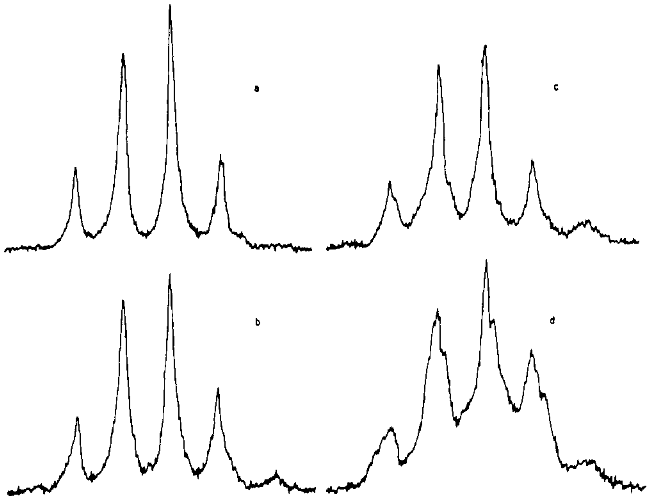


Figure 6. Nmr spectra of the methylene protons in poly(propylene-α-*d* oxide): (a-c) *n*-hexane-insoluble polymer fractions obtained by $Me_2AlOAlMe_2$, *i*-Bu_2AlOAl-*i*-Bu_2, and $Et_2AlOAlEt_2$ catalysts, respectively; (d) *n*-hexane-soluble polymer fraction obtained by *i*-Bu_2AlOAl-*i*-Bu_2 catalyst. Polymerization conditions: monomer, propylene-α-*d* oxide, 1 ml; catalyst:monomer ratio, 0.01 mol/mol; temperature, −5°; time, 48 hr.

A polymerization catalyzed by *i*-Bu_2AlOAl-*i*-Bu_2 containing a 0.2 molar equiv of added Al-*i*-Bu_3 (Table IV) resulted in a significant decrease in the total polymer yield and hexane-insoluble polymer yield. Intrinsic viscosities of the hexane-insoluble polymers obtained at −5 and −15° fell to the lowest limits of the viscosity ranges for the polymers made with the catalyst system without additive. Examples of similar inhibiting effects caused from addition of Me_2AlCl are shown also in the table. These effects can be related to the observation that only low polymers were obtained with such catalysts as $AlEt_3$,[12,13] $AlMe_3$,[9,14] Al-*i*-Bu_3,[15] Me_2AlCl,[8] and Et_2AlCl.[2a,3] (Some detailed investigations have been reported for the reactions occurring with $AlEt_3$[16] and Me_2AlCl.[8])

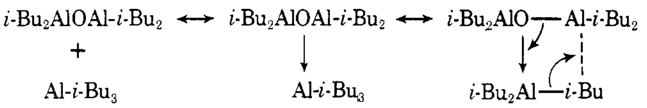
Addition of Al-*i*-Bu_3 to the *i*-Bu_2AlOAl-*i*-Bu_2 compound caused a decrease in the value of the internal chemical shift ($\delta(CH_3)$-$\delta(CH_2)$) without showing any dual reso-

Table IV
Effect of the Addition of AlR_3 and R_2AlCl upon the Polymerization of Propylene Oxide Catalyzed by $R_2AlOAlR_2$ Compounds[a]

Catalyst	Additive	Molar Equiv	Temp (°C)	T^b (%)	II + III[c] (%)	I[d] %	I[d] [η]	IS[e]
i-Bu_2AlOAl-i-Bu_2	None		30	79	56	23	2.3	29
i-Bu_2AlOAl-i-Bu_2	Al-i-Bu_3	0.2	30	47	37.6	9.4	2.2	20
i-Bu_2AlOAl-i-Bu_2	None		−5	81	49	32	3.3–5.2	40
i-Bu_2AlOAl-i-Bu_2	Al-i-Bu_3	0.2	−5	55	36	19	3.1	35
i-Bu_2AlOAl-i-Bu_2	None		−15	85	11	74	5.6–6.2	87
i-Bu_2AlOAl-i-Bu_2	Al-i-Bu_3	0.2	−15	32	12	20	5.6	63
$Me_2AlOAlMe_2$	None		−5	70	46	24	1.9	35
$Me_2AlOAlMe_2$	Me_2AlCl	0.5	−5	10	8	2	Very low	20
$Me_2AlOAlMe_2$	Me_2AlCl	1.0	−5	5–10	5–10	tr	Very low	Very low

[a] Polymerization conditions: monomer, propylene oxide, 2 ml; solvent, n-heptane, 2 ml; catalyst:monomer ratio, 0.01 mol/mol; time, 48 hr. [b] Total polymer yield. [c] Hexane-soluble fraction. [d] Hexane-insoluble fraction. [e] Index of stereospecificity of the polymerization.

nances of the i-Bu protons as illustrated in Figure 7. This indicates that the Al-i-Bu_3 molecule interacted with the i-Bu_2AlOAl-i-Bu_2 molecule in an alkyl exchange process



Thus, the Al-i-Bu_3 molecule can migrate between i-Bu_2-$AlOAl$-i-Bu_2 molecules. When an incoming monomer molecule attacks this Al-i-Bu_3-containing species, termination and/or disorder in the chain could result. In this process Al-i-Bu_3 would be converted into an inactive species by its reaction with propylene oxide or its derivatives to decrease the concentration of the Al-i-Bu_3 with time.

The effect of addition of 0.1 molar equiv of water to the i-Bu_2AlOAl-i-Bu_2 was investigated in a vacuum system employing carefully dried monomer and solvent. (Results are described in the Experimental Section.) In the absence of added water, no significant changes were observed for stereospecificity of the polymerization and molecular weight of the polymer formed when compared with cases observed for the polymerization under argon atmosphere. The addition of the amount of water above mentioned, however, resulted in a considerable decrease in the molecular weight of the hexane-insoluble polymer, while the stereospecificity of the polymerization was only slightly decreased. Hence, the free water molecule contributes to termination of the growing polymer.

Relation between Polymerization Activity and Properties of $R_2AlOAlR_2$ Compound. In the study of the organoaluminum chemistry of $R_2AlOAlR_2$ compounds,[2b] we have disclosed that the compounds show considerable conductivity due to polarization of the Al–O–Al linkages into $R_2Al^{\delta+}$----$O^{\delta-}$----AlR_2. From the infrared absorption frequencies of the ν_{AlOAl} bands a decreasing order of the polarizabilities of the compounds has been estimated as: i-Bu_2AlOAl-i-Bu_2 > $Et_2AlOAlEt_2$ > $Me_2AlOAlMe_2$. This order did not correlate directly with their catalytic behaviors in terms of polymer yields, stereospecificity, molecular weight, and tacticity of the polymer. Thus, the ionization into R_2AlO^- and R_2Al^+ species appears less important in the isotactic propagation than in the termination reaction.[9] (The polarization may take part in the initiation reaction, but the complicated nature of the initiation reaction precludes a depiction of the true initiation reaction of the polymerization.) Furthermore, we have already shown that an ionization of the compounds into ions R^- and $[R_2AlOAlR]^+$ is less likely.[2b]

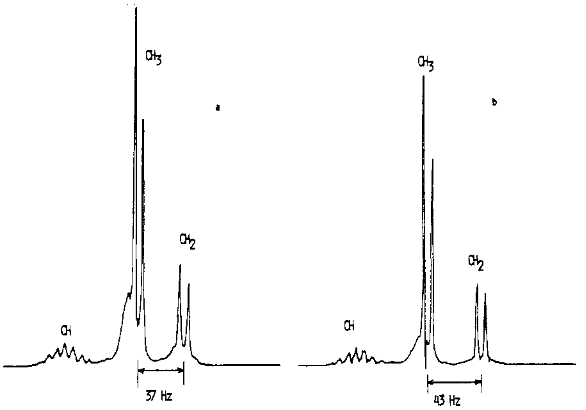
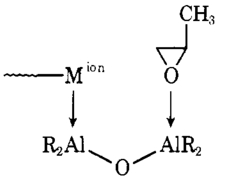


Figure 7. Nmr spectra of i-Bu_2AlOAl-i-Bu_2 (a) and i-Bu_2AlOAl-i-Bu_2 + Al-i-Bu_3 (1:0.2) (b) in benzene-d_6 at room temperature.

We have determined the degree of association to be ~4 for $Et_2AlOAlEt_2$[3] and ~1 for i-Bu_2AlOAl-i-Bu_2[2b] compounds, respectively. From the results of stereocontrol in the polymerizations, the increased association in the catalyst molecules appears not to correlate with the stereoregulation. One might consider that the alkyl groups on the catalyst molecule take part in the stereoregulation in the coordination polymerization. However, this possibility is excluded as we have mentioned above that the bulkiness of the alkyl groups in the catalyst is also not an important stereoregulating factor. In view of these aspects one may postulate that the Al–O–Al bonding unit in the catalyst satisfies the requirements for isotactic propagation.

It seems reasonable that the binuclear organoaluminum bidentate electron accepting nature[2b] of the catalyst compound allows a structure in which an incoming monomer molecule attacks an Al atom retaining a chain-end monomer unit on the other atom



This structure has been shown to be possible with an example of bisbenzoquinolinate of $Et_2AlOAlEt_2$ compound.[2b] The biscoordinated compound was relatively unstable compared with the monocoordinated compound, indicating that the vacant orbitals on the Al atoms are directed upward along an axis perpendicular to the line connecting two Al atoms (where the oxygen atom in the Al–

O-Al linkage is placed beneath the plane of Et_2Al- - - $AlEt_2$). This situation affords a closeness in the distance between the two substances coordinated, and consequently, the reaction of the active end with the incoming monomer will be rapid when this situation exists.

The structure of the reaction intermediate is stereochemically similar to those proposed by Vandenberg[17] and Price *et al.*[18] for stereoregular anionic polymerizations. We prefer, however, a cationic mechanism[9] for the polymerization catalyzed by $R_2AlOAlR_2$ compounds, since cyclic dimers, *i.e.*, *cis*-2,5-, *trans*-2,5-, and *cis*-2,6-dimethyldioxanes, apart from anionic side reaction products, were detected in the reaction with these catalysts at various temperatures. In addition, styrene oxide (phenyl group stabilizes secondary carbonium ion) gave higher amounts of dimers than polymers with this type of catalyst.[19] On considering the free space around the aluminum atoms in a $R_2AlOAlR_2$ molecule, some other yet undetermined factors must help to give such highly isotactic stereoregulation, repeating until a high molecular weight polymer is formed, as has been observed in this study.

We must mention here the cationic mechanism in the coordination polymerization, which has not been widely accepted when an oxonium ion is involved. It seems unlikely that a cationic species and an anionic species give two kinds of polymers simultaneously in one polymerization system, because they will react each other to terminate the polymerization in a short period. Since the side reactions involved in our systems were cationic in nature, we assume that the stereoregular polymerization is also conducted by either of the following two possibilities. (i) A less cationic species produces stereoregular polymer while a more cationic species forms various side reaction products. (ii) An anionic species which is formed as a result of the initial reaction of a cationic species with the monomer catalyze the stereoregular polymerization. In our recent study on the reaction of styrene oxide with a variety of organoaluminum compounds, we have found that the latter possibility is low as a universal mode of reaction in the cases of organoaluminum catalysis.[20]

The most important problem to be solved for elucidation of the cationic mechanism in the stereoregular polymerization is whether the oxonium ion can readily coordinate to the catalyst or not. Unfortunately, we have no definite evidence for this. However, when a molecule of precoordinated monomer undergoes attack of an electrophilic reagent on its oxygen atom, an oxonium ion retaining a somewhat weakened interaction with the catalyst can be formed. This state is not a stable coordination complex but can be regarded as a type of coordination. The oxonium cation thus "coordinated" must be highly reactive because of instability in the electronic arrangement at the oxygen atom where all of the lone pair electrons are losened from the nucleus. The formation of the highly active cation may explain the higher activity of $R_2AlOAlR_2$ catalyst, which can catalyze polymerization at a considerably low temperature, when compared with that of Et_2Zn-alcohol,[21,22] Et_2Zn-water,[22,23] or $Et_2ZnNBu^tZnEt_2$[1,24] catalytic systems.

Experimental Section

All of experiments were carried out under argon atmosphere.

Materials. Propylene oxide was refluxed over KOH, distilled, dried over CaH_2, fractionally distilled, dried over CaH_2, and then distilled just before use. Propylene-α-*d* oxide was prepared according to the method developed in our laboratory[5] and was refluxed over CaH_2 and distilled just before use. Solvents were purified by ordinary methods and then refluxed over K-Na alloy and distilled. $R_2AlOAlR_2$ catalysts were prepared by the reactions of R_2AlOLi with R_2AlCl compounds according to the method described in the preceding paper.[2b]

Preparation of AlR_3-H_2O catalyst was undertaken as follows. To a chilled suspension of water (0.0028 mol) in pentane (20 ml) a solution of AlR_3 (0.0056 mol) in *n*-pentane (20 ml) was added dropwise for 10 min at −78°, and it was warmed to 30° by controlling the temperature carefully. After stirring at 30° for 12 hr, the solvent was carefully removed at 0° under reduced pressure.

Polymerization Procedures. In a flask filled with argon, propylene oxide (2 ml) was added with stirring at −78° to a solution of the catalyst. The flask was sealed off and kept at a given temperature for a given period as indicated.

Termination of the polymerization was performed by two different methods. (a) The polymerization mixture was poured into a stirred mixture of a large amount of benzene and a small amount of ammoniacal water at room temperature. A small amount of undissolved material was removed by centrifugation. (b) The polymerization mixture which was treated with a small amount of methanol containing hydrochloric acid was poured into a large volume of benzene. The benzene solution was washed with water in order to remove the catalyst residue. Method a was applied in most of the cases studied except for the results obtained by Et_2AlOLi-Et_2AlCl and Et_2AlONa-Et_2AlCl catalytic systems, which are shown in Figure 1, because some water soluble oligomers were lost in method b. The benzene solutions obtained by methods a and b were then freeze-dried. Total yield of the polymer is based on the crude polymer obtained by freeze-drying.

Fractionation of the Polymer. The crude freeze-dried polymer was dissolved in acetone or *n*-hexane (150 ml/g of polymer) at 40°. The solution was stored at 0° for 24 hr without agitation. The acetone- or *n*-hexane-insoluble fraction formed was separated from the solution by centrifugation. (The crude polymer was fractionated more readily with *n*-hexane than with acetone.) From the filtrate, the *n*-hexane-soluble fraction was obtained after evaporation. Index of stereospecificity of the polymerization was defined as the percentage of the *n*-hexane-insoluble fraction to the crude polymer.

Characterization of the Polymers. Intrinsic viscosity of the polymer in benzene was determined at 25 ± 0.1° by the measurements of specific viscosity in the concentration range of 0.02–0.10 g/dl. GPC of the polymer fractions was carried out at room temperature with a Shimadzu GPC-1A-type instrument, using 4-m columns composed of 6:4:2:1 column arrangement. Two milliliters of 0.05% solutions of the polymers in benzene solution was charged and then eluted by benzene. The lower limit of the elution volume was 19 counts; polymers with molecular weight higher than 1×10^5 were eluted between 19 and 24 counts. The viscosity average molecular weights, $\overline{M_v}$, were determined by viscosity measurements with the equation: $[\eta] = 1.12 \times 10^{-4}\, \overline{M_v}^{0.77}$.[25]

Nmr-dyad analysis of poly(propylene-α-*d* oxide) was carried out with the aid of Varian 310 type curve resolver on the spectra recorded by a Japan Optics Laboratory Co. Ltd. JMN-4H-100 spectrometer. The accuracy of the analysis was at best ±5%.

Infrared crystallinity index of the polymer was determined on a film (for high molecular weight polymer) or KBr disk (for powdery polymer), using the D_{1038}:D_{1016} ratio.[26]

Experiments in Relation to the Effect of Water on the Polymerization. A toluene solution containing *i*-Bu_2AlOAl-*i*-Bu_2 catalyst was prepared under an argon atmosphere and sealed after evacuation at room temperature. The solution was introduced at −78° into a polymerization flask *in vacuo*. Propylene oxide which was dried under an argon atmosphere with CaH_2 or Zeolite was distilled *in vacuo* into the polymerization flask. The polymerization flask was sealed, and then allowed to stand in a thermostated bath (−5°). After the polymerization the reaction mixture was treated in the usual way. Polymerization conditions were as follows: solvent, toluene, 5 ml; propylene oxide, 2 ml; catalyst: monomer ratio, 0.01 mol/mol; polymerization time, 48 hr. The CaH_2-dried monomer (without addition of water) gave 26% of hexane-insoluble polymer as a film having *ca.* 1×10^6 $\overline{M_v}$. A similar polymer was obtained in 20% yield from the Zeolite-dried monomer (without addition of water). Addition of 0.1 molar equiv (for the catalyst) of water to the CaH_2- and Zeolite-dried monomers resulted in powdery polymers having *ca.* 1×10^5 M_v in 24 and 25% yields, respectively.

Acknowledgments. The authors thank Messers. K. Kawai and T. Uemura of Shimadzu Seisakusho Ltd., and Mr. T. Hashimoto of Toyo Soda Co., Ltd., for the use of GPC instrument. We also thank Mr. S. Watanabe for preparation of propylene-α-*d* oxide, and Dr. M. Kobayashi for discussions on the infrared crystallinity of the polymer.

References and Notes

(1) This paper comprises a part of the Ph.D. Thesis of Dr. N. Ueyama 1970, Osaka University.
(2) (a) H. Tani, T. Araki, N. Oguni, and N. Ueyama, *J. Amer. Chem. Soc.*, **89**, 173 (1967). (b) N. Ueyama, T.Araki, and H. Tani, *Inorg. Chem.*, **12**, 2218 (1973).
(3) T. Araki, T. Aoyagi, N. Ueyama, T. Aoyama, and H. Tani, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 699 (1973).
(4) The polymer yields for $Et_2AlOLi(Na)$-Et_2AlCl catalyses in Figure 1 were obtained by the procedure ii.
(5) H. Tani, N. Oguni, and S. Watanabe, *J. Polym. Sci., Part B*, **6**, 577 (1968).
(6) Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Part B*, **5**, 753 (1967).
(7) (a) R. J. Katnick and J. Schaefer, *J. Org. Chem.*, **33**, 384 (1968). (b) R. J. Kern, *ibid.*, **33**, 388 (1968).
(8) R. O. Colclough and I. N. Simpson, Abstract of papers presented at the International Symposium on Macromolecular Chemistry, IUPAC, Tokyo-Kyoto, Japan, Sept 28-Oct 4, 1966, Vol. I, p 219.
(9) R. O. Colclough and K. Wilkinson, *J. Polym. Sci., Part C*, **4**, 311 (1964).
(10) T. Saegusa, H. Imai, and S. Matsumoto, *J. Polym. Sci., Part A1*, **6**, 459 (1968).
(11) A. Storr, K. Jones, and W. Laubengayer, *J. Amer. Chem. Soc.*, **90**, 311 (1968).
(12) H. Imai, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **82**, 25 (1965).
(13) S. Kambara and T. Takahashi, *Makromol. Chem.*, **63**, 89 (1964).
(14) R. O. Colclough, G. Gee, and A. H. Jagger, *J. Polym. Sci.*, **48**, 273 (1960).
(15) P. E. Ebert and C. C. Price, *J. Polym. Sci.*, **34**, 157 (1959).
(16) A. J. Lundeen and A. C. Oehlschlager, *J. Organometal. Chem.*, **25**, 337 (1970).
(17) (a) E. J. Vandenberg, *J. Amer. Chem. Soc.*, **83**, 3538 (1961). (b) E. J. Vandenberg, *J. Polym. Sci., Part B*, **2**, 1085 (1964). (c) E. J. Vandenberg, *ibid., Part A1*, **7**, 525 (1969).
(18) C. C. Price and R. Spector, *J. Amer. Chem. Soc.*, **87**, 2070 (1965).
(19) N. Ueyama, T. Araki, and H. Tani, Abstract of Papers presented at 17th Annual Meeting of High Polymer Society of Japan, Tokyo, 1968, p 237. N. Ueyama, Ph.D. Thesis, Osaka University, 1970.
(20) T. Araki and T. Koshida, unpublished results.
(21) (a) M. Ishimori, T. Tomoshige, and T. Tsuruta, *Makromol. Chem.*, **120**, 161 (1968). (b) M. Ishimori and T. Tsuruta, *ibid.*, **64**, 190 (1963).
(22) A. J. Burgess and R. O. Colclough, *SCI (Soc. Chem. Ind., London) Monogr.*, **20**, 41 (1966).
(23) C. Booth, W. C. E. Higginson, and E. Powell, *Polymer*, **5**, 479 (1964).
(24) N. Oguni and H. Tani, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 573 (1973).
(25) G. Allen, C. Booth, and M. N. Jones, *Polymer*, **5**, 195 (1964).
(26) A. Kawasaki, J. Furukawa, T. Tsuruta, T. Saegusa, G. Kakogawa, and R. Sakata, *Polymer*, **1**, 315 (1960).

Catalytic Activity of Poly(4(5)-vinylimidazole-*co*-acrylic acid) in the Hydrolyses of 3-Acetoxy-*N*-trimethylanilinium Iodide and *p*-Nitrophenyl Acetate in Aqueous Solution

Takeo Shimidzu,* Akihiro Furuta, and Yukimasa Nakamoto

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

Received May 23, 1973

ABSTRACT: The catalytic activity of poly(4(5)-vinylimidazole-*co*-acrylic acid) (copoly(VI-AA)) in hydrolyses of 3-acetoxy-*N*-trimethylanilinium iodide (ANTI) and *p*-nitrophenyl acetate (PNPA) in an aqueous solution containing no metal ion has been studied. The copolymer had random sequence. The neutral imidazole fraction as well as the carboxylate fraction in the copolymer were estimated by potentiometric titrations. Both fractions increased with VI content in the copolymer, even in the same pH solution. The hydrolysis of ANTI followed the Michaelis-Menten-type kinetics, and that of PNPA followed the second-order kinetics. Though profiles of total hydrolyis rates for ANTI and PNPA were different, rates of hydrolytic step gave similar profiles; that is, the rates decreased sharply with the VI content in the copolymer in which the VI content was lower than 30 mol %. The effective interaction of ANTI on the copolymer appeared at 30 mol % VI content in the copolymer. The slope in the Brönsted plots with the present reaction was steeper than that obtained in the nucleophilic hydrolysis by Bruice. The molar extinction coefficients of the imidazole moiety in the copolymers also changed decreasingly with VI content in the copolymers. Those results lead to a tentative scheme of the cooperation between imidazole and carboxylic acid moieties. A carboxylic acid moiety not only changes the fraction of the neutral imidazole moiety in the copolymer, but also the nucleophilicity of the imidazole moiety. Such a multiple effect can be considered as the special province of the polymer catalyst.

As a model of catalysis by α-chymotrypsin, many esterolytic catalyses by copolymers containing imidazole or the other nucleophile have been studied.[1-19]

Generally speaking, the role of enzyme consists of the attraction of substrate and the catalysis. On this point, copolymer of 4(5)-vinylimidazole (VI) and acrylic acid (AA) can be thought to be one of the model of the enzyme, because it has an electrostatic attractive moiety and a catalytic moiety. The hydrolysis reaction of a positively charged substrate, of which charge is opposite in sign to the copolymer, will realize a model reaction system. The farseeing study of the catalytic reaction using copoly(VI-AA) has been made by Overberger and Maki.[7] However, the above-mentioned two roles had not been separated. In the present study, to simplify the reaction condition, an aqueous solution containing no metal ion was adopted as a reaction medium. As a result, the above-mentioned two roles in the hydrolysis have been separated. Additionally, an interesting result with respect to an cooperative action between imidazolyl and carboxyl groups in the copoly(VI-AA) is found in the present study.

Experimental Section

Substrate. ANTI was synthetized by the method of Overberger *et al.*,[5] and was purified by recrystallization in nitromethane, twice, mp 210.2-212.0° (lit.[5] mp 209-210°). PNPA was purchased from Tokyo Kasei Ltd., and was purified in the usual manner.

Copoly(VI-AA). Copoly(VI-AA)'s with various copolymer compositions were obtained by radical copolymerization of 4(5)-vinylimidazole (VI) and acrylic acid (AA).

Compound VI was synthetized *via* decarbonation of urocanic acid as shown in Scheme I. The decarbonation was achieved under the pressure of 2-3 mm, and the product, 4(5)-vinylimidazole, was distilled immediately at the same condition. The copolymerization was achieved as follows. Monomers were placed in an ampoule with methanol, where the concentration of the monomer in the solution was about 17 mol %. AIBN (0.01 mol %) (for monomer) was added to the solution. The ampoule was sealed under nitrogen and the polymerization was carried out at 70° with vigorous shaking agitation. A copolymer was precipitated with