Polymerization of Alkylene Oxides with Trialkylaluminum, Metal Acetylacetonates, and Water

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Synopsis

Trialkylaluminum and acetylacetonates of Groups II and III metals are very effective polymerization catalysts for alkylene oxides. Addition of water increased both polymerization rate and yield. Among many combinations examined, a combination of triisobutylaluminum, zinc acetylacetonate, and water is outstanding. It gives high rate, high yield, and high degree of polymerization. The mole ratio of these three components was extensively studied and shown to be less critical than for other systems. Order of addition was not important. Elastomeric products based on propylene oxide, ethylene oxide, epichlorohydrin, and allyl glycidyl ether were prepared in high yield in relatively short reaction times. Copolymerization rates for epichlorohydrin–ethylene oxide and epichlorohydrin–propylene oxide were determined and indicated that this catalyst is anionic in character. It is concluded that the bimetallic nature of this catalyst is responsible for its high reactivity, versatility and stereochemistry.

INTRODUCTION

Organometallic compounds such as trialkylaluminum and dialkylzinc have been used in conjunction with water as a polymerization catalyst for alkylene oxides.[1-9] For the polymerization of propylene oxide, trialkylaluminum and water gave a high polymerization rate and high final conversion, but a low degree of polymerization. On the other hand, dialkylzinc and water gave a medium rate of polymerization, high conversion, and high degree of polymerization. The ratio of zinc and water is extremely critical in obtaining high conversion, as shown by Furukawa.[5,6] We have found that for combinations of both the aluminum and zinc compounds, the ratio of metal to water is far less critical and that high polymerization rate, high conversion, as well as high molecular weight are obtained.[10] It was speculated that the bimetallic nature of this catalyst was responsible. Kambara et al. reported that propylene oxide could be polymerized to a soft solid by use of trialkylaluminum and acetylacetonates of transition metals.[11] In this report, we wish to discuss our extensive study of a family of polymerization catalysts for alkylene oxides resulting from combining trialkylaluminum, a metal (particularly zinc) acetylacetonate, and water. This combination provides an unusually active and versatile polymerization catalyst for the preparation of high molecular weight alkylene oxide polymers and copolymers.

EXPERIMENTAL

Epichlorohydrin (ECH), propylene oxide (PO), ethylene oxide (EO), and allyl glycidyl ether (AGE) were obtained from Eastman Chemicals; EO (reagent grade) was used as received. Other epoxides were distilled and stored over a molecular sieve. Triisobutylaluminum was purchased from Texas Alkyls, and metal acetylacetonates from Mackenzie Chemical Works. The acetylacetonates have very limited solubility in cyclohexane and toluene, and were generally dispersed in cyclohexane at 0.2 molar concentrations. The solvents employed, petroleum-derived toluene and Phillips polymerization-grade cyclohexane, were dried by countercurrent scrubbing with prepurified nitrogen followed by passage over activated alumina.

Bottle polymerization procedure was followed, the details of which have been described before.[12] The charge order was solvent, monomers, triisobutylaluminum, metal acetylacetonate, and water. However, the order of addition of the catalyst components was not critical. Polymers containing less than 40% propylene oxide were coagulated in isopropyl alcohol. Those containing more were recovered by evaporating the cements to dryness after they were first washed with acidified water. About one part of antioxidant, 2,2'-methylenebis(4-methyl-6-tert-butylphenol), was used in all the samples.

Inherent viscosity was determined at 25°C in toluene for PO-based rubbers and in tetrahydrofuran for ECH-based rubbers. Unsaturation was determined by iodine monochloride titration.

For the calculation of reactivity ratios, all components of the polymerization mixture were added to 26-oz bottles and heated to the desired temperature. At zero time, triisobutylaluminum was added to initiate copolymerization. Reactions were terminated at 10% or less conversion. Products were recovered by washing in water and then drying. Mole fractions of epichlorohydrin incorporated were calculated from the percentage of chlorine in the copolymer.

RESULTS AND DISCUSSION

Preparation of Poly(propylene Oxide) Rubbers

Combinations of aluminum compound and acetylacetonate of transition metals in the absence of water gave soft to fairly tough rubber depending on the nature of the aluminum compound, metal acetylacetonate, and solvent. Reaction rate was quite low, even at 70°C, and final conversion was low. The results are summarized in Tables I and II.

It was soon discovered that acetylacetonates of zinc, copper, and aluminum were cocatalysts as effective as, or more so than, the transition metal compounds[13] and that small amounts of water greatly accelerated polymerization and increased yield.[14] The results are shown in Tables III and IV. The amount of water in the polymerization recipe was quite critical for most of the acetylacetonates, with the exception of zinc and, to a lesser

TABLE I

Polymerization of Propylene Oxide by Triisobutylaluminum
and Acetylacetonate of Transition Metals[a]

Cocatalyst		Solvent	Conversion, %	Inherent viscosity
Compound	mmoles			
Co(AcAc)₃	1	toluene	38	—
	3	toluene	41	3.19
	5	toluene	35	3.77
Fe(AcAc)₃	1	toluene	45	—
	3	toluene	45	3.73
	5	toluene	50	5.11
Fe(AcAc)₃	1	cyclohexane	60	1.65
	3	cyclohexane	65	2.70
	5	cyclohexane	78	3.19
V(AcAc)₃	1	toluene	42	1.48
	3	toluene	45	2.54
	5	toluene	35	3.20
Cr(AcAc)₃	1	toluene	38	0.68
	3	toluene	38	0.92
	5	toluene	43	—
Zr(AcAc)₄	1	toluene	40	1.95
	3	toluene	50	2.87
	5	toluene	43	3.60
Mn(AcAc)₃	1	toluene	47	2.42
	3	toluene	40	2.46
	5	toluene	36	6.66
Mn(AcAc)₃	1	cyclohexane	38	2.17
	3	cyclohexane	45	3.61
	5	cyclohexane	46	4.83
Ni(AcAc)₃	1	toluene	59	1.49
	3	toluene	49	2.12
	5	toluene	24	3.01

[a] With 100 g propylene oxide and 30 mmoles $(i\text{-Bu})_3\text{Al}$ in 500 ml solvent at 70°C for 24 hr.

degree, zirconium. It was concluded that the combination of triisobutyl-aluminum, zinc acetylacetonate, and water is an outstanding catalyst for the polymerization of propylene oxide because its use results in high conversion, high reaction rate (Fig. 1), and high molecular weight polymer. The mole ratio of these three components is less critical than for most of the initiator combinations tested. Charge order seemed to be unimportant. Allyl glycidyl ether (AGE), an unsaturated epoxide, could be incorporated in the polymer without difficulty (Table V).

Preparation of Epichlorohydrin-Based Rubbers

The reaction mechanism of polymerization of epichlorohydrin should be the same as for propylene oxide. In practice, polymerizations of epichlorohydrin have two distinct features; namely, the monomer contains an active chlorine and the polymer is insoluble in alkanes and cycloalkanes. The

TABLE II
Polymerization of Propylene Oxide by Diethylaluminum Chloride
and Acetylacetonates of Transition Metals[a]

Cocatalyst		Conversion, %	Inherent viscosity
Compound	mmoles		
Co(AcAc)₃	1	68	2.36
	3	51	2.73
	5	26	3.55
Fe(AcAc)₃	1	70	2.18
	3	70	2.92
	5	68	2.67
V(AcAc)₃	1	63	1.67
	3	50	2.73
	5	47	2.96
Zr(AcAc)₄	1	69	2.85
	3	65	4.08
	5	63	3.74
Mn(AcAc)₃	1	64	3.14
	3	64	2.19
	5	64	4.46
Ni(AcAc)₃	1	61	2.58
	3	40	3.81
	5	24	4.50

[a] With 100 g propylene oxide and 30 mmoles Et₂AlCl in 500 ml toluene at 70°C for 24 hr.

TABLE III
Polymerization of Propylene Oxide by Acetylacetonates
of Copper, Zinc, and Aluminum as Cocatalyst[a]

Catalyst[b]	Cocatalyst		Conversion, %	Inherent viscosity
	Compound	mmoles		
(i-Bu)₃Al	Cu(AcAc)₂	2	88	3.21
		4	88	4.46
		6	86	4.48
	Zn(AcAc)₂	2	74	3.94
		4	83	3.75
		6	82	6.68
	Al(AcAc)₃	2	73	2.08
		4	78	2.88
		6	82	3.66
Et₂AlCl	Cu(AcAc)₂	2	73	3.36
		4	73	4.54
	Zn(AcAc)₂	2	63	7.40
		4	62	8.28
	Al(AcAc)₃	2	78	3.33
		4	83	4.75

[a] With 100 g propylene oxide in 500 ml toluene at 70°C for 48 hr.
[b] 30 mmoles.

former feature eliminates the use of initiators that are reactive toward chlorine. This was true with the Et_2Zn-H_2O system.

Homopolymer, copolymer, and terpolymer based on epichlorohydrin could be satisfactorily produced using $(i\text{-}Bu)_3Al-Zn(AcAc)_2-H_2O$ as catalyst (Tables VI to X). Formation of terpolymer was slower and more diffi-

TABLE IV
Polymerization of Propylene Oxide with Water as the Third Component[a]

Cocatalyst[b]	H_2O, mmoles	Conversion, %	Inherent viscosity
$Co(AcAc)_2$	0	26	—
	5	49	—
	10	71	—
	15	99	5.73
	20	99	—
	30	13	—
$Fe(AcAc)_3$	0	12	—
	5	29	—
	10	61	—
	15	94	—
	20	100	3.10
	30	51	—
$V(AcAc)_3$	0	22	2.01
	5	24	2.20
	10	30	2.53
	15	41	3.51
	30	9	2.50
$Mn(AcAc)_3$	0	7	—
	5	24	—
	10	64	—
	20	97	9.17
	30	25	3.76
$Zr(AcAc)_4$	0	66	5.07
	5	89	4.99
	10	89	5.06
	15	97	4.34
	20	97	4.22
	30	16	3.13
$Cu(AcAc)_2$	0	10	—
	5	24	—
	10	52	—
	15	73	—
	20	85	2.47
	30	39	—
$Zn(AcAc)_2$	0	65	5.51
	5	90	3.82
	10	90	2.66
	15	99	3.59
	20	100	—
	30	90	2.80

[a] With 100 g propylene oxide and 30 mmoles $(i\text{-}Bu)_3Al$ in 1 liter cyclohexane at 70°C for 7 hr.
[b] 5 mmoles.

TABLE V
Preparation of Unsaturated Copolymer[a]

(i-Bu)$_3$Al, mmoles	Zn(AcAc)$_2$, mmoles	H$_2$O, mmoles	Conversion, %	Inherent viscosity
In Toluene				
30	6	20	96	4.85
20	4	14	90	3.50[b]
15	3	10	90	3.43
10	2	7	72	6.15
In Cyclohexane				
30	6	20	97	3.62
20	4	14	99	3.16[c]
15	3	10	84	5.04
10	2	7	81	3.69
10	4	7	100	5.17[d]

[a] With 92 g propylene oxide and 8 g allyl glycidyl ether in 1 liter solvent at 70°C for 15 hr.
[b] Unsaturation 0.70 mmole/g.
[c] Unsaturation 0.82 mmole/g.
[d] Unsaturation 0.74 mmole/g.

cult than that of copolymer which in turn was slower and more difficult than homopolymerization. The higher the comonomer content, the slower was the polymerization and the lower was the final conversion for a given catalyst level. Small amounts of tetrahydrofuran had a significantly beneficial effect on rate and conversion. This was particularly true in the formation of terpolymers.

TABLE VI
Polymerization of Epichlorohydrin[a]

H$_2$O, mmoles	THF, ml	Conversion, %	
		1.0 liter Toluene	1.5 liter Toluene
5	0	76	76
10	0	100	98
15	0	100	98
5	50	93	85
10	50	100	96
15	50	100	97
5	100	70	78
10	100	95	96
15	100	100	96
5	200	57	73
10	200	78	88
15	200	83	75

[a] With 100 g epichlorohydrin, 20 mmoles (i-Bu)$_3$Al, and 4 mmoles Zn(AcAc)$_2$ at 70°C for 8 hr.

Copolymerization Rates

The rates of homopolymerization of propylene oxide and epichlorohydrin were fairly close. At low catalyst levels they were almost identical, and at

TABLE VII
Copolymerization of Epichlorohydrin and Allyl Glycidyl Ether[a]

Catalyst, mmoles				
$(i\text{-Bu})_3\text{Al}$	Zn(AcAc)_2	H_2O	THF, ml	Conversion, %
Toluene = 1 liter, Reaction Time = 6 hr				
24	3	10	0	16
24	3	16	0	35
24	5	10	0	32
24	5	16	0	69
36	4	15	0	22
36	4	24	0	69
36	8	15	0	59
36	8	24	0	100
Toluene = 1 liter, Reaction Time = 16 hr				
24	5	16	0	95
24	6	16	0	100
24	7	16	0	100
Toluene = 1.5 liter, Reaction Time = 4 hr				
25	3	16	50	75 (62)[b]
25	6	16	50	90 (54)
25	3	16	100	62 (61)
25	6	16	100	83 (57)
25	3	16	200	48 (56)
25	6	16	200	73 (56)
Toluene = 1.5 liter, Reaction Time = 6 hr				
20	0	5	50	6 (10)
20	2	5	50	28 (31)
20	4	5	50	54 (38)
20	6	5	50	67 (36)
20	0	10	50	19 (21)
20	2	10	50	62 (52)
20	4	10	50	84 (53)
20	6	10	50	73 (46)
20	0	15	50	11 (24)
20	2	15	50	63 (54)
20	4	15	50	68 (43)
20	6	15	50	36 (6)
Toluene = 1.5 liter, Reaction Time = 16 hr				
25	6	15	200	100 (92)
30	6	20	200	100 (99)

[a] With 90 g epichlorohydrin and 10 g allyl glycidyl ether at 70°C.
[b] Parenthetical values are for $(\text{Et})_3\text{Al}$.

TABLE VIII
Terpolymerization of Epichlorohydrin, Propylene Oxide, and Allyl Glycidyl Ether[a]

ECH– PO–AGE	Zn(Ac-Ac)₂, mmoles	Con-version, %	Chlorine, %	Inherent viscosity	In-soluble, %	Mooney viscosity ML-4	
						212°F	250°F
			$(i\text{-Bu})_3\text{Al} = 25$ mmoles; $H_2O = 20$ mmoles				
90–0–10	4	100	—	—	—		
90–0–10	6	100	34 (34)[c]	5.29	41		
80–10–10	4	65	—	—	—		
80–10–10	6	95	29 (30)	4.23	4		
70–20–10	4	60	—	—	—		
70–20–10	6	85[b]	26 (27)	5.58	4		
60–30–10	4	65	—	—	—		
60–30–10	6	85[e]	22 (23)	4.11	0		
50–40–10	4	65	—	—	—		
50–40–10	6	90[d]	19 (19)	6.28	0		
			$(i\text{-Bu})_3\text{Al} = 30$ mmoles, $H_2O = 20$ mmoles				
92–0–8	4	96				87	87
92–0–8	6	100				96	100
92–0–8	8	100				119	102
60–32–8	4	79				50	—
60–32–8	6	95				68	—
60–32–8	8	100				78	—

[a] In 1 liter toluene at 70°C for 16 hr.
[b] Unsaturation 0.56 mmole/g.
[c] Unsaturation 0.51 mmole/g.
[d] Unsaturation 0.64 mmole/g.
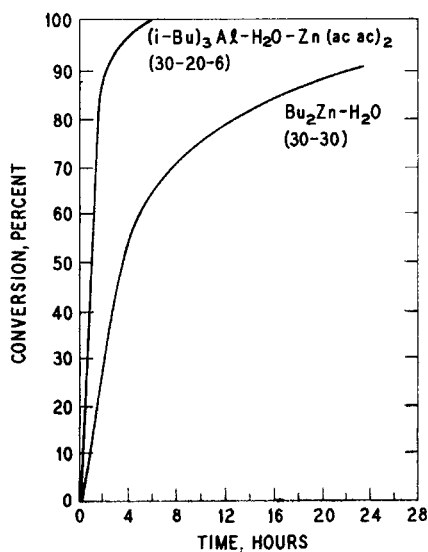[e] Parenthetical values are calculated.

Fig. 1. Polymerization of propylene oxide in toulene at 70°C.

TABLE IX
Copolymerization of Epichlorohydrin and Ethylene Oxide[a]

ECH–EO	Conversion, %	Chlorine, %		Mooney viscosity ML-4 at 250°F
		Found	Calculated	
95–5	100	36	36	88
90–10	100	33	34	113
80–20	100	30	30	134
70–30	96	26	27	148
60–40	83	20	23	150

[a] In 1 liter toluene and 50 ml THF with 30 mmoles $(i\text{-Bu})_3\text{Al}$, 6 mmoles $\text{Zn}(\text{AcAc})_2$, and 12 mmoles H_2O at 70°C for 20 hr.

TABLE X
Terpolymerization of Epichlorohydrin, Ethylene Oxide, and Allyl Glycidyl Ether[a]

ECH–EO–AGE	$\text{Zn}(\text{AcAc})_2$, mmoles	Conversion, %, with water, mmoles			
		0 mmole	5 mmoles	10 mmoles	20 mmoles
100–0–0	5	34	94	100	100
100–0–0	8	67	97	98	82
90–0–10	5	33	97	97	84
90–0–10	8	45	95	96	77
70–20–10	5	22	60	77	46
70–20–10	8	33	73	80	48
50–40–10	5	45	71	68	55
50–40–10	8	36	64	66	33

[a] In 1.5 liter toluene and 50 ml THF with 25 mmoles $(i\text{-Bu})_3\text{Al}$ at 70°C for 16 hr.

higher catalyst levels, the chlorohydrin polymerized somewhat faster (Figs. 2 and 3). Copolymerization, however, proceeded at a much reduced rate.

The copolymerization ratios for epichlorohydrin–propylene oxide and for epichlorohydrin–ethylene oxide were determined (Figs. 4 and 5). The points were experimentally determined by analyzing chlorine contents, and the reactivity ratios were determined by fitting the experimental data to copolymer–monomer composition curves using the method of Mayo and Lewis.[15] Values obtained were r_1 (PO) = 4.5 ± 1.5 and r_2 (ECH) = 0.05 ± 0.03, and r_1 (EO) = 14 and r_2 (ECH) = 0.02. As a comparison, the values of r_1 (PO) = 0.6 ± 0.5 and r_2 (ECH) = 1.8 ± 0.3 were reported by Ishida[16] for FeCl_3–PO catalyst at 85°C. The opposite results obtained for $(i\text{-Bu})_3\text{Al}$–$\text{Zn}(\text{AcAc})_2$–H_2O support the idea that the aluminum–zinc is an anionic (coordinated) system, whereas the ferric chloride catalyst is generally agreed to be cationic in nature.

The very large differences between r_1 and r_2 for either pair indicated that true random copolymers could not be formed. Indeed, when ethylene oxide (30 wt-% or 47 mole-%) and epichlorohydrin (70 wt-% or 53 mole-%) were copolymerized, ethylene oxide polymerized more rapidly, and by the time polymerization reached about 69% conversion, there was no EO monomer left in the solution (Fig. 6). Propylene oxide would be more randomly
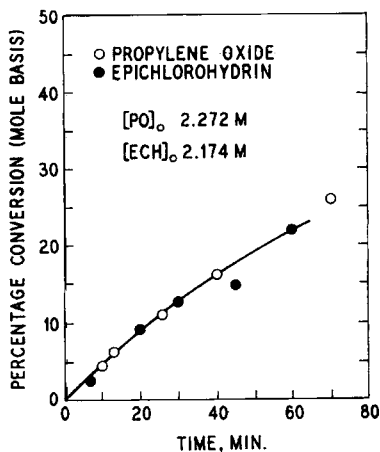
Fig. 2. Rate of polymerization in toulene with $(i\text{-Bu})_3\text{Al}$ (14 mmoles), Zn(AcAc)_2 (3 mmoles), and H_2O (10 mmoles) at 70°C.
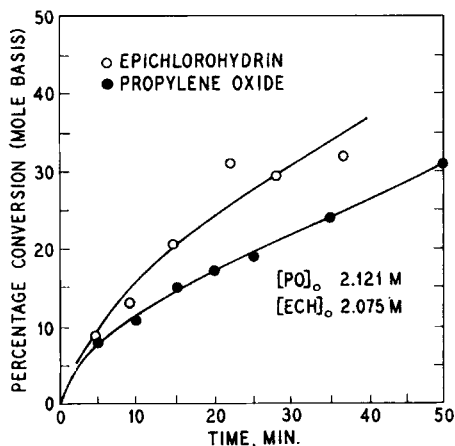

Fig. 3. Rate of polymerization in toulene with $(i\text{-Bu})_3\text{Al}$ (30 mmoles), Zn(AcAc)_2 (6 mmoles), and H_2 (20 mmoles) at 70°C

distributed than ethylene oxide because of the relatively smaller difference between r_1 and r_2. Preparation of a terpolymer of epichlorohydrin, propylene oxide, and allyl glycidyl ether (80-14-6) resulted in much more uniform composition (Fig. 7).

Comparison of Acetylacetone and Zinc Acetylacetonate as Cocatalyst

Vandenberg[9,17] reported that catalysts composed of organoaluminum compound, water, and a chelating agent such as acetylacetone are very active for polymerization of various alkylene oxides. We found that the use of the zinc salt gave even faster polymerization (Tables XI and XII).

The uniqueness of this bimetallic (a combination of aluminum and zinc) composition was demonstrated in another way. Diethylzinc and water,

with or without acetylacetone, reacted with the chlorine in epichlorohydrin rapidly and were not an active catalyst. By mixing R_3Al, R_2Zn, H_2O, and acetylacetone, we obtained a combination[18] superior to catalyst without the

TABLE XI

Comparison of Zinc Acetylacetonate and Acetylacetone
as Cocatalyst for Propylene Oxide Polymerization[a]

Acetylacetone		Zinc acetylacetonate	
mmoles	Conversion, %	mmoles	Conversion, %
2	19	2	22
3	18	3	32
5	19	5	54
7	21	7	48

[a] With 100 g propylene oxide in 1 liter toluene, 30 mmoles $(i\text{-Bu})_3Al$, and 20 mmoles H_2O at 70°C for 40 min.

TABLE XII

Comparison of Zinc Acetylacetonate and Acetylacetone
as Cocatalyst for Epichlorohydrin Polymerization[a]

Acetyl-acetone, mmoles	Zn(AcAc)$_2$, mmoles	H$_2$O, mmoles	Conversion, %
4	0	8	14
4	0	16	18
8	0	8	13
8	0	16	26
16	0	8	20
16	0	16	6
0	4	8	31
0	4	16	78

[a] With 100 g epichlorohydrin in 1 liter toluene and 20 mmoles $(i\text{-Bu})_3Al$ at 70°C for 90 min.
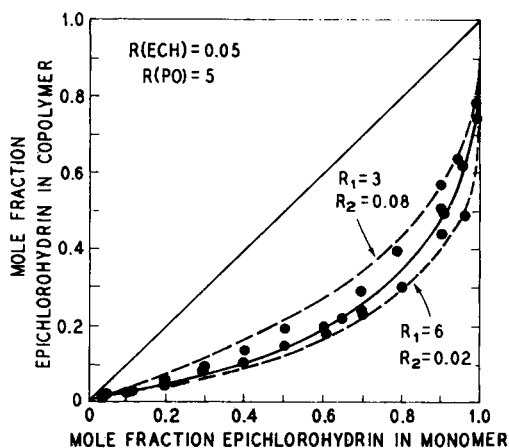

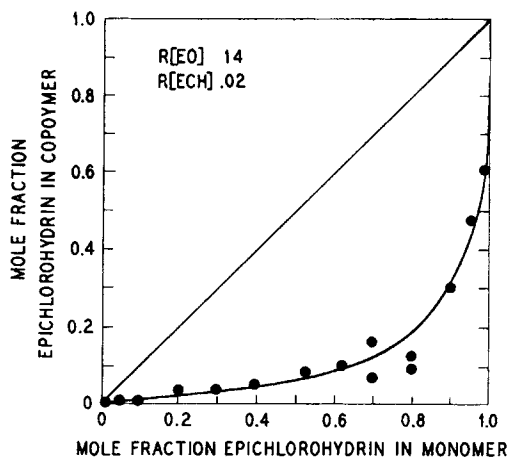Fig. 4. Copolymer composition curve of copolymerization of epichlorohydrin and propylene oxide by $(i\text{-Bu})_3Al$–H_2O–Zn $(AcAc)_2$.

Fig. 5. Copolymer composition curve of copolymerization of epichlorohydrin and ethylene oxide by $(i\text{-Bu})_3\text{Al}-\text{H}_2\text{O}-\text{Zn (AcAc)}_2$.

TABLE XIII
Polymerization of Epichlorohydrin by Triisobutylaluminum,
Diethylzinc, Water, and Acetylacetone[a]

$(i\text{-Bu})_3\text{Al}$, mmoles	Et_2Zn, mmoles	H_2O, mmoles	AcAc, mmoles	Conversion, %
25	0	20	4	59
0	25	20	4	0
20	2	20	4	93
20	4	20	4	77
4	20	20	4	0
20	0	15	4	69
0	20	15	4	3
18	2	15	4	89
16	4	15	4	88
14	6	15	4	63
10	10	15	4	6

[a] With 100 g ECH in 1 liter toluene. Acetylacetone (AcAc) was mixed with Et_2Zn at room temp. for 45 min before the addition of $(i\text{-Bu})_3\text{Al}$, H_2O, and ECH. Polymerization was carried out at 70°C for 4 hr.

presence of zinc (Table XIII). The fact that a high zinc-to-aluminum ratio resulted in low or no yield suggested that the primary site for chain growth is centered on aluminum atoms. Recently, Kuntz and Kroll[19] reported that $\text{R}_2\text{Al(AcAc)}-\text{H}_2\text{O}-\text{R}_2\text{Zn}$ is an active catalyst and proposed a mechanism involving bimetallic catalyst species.

Crystallinity

Epichlorohydrin can be polymerized to a highly crystalline product as well as to an amorphous polymer, depending on the nature of the catalyst. In a bimetallic catalyst, it is believed that two metals can function separately. A direct comparison of two-catalyst systems (Table XIV), one with and one without zinc, strongly suggested that zinc atoms in the bi-
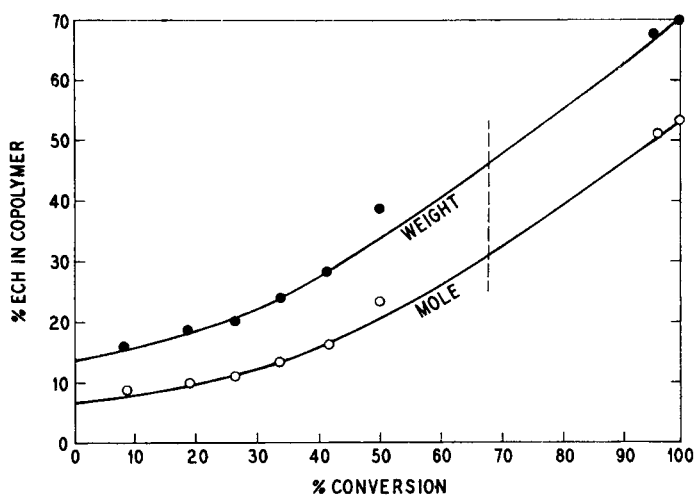
Fig. 6. Solution copolymerization of epichlorohydrin (70 wt-%, 53 moles-%) and ethylene oxide (30 wt-%, 47 mole-%) in toluene at 73°C.
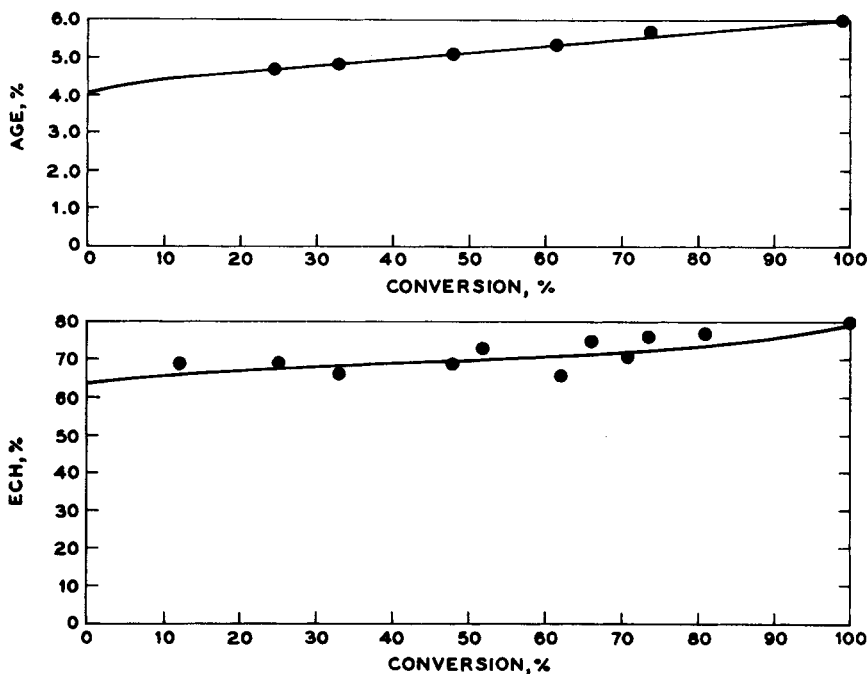

Fig. 7. Epichlorohydrin–propylene oxide–allyl glycidyl ether (80–14–6) copolymerization.

metallic catalyst species coordinate with the monomer and direct its incorporation into the polymer chain, while aluminum is responsible for the chain growth. Kuntz and Kroll have come to the same conclusion and speculated that the mechanism of propagation involved a five-coordinate aluminum.[19]

TABLE XIV
Crystallinity of Epichlorohydrin-Based Polymers

Sample	Catalyst	Crystal-linity,[a] %	Insoluble, %, in		
			Benzene	Acetone	THF
ECH (100)	$(i\text{-Bu})_3\text{Al–H}_2\text{O–AcAc}$	28	49	40	14
ECH (100)	$(i\text{-Bu})_3\text{Al–H}_2\text{O–Zn(AcAc)}_2$	60–78	73–84	63–82	65–81
ECH–EO (70–30)	$(i\text{-Bu})_3\text{Al–H}_2\text{O–AcAc}$	trace	3	5	0
ECH–EO (70–30)	$(i\text{-Bu})_3\text{Al–H}_2\text{O–Zn(AcAc)}_2$	48	60	60	66

[a] By dissolving the mixture of polymers in hot acetone (65°C) in a closed vessel under nitrogen pressure and then cooling the solution to about −18°C for at least 16 hr, whereby the crystalline polymer crystallizes out of solution.[17]

CONCLUSION

A catalyst system consisting of triisobutylaluminum, zinc acetylacetonate, and water is effective and versatile for the polymerization of alkylene oxides. It gives high rate, high yield, and high degree of polymerization. Each metal atom plays an important and independent role in the polymerization. Elastomers based on propylene oxide, ethylene oxide, epichlorohydrin, and allyl glycidyl ether can be successfully prepared with this catalyst.

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