

Molecular Weight and Molecular Weight Distribution Control in HDPE with VOCl_3 -Based Ziegler—Natta Catalysts

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Synopsis

Some characteristics of alkoxyated catalysts derived from VOCl_3 and trialkylaluminum compounds have been examined for ethylene polymerization. Specifically studied were catalysts resulting from reaction of VOCl_3 with either an alcohol or an alkylaluminum alkoxide, or both, prior to reduction with a trialkylaluminum compound (R_3Al). Although the two methods of preparing alkoxyated catalysts did not give identical results, certain overall generalizations can be drawn. In general, as the alkoxide content was increased, the molecular weight distribution was narrowed (by a simultaneous increase in \bar{M}_n and decrease in \bar{M}_w), polymerization rate was decreased, and the polymer melt index increased at a constant hydrogen level. Alkoxides had a negative effect on rate which could largely be overcome by raising the $\text{R}_3\text{Al}/\text{V}$ ratio or using continuous addition of R_3Al . By suitably adjusting the alkoxide and hydrogen amounts, the complete range of molecular weights and molecular weight distributions of current commercial HDPE products can be made.

INTRODUCTION

Vanadium-based Ziegler-Natta catalysts generally have high catalytic activity for polymerizing olefins. They have been studied extensively for ethylene copolymerization, though not so extensively for ethylene homopolymerization. Available data suggest that molecular weight distribution (MWD) is narrow for both copolymers^{1,2} and homopolymers,³⁻⁶ although at least one report of broad MWD (without data) exists.²

Commercial linear ethylene homopolymer (HDPE) is available in a wide variety of molecular weight levels (MW) and MWD's. It would be advantageous to utilize the high activity of vanadium-based catalysts for HDPE manufacture if MW and MWD could be widely varied and independently controlled. This paper reports that catalysts derived from VOCl_3 and trialkylaluminum compounds give broad MWD. Suitably modified with alkoxides, these catalysts can cover the span of MWD of present commercial interest. Hydrogen is an effective chain-transfer agent, especially with the alkoxide-containing catalysts, so MW can be varied independently of MWD over the range of interest. Furthermore, this can be accomplished without raising the halogen content of the catalyst.

EXPERIMENTAL

General Polymerization Method

Polymerizations were conducted in a jacketed, baffled glass reactor fitted with a high-speed stirrer, gas inlet, liquid drain, immersed thermocouple, serum-capped entry, and mercury manometer. All gases and liquids were dried over 3-Å molecular sieves and analyzed at less than 10 ppm H₂O. Gases were analyzed at 0.5–2 ppm O₂; liquids were purged with dried N₂ or Ar until no more oxygen could be stripped out of them.

After a rinse with dilute R₃Al, the reactor was filled with fresh Isopar-E (an aliphatic solvent from Exxon) under either Ar or N₂ (equivalent polymerization results were obtained with either), brought to temperature, and a partial vacuum pulled. Hydrogen was measured into the reactor by manometer pressure with stirring. Ethylene was then added from a high-pressure reservoir upon demand to keep the manometer at a predetermined level, generally about 800 torr. Solution concentrations of the gases were calculated from the partial pressures using previously determined solubility equations derived from our own solubility data.

When the solution was saturated with the gases at the desired temperature, the catalyst components were added individually. Generally, the alkoxide compound and VOCl₃ were reacted for 2 min before the trialkylaluminum compound was added. Isoprenylaluminum (IPA) was always added all at once. Triethylaluminum (TEA) was sometimes added all at once, but other times TEA was added quickly until polymerization commenced at what experience suggested was a near maximum rate and then slowly added via syringe pump just fast enough to eliminate or nearly eliminate the otherwise rapid rate loss.⁷ Rate was determined from the pressure drop, volume, and temperature of the ethylene reservoir and checked by polymer recovery. Stirring was not rate limiting. Hydrogen consumption during the run was negligible. The rate constant *k* in the tables was calculated assuming

$$-d[E]/dt = k[E][VOCl_3]$$

where *E* is ethylene and, unless otherwise specified, was calculated from the initial (highest) rate. Yields of polymer are expressed as moles of ethylene consumed per mmole of VOCl₃.

Reagents

The VOCl₃ was redistilled before use. TEA and IPA were used as received (Texas Alkyls). Ethylaluminum diethoxide (EADE) and ethylaluminum sesquiethoxide (EASE) were synthesized and their compositions established by NMR and quantitative ethane evolution.⁸ Dodecanol (ROH) added to an equimolar amount of VOCl₃ in Isopar-E gave quantitative evolution of one mole of HCl at room temperature and ROVOCl₂ was formed. (RO)₂VOCl was prepared by heating 2 moles of ROH per mole of VOCl₃ until 2 moles of HCl were evolved, at which point HCl evolution ceased.⁹

Polymer Handling

The polymer was recovered by filtration, boiled in isopropanol containing a small amount of HCl, filtered, rinsed with isopropanol, and vacuum dried at

60°C. Molecular weight data were obtained by gel permeation chromatography. MI_2 is the standard 190°C melt index using the standard 2160-g plunger; MI_{10} was measured using a 10-kg plunger. Since the same melt flow results were found whether 2,6-di-*t*-butyl-4-methyl phenol was added as stabilizer or not, most samples were not stabilized.

RESULTS AND DISCUSSION

First, the reproducibility of our procedures was checked (see Tables I and II). The run-to-run variability was substantially less than the effects of the variables studied. Interesting was the observation that MW and MWD were not greatly affected by the fourfold difference in rate shown in the runs of Table II. It is well known that rates are difficult to reproduce when the transition metal compound is very dilute, as it was in Table II. Data not shown in the tables indicated that MW tended to drift downward at long times (or high conversions), especially with continuous Et_3Al addition. To avoid the need for corrections, the runs shown in the later tables were run at yields or times close enough to each other that the extent of drift was small compared with the effects being studied.

The unique behavior of catalysts prepared by reacting an aluminum alkoxide with $VOCl_3$ prior to reduction with a trialkylaluminum compound has re-

TABLE I
Reproducibility Runs with $VOCl_3$ -IPA^a

Run	Run time, min	Yield, mole/mmole	k , l./mole/sec	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	MWD	MI_2	MI_{10}	MI_{10}/MI_2
155 ^b	51	1.9	138	15.3	248	16	0.055	0.99	18
186 ^b	42	1.9	101	21.6	249	12			
187 ^b	52	2.2	116	15.9	234	15			
Average ^b			118 ± 19	17.6 ± 3.5	244 ± 8	14 ± 2			
151 ^c	67	1.8	88	8.9	165	18	0.52	9.4	18
180 ^c	62	1.5	93	8.6	—	—	0.89	14.5	16
183 ^c	66	2.0	73	9.8	145	15			
185 ^c	73	2.1	78	9.4	170	18			
188 ^c	73	2.1	86	9.8	151	15			
Average ^c			84 ± 8	9.3 ± 0.5	158 ± 12	17 ± 2			

^a Standard conditions were: 0.40 mmole/l. $VOCl_3$, 2.40 mmole/l. IPA, 28.3–28.9 mmole/l. ethylene, 60.0–61.5°C.

^b 0.52 mmole/l. hydrogen.

^c 1.56 mmole/l. hydrogen.

TABLE II
Reproducibility Runs with $VOCl_3$ -TEA^a

Run	Run time, min	Yield, mole/mmole	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	MWD	MI_2	MI_{10}	MI_{10}/MI_2
182	14	0.3	17.0	202	12	0.09	1.4	16
			18.5 ^b	238 ^b	13 ^b			
184	21	0.1	16.4	169	10	0.08	1.3	17

^a Standard conditions were: 0.03 mmole/l. $VOCl_3$, 0.12 mmole/l. TEA all added at beginning, 51.0 mmole/l. ethylene, 1.50 mmole/l. hydrogen, 22°C.

^b Duplicate determination on same sample.

cently been reported.¹⁰ Tables III and IV show the effect of varying the concentration of the alkoxide species while holding all other concentrations constant. As concentration of alkoxide increased, polymerization rate and MWD decreased. Comparison of EASE and EADE is not direct between the tables because the lower IPA concentration gave a broader MWD than the higher one. EADE usually reduced both MWD and rate more than EASE at otherwise identical conditions. It is noteworthy that, in the narrowing of MWD, \bar{M}_n increased slightly while \bar{M}_w decreased.

TABLE III
Effect of EASE^a

Run	EASE, mmole/l.	Run time, min	Yield, mole/mmole	k , l./mole/sec	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	MWD
124	0.30	76	1.6	19	9.4	159	17
125	0.60	85	1.5	20	13.3	154	12
130	1.00	106	1.5	15	12.8	143	11

^a Standard conditions were: 0.48 mmole/l. VOCl_3 , 3.56 mmole/l. IPA, 52.3–52.7 mmole/l. ethylene, 1.99 mmole/l. hydrogen, 20.0–20.5°C.

TABLE IV
Effect of EADE^a

Run	EADE, mmole/l.	Run time, min	Yield, mole/mmole	k , l./mole/sec	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	MWD
149	0.30	49	1.7	43	10.1	189	19
144	0.70	53	1.5	39	11.3	179	16
150	1.40	17	0.4	35	11.3	154	14
148	2.00	94	1.2	15	12.2	165	13

^a Standard conditions were: 0.48 mmole/l. VOCl_3 , 2.74 mmole/l. IPA, 51.0–52.3 mmole/l. ethylene, 1.99 mmole/l. hydrogen, 20.5–22.0°C.

TABLE V
Runs Made with VOCl_3 -(i-PrO)_nAlEt_{3-n}-TEA^a

Run	n	Total TEA, mmole/l.	Run time, min	Yield, mole/mmole	k , l./mole/sec	Overall rate, mole/mmole/hr	MI_2	MI_{10}	MI_{10}/MI_2
227	0.0	0.54	8	0.4	41	2.8	0.26 ^b	5.1 ^b	20
258	1.0	0.40	31	0.4	14	0.7	0.19	4.3	22
267	1.3	0.40	19	0.4	16	1.2	1.0	17	17
257	1.5	0.40	17	0.4	23	1.3	2.9	47	16
261	1.8	0.70	29	0.4	12	0.8	15	210	14
259	2.0	0.70	29	0.4	15	0.8	35	470	13
260	2.2	0.80	32	0.4	12	0.7	56		
265	2.5	1.00	36	0.3	13	0.6	67		

^a Standard conditions were: 0.40 mmole/l. VOCl_3 , 28.3–29.3 mmole/l. ethylene, 1.55–1.56 mmole/l. hydrogen, 0.40 mmole/l. (i-PrO)_nAlEt_{3-n} at 59.0–61.5°C. Run procedure was: i-PrOH and TEA added to the reactor to form (i-PrO)_nAlEt_{3-n} *in situ* and reacted 2 min at reaction temperature, VOCl_3 added and reacted 2 min, 0.2 mmole TEA added and reacted 15 min before ethylene and hydrogen added. Extra TEA added rapidly until further addition gave no rate increase and continuously at reduced rate thereafter.

^b Hydrogen was 2.34 mmole/l.

TABLE VI
 Comparison of VOCl_3 and ROVOCl_2 ^a

Run	VOCl_3 , mmole/l.	ROVOCl_2 , mmole/l.	TEA mmole/l.	H_2 , mmole/l.	Run time, min	Yield, mole/ mmole	k , l./ mole/ sec	MI_2	$MI_{1.0}$	$MI_{1.0}/MI_2$
194	0.40		0.70	2.07	45	0.8	19	0.09	2.5	27
200	0.20	0.20	0.66	2.08	130	5.0	30	0.29	6.2	22
201	0.20	0.20	0.64	2.08	132	5.8	34	0.18	3.8	21
199		0.40	1.12	2.07	134	4.9	26	16.	202.	13
202		0.40	0.70	1.30	119	5.8	34	1.8	22.	13
204		0.40	0.70	0.78	159	5.3	24	0.75	9.7	13
205		0.40	0.70	0.52	158	5.5	26	0.17	2.3	13
203	0.40		0.70	0.52	134	5.1	33	—	0.015	—

^a Standard conditions were: 27.2–28.7 mmole/l. ethylene at 60.5–64.5°C with continuous TEA addition.

 TABLE VII
 Effect of Mixed Alkoxides^a

Run	Vanadium compound	Aluminum alkoxide	TEA, mmole/l.	Hydrogen, mmole/l.	Run time, min	k , l./ mole/ sec	MI_2	$MI_{1.0}$	$MI_2/$ $MI_{1.0}$	$\bar{M}_n \times$ 10^{-3}	$\bar{M}_w \times$ 10^{-3}	MWD
238	$(\text{RO})_2\text{VOCl}$	None	0.94	0.52	21	15	14	125	9	9.6	53	6
248	ROVOCl_2	Et_2AlOEt	0.40	0.52	15	22	7.5	80	11	10.6	64	6
249	ROVOCl_2	EtAl(OEt)_2	0.60	0.26	16	23	1.6	15	10	15.9	120	8
253	$(\text{RO})_2\text{VOCl}$	Et_2AlOEt	0.60	0.13	18	25	0.23	2.0	9	34.1	199	6
254	$(\text{RO})_2\text{VOCl}$	EtAl(OEt)_2	0.90	0.13	13	25	0.31	2.4	8	32.5	167	5

^a Standard conditions were: 0.40 mmole/l. vanadium compound, 0.40 mmole/l. aluminum alkoxide, 28.5–29.1 mmole/l. ethylene at 59.5–61.0°C, continuous TEA addition. All runs terminated at 0.4 mole/mmole yield.

The series of runs shown in Table V was made to directly determine the effects of extent of alkoxylation of the alkylaluminum alkoxide. It can be seen that polymerization rate was highest for the alkoxide-free run and was maximum for the alkoxide-containing catalysts at about the formula for the sesquialkoxide. MW and MWD (as inferred from MI_{10} and MI_2) did not change significantly until more than one alkoxy group/Al was present and then decreased monotonically with increased alkoxide. MI_2 increased steadily as n increased, suggesting that hydrogen was more effective at higher n . The runs were made in random order to avoid any unknown systematic changes as n varied.

The catalytic behavior of catalysts derived from partially esterified (alkoxylated) $VOCl_3$ with trialkylaluminums was also investigated. This combination appears not to have been recognized in ethylene polymerization. Although the literature is replete with references on the use of orthovanadates or halovanadyl esters with alkylaluminum halides, relatively few references were found to the use of trialkylaluminums, and all were patents directed at "halogen-free" catalysts and used orthovanadate esters.¹¹⁻¹⁵ However, in very careful work, Kahle and Buck¹⁶ showed that pure $R_3VO_4 \cdot R_3Al$ mixtures do not polymerize olefins in the absence of a halogen compound; but when the orthovanadate was treated with a halogen-containing compound (such as HCl), polymerization occurred. Clearly, Kahle and Buck produced $(RO)_2VOCl$ and $ROVOCl_2$ in their work. Whether the earlier workers had impure R_3VO_4 or impure R_3Al is not known. Matkovski et al.¹⁷ report a single experiment in which ethylene was polymerized by a catalyst prepared by combining $VOCl_3$, *i*-BuOH, and *i*-Bu₃Al in that order. From our work, it seems clear that *i*-BuOVOCl₂ was formed since we obtained the same results using either $VOCl_3$ plus dodecanol or presynthesized dodecyloxyvanadium oxydichloride.

This alkoxide (R = dodecyl) was studied briefly (see Table VI) to determine its characteristics in comparison with the aluminum alkoxide catalysts described above. It can be seen that the presence of the dodecyloxy group lowered the MI_{10}/MI_2 ratio and increased the effectiveness of hydrogen as an MI_2 -controlling agent. Because there was scatter introduced into the rate data due to variation in the timing and method of continuous TEA addition, about all that can be said about polymerization rate is that no major effects due to variation in alkoxide or hydrogen levels were discernable.

Finally, the effects of adding alkoxide to both the vanadium and aluminum components of the catalyst were briefly examined (Table VII). This apparently has not been reported before. In general, the polymers obtained would be classified as ultranarrow-MWD polyethylene products. By adjusting TEA, the reaction rates were kept comparable. Only a small amount of hydrogen was required to make a high MI_2 product.

CONCLUSIONS

It has been shown that by appropriate addition of alkoxide to a $VOCl_3 \cdot R_3Al$ catalyst, MWD may be varied from very broad to very narrow (for HDPE). The molecular weight level can be controlled with hydrogen to give either high or low MI_2 at all MWD levels. Finally, the negative effect of in-

creased alkoxide content on rate can be largely overcome by continuous addition of increasing amounts of R_3Al .

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References

1. G. I. Keim, D. L. Christman, L. R. Kangas, and S. K. Keahey, *Macromolecules*, **5**, 217 (1972).
2. G. W. Phillips and W. L. Carrick, *J. Amer. Chem. Soc.*, **84**, 920 (1962).
3. D. L. Christman, *J. Polym. Sci. A-1*, **10**, 471 (1972).
4. W. L. Carrick, R. W. Kluiber, E. F. Bouner, L. H. Wartman, F. M. Rugg, and J. J. Smith, *J. Amer. Chem. Soc.*, **82**, 3883 (1960).
5. L. L. Stotskaya, I. F. Leshcheva, and B. A. Krentsel, *Neftikhimiya*, **4**, 43 (1964).
6. A. K. Shilova, S. V. Shulyndin, and G. I. Sotnikova, *Vysokomol. Soedin.*, **A9**, 808 (1967).
7. I. N. Meshkova, N. G. Kudryakova, and N. M. Chirkov, *Vysokomol. Soedin.*, **A15**, 1087 (1973); *Polym. Sci. USSR*, **15**, 1220 (1974).
8. M. R. Ort and G. A. Mortimer, to be published.
9. M. R. Ort, private communication.
10. M. R. Ort, U.S. Pat. 3,784,539 (1974).
11. G. Natta, G. Mazzanti, and C. M. Capucci, Ital. Pat. 564,922 (1957).
12. G. Natta, G. Mazzanti, A. Valvassori, and G. Sartori, Belg. Pat. 632,635 (1963).
13. G. B. Stampa and A. G. Farnham, U.S. Pat. 3,008,948 (1961).
14. V. L. Bell, Jr., Belg. Pat. 616,171 (1962).
15. Hercules Powder Co., Brit. Pat. 902,385 (1962).
16. G. R. Kahle and D. G. Buck, French Pat. 1,454,525 (1966).
17. P. E. Matkovskii, G. A. Beikhold, and A. D. Pomogailo, *Izv. Akad. Nauk. Kaz. SSR, Ser. Khim.*, **19**(4), 63 (1969).

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