

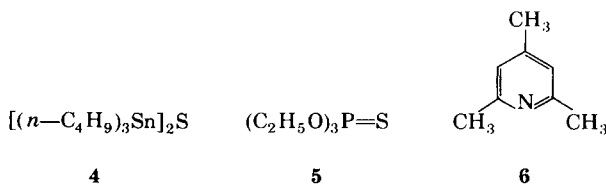
Modification of Ziegler-Type Propylene Polymerization Catalysts with Orthosilicate Alkylesters

INTRODUCTION

The activation of the propylene polymerization catalyst system based on TiCl_3 and $(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ with various organosilicon compounds has been demonstrated in the past.¹⁻⁴ Systems consisting of TiCl_3 and alkylaluminum dihalides are practically ineffective for the polymerization of propylene to solid polymer, but can be converted to stereospecific systems by inclusion of a third component.⁴ Among organosilicon compounds, orthosilicate alkylesters ($\text{Si}(\text{OR})_4$), alkyl- or aryl-alkoxysilanes ($\text{R}'_n\text{Si}(\text{OR})_{4-n}$; $\text{R} = \text{alkyl}$, $\text{R}' = \text{alkyl, aryl}$),¹⁻³ and $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ ⁴ were found to be effective in this connection. Other types of third components that can be used as activators of the system include tertiary amines and phosphines and hexamethylphosphoric triamide.⁵⁻⁹ Regarding the species responsible for the activation of the catalyst system by amines, phosphines and hexamethylphosphoric triamide, two differing views were advanced: i.e., a dismutation reaction of $(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ in the presence of the third component, leading to formation of AlCl_3 and $(\text{C}_2\text{H}_5)_2\text{AlCl}$, with the latter compound contributing to the activation of the system^{5,6,9}; and formation of a stable complex between $(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ and the third component, and activation of the system by this complex.^{7,8} In the case of organosilicon third components, stable complexes with $(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ are formed. Actually, a 1 : 2 complex of $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ and $(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ has been isolated; Matsumura et al. demonstrated that this complex does not undergo dismutation reactions but has the ability to alkylate TiCl_3 and thus activate the catalyst system.⁴ Following studies of the effects of various types of modifiers on catalyst systems based on Stauffer's AATiCl_3 and $(\text{C}_2\text{H}_5)_2\text{AlCl}$,¹⁰⁻¹⁷ we became interested in investigating the modification of these systems with organosilicon compounds, which had been found to produce quite active systems when used with TiCl_3 and $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$.¹⁻³ Accordingly, research in this direction was undertaken, and this communication deals with our results on various orthosilicate alkylesters (**1a-f**), hexamethyldisilazane (**2**), and diphenylsilanediol (**3**) as potential catalyst modifiers in systems involving either a single organosilicon compound, as well as systems containing both an organosilicon and an additional modifier^{15,16,18}:

$\text{Si}(\text{OR})_4$	1a	b	c	d	e	f
1	C_2H_5	$(\text{CH}_2)_3\text{CH}_3$	$(\text{CH}_2)_4\text{CH}_3$	$(\text{CH}_2)_5\text{CH}_3$	$(\text{CH}_2)_6\text{CH}_3$	$(\text{CH}_2)_7\text{CH}_3$
		$\text{HN}[\text{Si}(\text{CH}_3)_3]_2$		$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$		
		2		3		

Additional modifiers of other types investigated in combination with organosilicon modifiers were bis(tri-*n* butyltin)sulfide (**4**),^{15,19,20} and, to a lesser extent, triethyl thiophosphate (**5**).^{16,18} The performance of catalyst systems modified with the binary **1a-4** system was compared to that of the corresponding system modified with **4** and 2,4,6-trimethylpyridine (**6**)^{10,20}:



RESULTS AND DISCUSSION

Propylene polymerization results given in Tables I-III are generally reproducible within a given set of experiments¹⁵ and represent average values of 2-3 runs. Table I summarizes the results of screening studies of various organosilicon compounds in pressure-bottle (catalyst systems A and B) and 1-gal reactor (catalyst systems C and D) slurry polymerizations. Use of any of the compounds **1a**, **1c-e**, and **3** as sole modifiers leads to improvements of both activity and stereospecificity, relative to the unmodified catalyst system. However, combination of the organosilicon compound with a second modifier, such as **4**, is necessary, in order to reduce the hexane solubles level to below 4% (catalyst system B vs. A). Inclusion of **4** in the catalyst system leads to intermediate catalyst activities between those realized with the unmodified and organosilicon compound-modified catalyst systems. Among the various compounds of type **1** studied at the pressure-bottle level, the ethyl ester **1a** is the most effective modifier, while the *n*-hexyl ester **1d** is superior to both the *n*-amyl (**1c**) and *n*-heptyl (**1e**) esters. It is not clear whether the performance differences observed with the latter three esters are due to chemical effects or the relative purities of the samples used. During later scale-up work, involving slurry polymerizations in 1-gal reactors, a number of additional organosilicon compounds (**1b**, **1f**, **2**, and **3**) were compared to **1a** (catalyst systems C and D). Again, substantial stereospecificity improvement was realized with the binary modifier **1a-4** system relative to the system using **1a** as the sole modifier, without any adverse effect on catalyst yield. In this set of experiments, modifiers **1a** and **2** gave the best results in binary modifier systems involving also **4**; actually the silazane **2** was found to lead to slightly improved yields and stereospecificities relative to **1a**, but it was decided to

TABLE I
Screening Studies of Organosilicon Compounds as Potential Modifiers
of Propylene Polymerization Catalysts^a

Modifier	Catalyst system ^b	Yield of isotactic polypropylene (g/g AATiCl ₃)	Hexane solubles (wt %)
None	A	195	7.26
1a	A	252	4.10
1c	A	262	6.35
1d	A	243	5.13
1e	A	265	6.96
3	A	265	6.37
1a	B	239	2.12
1c	B	233	3.28
1d	B	228	2.82
1e	B	225	3.23
1a	C	1048	6.50
1a	D	1056	4.00
1b	D	980	4.20
1f	D	966	4.60
2	D	1136	3.90
3	D	918	4.20

^a Catalyst systems A and B were used in 4-h pressure-bottle slurry propylene polymerizations in 190 mL hexane at 70°C; propylene pressure 40 psig (3.75 bar), in the absence of H₂. 0.2 g AATiCl₃ were used. Catalyst systems C and D were used in 2-hr 1-gal reactor slurry polymerizations in 1.5 L hexane at 70°C; 160 psig (11.66 bar) total pressure and 3.5 psig (1.3 bar) partial pressure of H₂. 0.6 g AATiCl₃ were used.

^b Catalyst systems: molar ratios: A = (C₂H₅)₂AlCl/AATiCl₃/organosilicon modifier 3.16/1/0.036; B = (C₂H₅)₂AlCl/AATiCl₃/4/organosilicon modifier 3.16/1/0.116/0.036; C = (C₂H₅)₂AlCl/AATiCl₃/organosilicon modifier 2.55/1/0.104; D = (C₂H₅)₂AlCl/AA TiCl₃/4/organosilicon modifier 2.55/1/0.089/0.104.

TABLE II
Propylene Slurry Polymerizations Using the $(C_2H_5)_2AlCl-AATiCl_3$
4-1a (or 6) Catalyst Systems^a

Modifier X	Molar ratios of $(C_2H_5)_2AlCl/AATiCl_3/4/X$	Yield of polypropylene in g/g $AATiCl_3$	Hexane solubles (wt %)
Series A ^b			
	1.5/1/—/—	980	7.20
1a	1.5/1/0.028/0.02	1102	5.00
1a	1.5/1/0.028/0.04	1152	6.80
1a	1.5/1/0.042/0.06	1012	4.30
1a	1.5/1/0.056/0.02	1016	4.50
1a	1.5/1/0.056/0.04	990	4.10
1a	1.5/1/0.056/0.08	800	4.80
1a	2.55/1/0.089/0.104	1056	4.00
1a	2.55/1/0.089/0.052	888	4.00
1a	2.55/1/0.134/0.104	896	3.60
1a	2.55/1/0.134/0.052	984	3.90
1a	2.55/1/0.178/0.104	894	3.50
6	2.55/1/0.023/0.046	824	2.90
6	2.55/1/0.115/0.023	786	4.10
Series B ^b			
1a	2.0/1/0.089/0.104	1410	6.00
1a	2.55/1/0.089/0.104	1438	3.50
1a	3.0/1/0.089/0.104	1266	4.70
1a	2.55/1/0.0445/0.104	1670	8.20
6	3.0/1/0.027/0.054	1224	2.60

^a2-h 1-gal reactor slurry polymerizations in 1.5 L hexane at 70°C.

^bSeries A involved polymerizations at 160 psig (11.66 bar) total pressure while in series B the total pressure was increased to 250 psig (18.22 bar). The partial pressure of H_2 was 3.5 psig (1.3 bar) in both cases.

TABLE III
Propylene Bulk Polymerizations Using Catalyst Systems
Involving Binary Modifier Packages^a

Modifier		Molar ratios of $(C_2H_5)_2Al/AATiCl_3/X/Y$	Yield of polypropylene in g/g $AATiCl_3$	Hexane extractables (wt %)
X	Y			
None	4	5.5/1/—/0.3	3042	2.59
1a	4	5.5/1/0.104/0.3	3722	2.72
1d	4	5.5/1/0.104/0.3	3635	2.97
1d	4	5.5/1/0.208/0.3	3120	4.50
None	5	5.5/1/—/0.1	2619	1.90
1a	5	5.5/1/0.07/0.1	2966	2.85
1a	5	5.5/1/0.14/0.1	2660	4.17
1d	5	5.5/1/0.07/0.1	2854	3.30
1d	5	5.5/1/0.14/0.1	2547	11.10

^a2-h propylene polymerizations in 1-L Parr reactors at 70°C. 485 psig (34.4 bar) total pressure, 3.5 psig (1.3 bar) H_2 partial pressure; 0.2375 mmol $AATiCl_3$ were used in each run.

continue our studies with the latter modifier, as we had already developed a substantial number of data with the 1a-4 binary system. The *n*-butyl (1b) and *n*-octyl (1f) orthosilicate esters and the silanediol 3 exhibited somewhat poorer yields and stereospecificities relative to 1a or 2.

Table II shows 1-gal reactor propylene slurry polymerization results with the $(C_2H_5)_2AlCl$ - $AATiCl_3$ -1a-4 catalyst system at various molar ratios and comparative data for the corresponding system that uses the binary 4-6 modifier package.²⁰ The use of 1a and 4 as modifiers leads generally to both activity and stereospecificity improvements relative to the unmodified catalyst system. By appropriate variation of the levels of 1a and 4 yields of 900-1050 and 1438 g/g $AATiCl_3$ at 11.66 and 18.22 bar total pressure, respectively, with hexane solubles of 3.5-4.0% can be attained. These yields are higher by 15-30% than those realized by the highly stereospecific $(C_2H_5)_2AlCl$ - $AATiCl_3$ -4-6 catalyst system, which produces lower hexane solubles (2.6-2.9%), however. An additional advantage of the latter system is that it requires substantially lower modifier levels for stereospecificity control, relative to the system modified with 1a and 4.

Table III gives bulk propylene polymerization results with catalyst systems modified with one organosilicon compound (1a or 1d) and the organotin sulfide 4 or the thiophosphate ester 5. Use of relatively low amounts of 1a or 1d along with 4 or 5 results in catalyst systems exhibiting substantially better activity but somewhat lower stereospecificity, relative to systems using 4 or 5 as the sole modifier. 1a is a more effective modifier than 1d, as would be expected from the data of Table I. When the levels of 1a or 1d are increased, an adverse effect on catalyst performance is observed. In fact, the beneficial effect of these modifiers on catalyst activity is lost, while the stereospecificity of the systems decreases to unacceptable levels.

Regarding the interactions of the orthosilicate alkylesters of type 1 with the components of the catalyst system, it appears that their ability to improve catalyst activity results from their complexation with $(C_2H_5)_2AlCl$, which facilitates the alkylation of $TiCl_3$.⁴ Adduct formation between 1 and the solid metal chlorides of the system ($TiCl_3$, $AlCl_3$) is possible,²¹ but unlikely to occur in the presence of the $(C_2H_5)_2AlCl$ component. As far as reactions between $Si(OR)_4$ and $(C_2H_5)_2AlCl$, leading to formation of $(C_2H_5)_nSi(OR)_{4-n}$ and $(C_2H_5)(OR)AlCl$, are concerned, they are known to take place at significantly higher temperatures²²⁻²⁴ than that used in propylene polymerization (70°C).

In conclusion, use of orthosilicate alkylesters (1) as the sole modifiers of propylene polymerization catalyst systems consisting of $AATiCl_3$ and $(C_2H_5)_2AlCl$ resulted in significant activity and modest stereospecificity improvements. These improvements are not sufficient as to allow practical application of $(C_2H_5)_2AlCl$ - $AATiCl_3$ -1 catalyst systems. However, systems containing a binary modifier package, consisting of one compound of type 1 (preferably the ethyl ester 1a) and the organotin sulfide 4, provide satisfactory activity-stereospecificity combinations. Practical application of these systems is considered possible, especially when high catalyst activities at some expense of the stereospecificity control which can be provided by lower activity systems, such as $(C_2H_5)_2AlCl$ - $AATiCl_3$ -4-6, are desired.

EXPERIMENTAL

Reagent grade modifiers (1a-f and 2-6) were used as received. $AATiCl_3$ (from Stauffer; composition $TiCl_3 \cdot 1/3AlCl_3$) and 25 wt % solutions of $(C_2H_5)_2AlCl$ in hexane (from Texas Alkyls) were used. Polymerization grade propylene and hexane were treated with molecular sieves 3A and 13X, respectively, prior to use. All operations were performed in a dry, deoxygenated nitrogen atmosphere. Propylene slurry polymerizations were performed in pressure bottles and 1-gal reactors. The polymerization techniques used and the calculations of yields of isotactic polypropylene and hexane solubles % were described elsewhere in detail.^{10,12,17} Propylene bulk polymerizations were performed in 1-L Parr reactors; the polymerization technique and the calculation of polypropylene yield and hexane extractables % were also previously described.¹² With respect to the sequence of combining the components of the catalyst systems investigated, it was established that comparable results are obtained when the organosilicon and additional modifiers are added to a mixture of $(C_2H_5)_2AlCl$ and $AATiCl_3$ or the modifiers are combined with the alkylaluminum chloride and then $AATiCl_3$ is added. Direct contact of the modifiers with $AATiCl_3$ in the absence of $(C_2H_5)_2AlCl$ is to be avoided, as it may lead to severe agglomeration of the solid catalyst. The molecular weight distributions of the polypropylene samples prepared in the presence of H_2 were generally normal (M_w/M_n range 6-8).

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