values for methyl acrylate, $e_M = 0.60$ and $Q_M = 0.42$, the average Q_{SO_2} value calculated from the data at -78 and 0 °C was found to be 0.67. Assuming that the rate constant of reaction 4 is equal to that of propagation in the homopolymerization of methyl acrylate, one can roughly estimate also other kinetic parameters characterizing the addition of SO_2 to $\sim MM^\bullet$ macroradicals (eq 1). As can be seen from Table IV this reaction is characterized by a lower Arrhenius activation energy (E_a) and lower value of the collision frequency factor (A) than the homopropagation of methyl acrylate. In terms of the active complex theory one can expect that the addition of SO_2 is connected with a lower enthalpy of activation ($\Delta H^\ddagger$) and a much larger entropy of activation ($\Delta S^\ddagger$), which indicates that the freedom of reagent movement in the active complex of the $\sim MM^\bullet$ macroradical with SO_2 is much less limited than that in the complex with methyl acrylate.

It should be noticed that also in other nonalternating copolymerizations of sulfur dioxide the occurrence of SO_2MSO_2 triads is not observed above a certain temperature. However, the number of experimental data available at present is insufficient for testing the applicability of eq 6 for the description of these systems.

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Isotactic-Specific Polymerization of Propene with Supported Catalysts in the Presence of Different Modifiers

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ABSTRACT: The behavior of several organic molecules in modifying the productivity and stereospecificity of two different supported Ziegler-Natta catalysts in the polymerization of propene has been investigated. Some correlation between the structure of the modifiers, the type of supported catalyst, and the polymerization results can be observed.

The "last generation" heterogeneous Ziegler-Natta catalysts for isotactic-specific polymerization of propene are rather complex systems consisting of (a) a solid precatalyst obtained from $MgCl_2$, $TiCl_4$, and an organic Lewis base (often referred to as the "internal modifier") and (b) a cocatalyst solution containing an alkylaluminum and an organic Lewis base (the "external modifier").[1] The function of the external modifier is to increase the stereospecificity of the catalytic system, which otherwise produces a mixture of isotactic and more or less stereoirregular macromolecules. While a great variety of Lewis bases are able to increase the stereospecificity of the polymerization, only three classes of external modifier are known that allow one to obtain polypropylene with a high isotactic index (e.g., >95%) without impracticably depressing the polymer productivity. These classes are (1) the esters of aromatic carboxylic acids (e.g., ethyl benzoate), (2) some sterically hindered amines (e.g., 2,2,6,6-tetramethylpiperidine), and (3) the alkoxysilanes of general formula $R_nSi(OR')_{4-n}$.

A considerable effort, with special attention to the aromatic esters, has been devoted by several research groups toward clarifying the stereoregulation mechanism of these modifiers.[2] A widely accepted hypothesis suggests selective coordination of the Lewis base to the nonstereospecific active sites of the solid precatalyst as the explana-

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tion of the increased stereospecificity of the system. A different mechanism was proposed by Goodall,[3] involving a reaction between the modifier and the titanium–polymer bonds of the active sites. In a previous paper by our research group[4] some evidence supporting the latter hypothesis was reported for the catalyst system $TiCl_4$/$MgCl_2$/ethyl benzoate/$Al(C_2H_5)_3$/methyl benzoate labeled with ^{14}C on the carboxylic carbon.

Very few reports[5,6] in the literature deal with the last two classes of external modifier (i.e., the alkoxysilanes and the hindered amines) despite the fact that the alkoxysilanes are the most commonly used modifiers in modern industrial processes.

This paper reports the results of a systematic investigation of the effect of the molecular shape of the alkoxysilane modifier on the catalytic system's performance. The performance of the catalytic system is estimated from polymer productivity, isotactic index, molecular weight distribution, and its interaction with hydrogen. The stereoregulation mechanism, previously proposed for benzoates, has been tested by using selectively ^{13}C-enriched alkoxysilanes and examining by NMR the obtained polymers. Some data concerning hindered amines are also reported.

Experimental Section

Materials. The $TiCl_4/MgCl_2$/diisobutyl phthalate (precatalyst 1) and the $TiCl_4/MgCl_2$/ethyl benzoate (precatalyst 2) systems were commercial products prepared according to the patent literature.[7,8] Triethylaluminum was purchased from Fluka. *n*-Heptane was dried by refluxing 48 h over Na–K alloy under a nitrogen atmosphere. Diphenyldimethoxysilane, dimethyldimethoxysilane, and phenyltriethoxysilane were purchased from Petrarch. The remaining alkoxysilanes were prepared according to a general procedure described in the literature.[9] Methylphenyldiethoxysilane enriched with ^{13}C on the methyl carbon was prepared by allowing phenyltriethoxysilane and ^{13}C-enriched methylmagnesium iodide to react. Diphenyldimethoxysilane enriched with ^{13}C on the methoxy substituent was synthesized from diphenyldichlorosilane and 90% ^{13}C-enriched methanol obtained from Aldrich. 2,2,6-Trimethylpiperidine was prepared according to the literature.[10] 1,2-Dimethylpiperidine was prepared by methylation of 2-methylpiperidine with methyl iodide. The remaining substituted piperidines were purchased from Fluka or Aldrich.

Polymerizations. Unless otherwise stated, polymerizations were carried out in a 2-L steel autoclave thermostated at 50 °C. In a typical run, 90–120 mg of solid precatalyst suspended in 0.7 L of anhydrous heptane containing 1.0 mL of triethylaluminum and the proper amount of the alkoxysilane or the substituted piperidine (the $Al(C_2H_5)_3$/modifier molar ratio was fixed at a value of 10) were introduced into the previously evacuated autoclave. Where specified (see Tables I and II), hydrogen, measured with a gas buret, was added in the amount as reported in the tables. Thereupon propene was fed to a pressure of 7 atm, held constant during the run. After 2 h the polymerization was stopped and the reaction mixture was poured into 0.8 L of acidified acetone. The polymers obtained were separated by filtration, washed twice with fresh acetone, and dried in vacuo.

Polymerizations in the presence of ^{13}C-enriched modifiers were performed as follows: Run 48: precatalyst 1, 0.5 g; $Al(C_2H_5)_3$, 1 mL; $C_6H_5Si(OC_2H_5)_2{}^{13}CH_3$ (90% ^{13}C enriched), 0.75 mL; hexane, 100 mL; C_3H_6 pressure, 0.5 atm; temperature, 50 °C; duration, 1 h; yield, 40 g; isotactic index, 98%. Run 49: precatalyst 1, 0.5 g; $Al(i\text{-}C_4H_9)_3$, 1 mL; $(C_6H_5)_2Si(O^{13}CH_3)_2$ (90% ^{13}C enriched), 0.2 mL; hexane, 200 mL; C_3H_6 pressure, 0.5 atm; temperature, 50 °C; duration, 3 h; yield, 34 g; isotactic index, 98%.

Polymer Characterization. The polymers were exhaustively extracted with boiling heptane in a Kumagawa extractor. The isotactic index (I.I.) reported in the tables for each sample is the percentage of insoluble polymer. Molecular weights were measured on the raw polymers by GPC on a Waters LC 150 at 140 °C in 1,2,4-trichlorobenzene using a Waters linear Ultrastyragel column.

The polymers obtained in runs 48 and 49 were sequentially extracted with boiling diethyl ether and *n*-heptane. The three fractions, namely, the ether-soluble fraction, the ether-insoluble, heptane-soluble fraction, and the heptane-insoluble fraction, were analyzed by ^{13}C NMR in tetrachlorodideuterioethane at 120 °C with a Bruker AM 250 spectrometer.

Results and Discussion

Several alkoxysilanes bearing alkyl and alkoxy substituents of different bulkiness were synthesized and tested as external modifiers in the polymerization of propene with a $TiCl_4/MgCl_2$/diisobutyl phthalate (precatalyst 1)/$Al(C_2H_5)_3$ catalytic system as described in the Experimental Section. Some commercially available alkoxysilanes were also tested for comparison. The polymerization conditions and results are summarized in Table I. A comparison of the data suggests the following considerations:

(1) The stereospecificity of the catalytic system is noticeably affected by the molecular shape of the alkoxysilane, but the bulkiness of the alkyl and of the alkoxy substituents on the silicon seems to play different roles in this respect. In fact, comparing the polymers produced with alkoxysilanes of formula $R_2Si(OCH_3)_2$, one can observe an increase of the I.I. that parallels the increase of bulkiness of the alkyl group R, following the order $CH_3 < n\text{-}C_4H_9 < i\text{-}C_4H_9 = C_6H_5 < i\text{-}C_3H_7$ (see, for example, runs 3, 9, 21, 11, and 19). On the contrary, comparing the I.I.'s of the polymers produced in the presence of alkoxysilanes of the general formula $(CH_3)_2Si(OR)_2$, $(C_6H_5)_2Si(OR)_2$, or $(C_6H_5)Si(OR)_3$, one finds the opposite trend. In this case, the I.I. decreases while the bulkiness of the alkoxy group OR increases, in the order $OCH_3 > OC_2H_5 > O\text{-}i\text{-}C_3H_7$ (for example, compare runs 3, 5, and 7, runs 21, 23, and 25, or runs 27, 29, and 31).

(2) The polymer productivity is marginally affected by the molecular structure of the alkoxysilane. The addition of hydrogen to the polymerization medium produces a considerable increase in productivity independently of the alkoxysilane used. At least in the range examined, this increase is proportional to the amount of H_2 added.

(3) The molecular weight distribution of the crude polymers seems to be sensitive to the bulkiness of the alkyl substituents of the silane. The M_w/M_n ratio decreases in the order $CH_3 > n\text{-}C_4H_9 > i\text{-}C_4H_9 > i\text{-}C_3H_7$. This is probably due to the decreasing amount of the stereoirregular low molecular weight fraction of the crude polymer. The molecular weight distribution is always broader for polymers prepared in the presence of hydrogen. Possibly this is due to the consumption of hydrogen during the polymerization.

(4) When deuterium is used instead of hydrogen (compare runs 13 and 14, runs 15 and 16, and runs 17 and 18), a very marginal isotope effect, if any, is observed on productivity, I.I., and molecular weight.

(5) Chain transfer with hydrogen seems to become less effective in the presence of silanes having bulkier alkyl substituents. In fact, the molecular weight of polymers prepared with the same amount of hydrogen increases in the order $n\text{-}C_4H_9 < C_6H_5 < i\text{-}C_4H_9 < i\text{-}C_3H_7$.

These experimental findings are compatible with both of the hypotheses concerning the stereoregulation mechanism mentioned in the introduction, i.e., (1) preferential coordination of the silane to the nonstereospecific sites vs (2) deactivation of the catalytic sites by some reaction of the silane with the titanium–polymer bonds, followed by reactivation through chain transfer with triethylaluminum; the different rates of the deactivation and/or reactivation processes for the two sorts of sites would account for the increased stereospecificity as described in ref 4.

In order to test the latter hypothesis, we have performed two polymerization runs in the presence of the precatalyst 1/$Al(C_2H_5)_3$ catalytic system and either (1) methylphenyldiethoxysilane enriched with ^{13}C on the methyl substituent or (2) diphenyldimethoxysilane enriched with ^{13}C on the methoxy substituents (runs 48 and 49). The polymers obtained were fractionated as described in the Experimental Section, and the frac-

Table I[a]
Polymerizations Performed with Precatalyst 1, $Al(C_2H_5)_3$, and Alkoxysilane

run	modifier	H_2, L	yield, g (g of cat.)$^{-1}$ h^{-1}	I.I., %	$M_w \times 10^{-3}$	M_w/M_n
1	none	none	1000	71	540	6.9
2	none	0.2	1430	74	320	7.0
3	$Me_2Si(OMe)_2$	none	630	86	570	6.1
4	$Me_2Si(OMe)_2$	0.2	1180	88	340	6.8
5	$Me_2Si(OEt)_2$	none	670	86	580	5.8
6	$Me_2Si(OEt)_2$	0.2	1070	84	270	7.3
7	$Me_2Si(O\text{-}i\text{-}Pr)_2$	none	900	80	360	6.6
8	$Me_2Si(O\text{-}i\text{-}Pr)_2$	0.2	1210	84	240	7.4
9	$(n\text{-}Bu)_2Si(OMe)_2$	none	730	97	590	4.6
10	$(n\text{-}Bu)_2Si(OMe)_2$	0.2	950	96	290	5.8
11	$(i\text{-}Bu)_2Si(OMe)_2$	none	710	98	560	3.8
12	$(i\text{-}Bu)_2Si(OMe)_2$	0.2	1140	97	382	6.1
13	$(i\text{-}Bu)_2Si(OMe)_2$	0.05	1090	97	480	6.0
14	$(i\text{-}Bu)_2Si(OMe)_2$	0.05[b]	1000	97	450	5.6
15	$(i\text{-}Bu)_2Si(OMe)_2$	0.03	1010	97	510	5.6
16	$(i\text{-}Bu)_2Si(OMe)_2$	0.03[b]	960	97	640	6.5
17	$(i\text{-}Bu)_2Si(OMe)_2$	0.015	780	97	490	4.7
18	$(i\text{-}Bu)_2Si(OMe)_2$	0.015[b]	740	97	570	5.4
19	$(i\text{-}Pr)_2Si(OMe)_2$	none	710	99	670	3.4
20	$(i\text{-}Pr)_2Si(OMe)_2$	0.2	1270	99	510	6.4
21	$Ph_2Si(OMe)_2$	none	740	98	610	8.5
22	$Ph_2Si(OMe)_2$	0.2	1040	97	360	7.0
23	$Ph_2Si(OEt)_2$	none	810	95	490	7.6
24	$Ph_2Si(OEt)_2$	0.2	1150	93	290	7.0
25	$Ph_2Si(O\text{-}i\text{-}Pr)_2$	none	740	85	570	7.2
26	$Ph_2Si(O\text{-}i\text{-}Pr)_2$	0.2	1090	84	250	7.6
27	$PhSi(OMe)_3$	none	670	98	280	5.3
28	$PhSi(OMe)_3$	0.2	970	96	360	4.7
29	$PhSi(OEt)_3$	none	730	97	360	5.3
30	$PhSi(OEt)_3$	0.2	1080	98	280	5.8
31	$PhSi(O\text{-}i\text{-}Pr)_3$	none	870	90	480	8.7
32	$PhSi(O\text{-}i\text{-}Pr)_3$	0.2	1100	91	340	7.0

[a] Polymerization conditions are reported in the Experimental Section. [b] D_2 was used instead of H_2.

Table II[a]
Polymerizations Performed with Precatalyst 1, $Al(C_2H_5)_3$, and Piperidines

run	modifier[b]	H_2, L	yield, g (g of cat.)$^{-1}$ h^{-1}	I.I., %	$M_w \times 10^{-3}$	M_w/M_n
1	none	none	1000	71	540	6.9
2	none	0.2	1430	74	320	7.0
33	P	none	700	77		
34	P	0.2	1060	82	270	6.9
35	2,6-MP	none	800	72	480	6.9
36	2,6-MP	0.2	1170	76	430	6.4
37	2,2,6-MP	none	630	87	230	6.2
38	2,2,6-MP	0.2	910	83	480	6.9
39	2,2,6,6-MP	none	750	95	240	7.9
40	2,2,6,6-MP	0.2	1250	95	440	4.9
41	1,2-MP	none	750	73	220	6.4
42	1,2,2,6,6-MP	none	1050	78	470	7.0

[a] See footnote *a* of Table I. [b] P = piperidine, 2-MP = 2-methylpiperidine, 2,6-MP = 2,6-dimethylpiperidine, 2,2,6-MP = 2,2,6-trimethylpiperidine, 2,2,6,6-MP = 2,2,6,6-tetramethylpiperidine, 1,2-MP = 1,2-dimethylpiperidine, 1,2,2,6,6-MP = 1,2,2,6,6-pentamethylpiperidine.

tions were examined by ^{13}C NMR. No peaks attributable to incorporation of labeled carbon in the polymer chains, in particular according to either one of the two possible deactivation reactions

$$\text{Ti–P} + {}^{13}CH_3(C_6H_5)Si(OC_2H_5)_2 \rightarrow \text{Ti–}OC_2H_5 + {}^{13}CH_3(C_6H_5)(\text{P})SiOC_2H_5 \quad (1)$$

$$\text{Ti–P} + (C_6H_5)_2Si(O{}^{13}CH_3)_2 \rightarrow \text{Ti–}OSi(C_6H_5)_2O{}^{13}CH_3 + {}^{13}CH_3\text{P} \quad (2)$$

were detected in any fraction of the two polymers.[11] Obviously, this result does not support the hypothesis that the stereoregulating effect of the alkoxysilanes is due to this kind of reaction.

The results of some polymerizations performed in the presence of the same solid precatalyst 1 using hindered amines as external modifiers are reported in Table II. For these modifiers one can observe a behavior similar to that of the alkoxysilanes. In particular, note the following:

(1) The amount of polymer insoluble in boiling heptane increases with bulkiness of the secondary amine.

(2) The tertiary amines tested (1,2,2,6,6-pentamethylpiperidine and 1,2-dimethylpiperidine) are essentially ineffective.

(3) Addition of hydrogen increases the polymerization yield. A final remark is that, as previously observed by Guyot et al.,[5] the performance of the different modifiers depends on the solid precatalyst (see Table III). In fact, with solid precatalyst prepared with ethyl benzoate as the internal modifier (precatalyst 2), the esters of aromatic carboxylic acids are very effective at increasing the stereospecificity of the system, while alkoxysilanes and secondary amines are not. On the other hand, when the solid precatalyst is prepared with diisobutyl phthalate, the performance of the alkoxysilanes and secondary amines as external modifiers is excellent while that of the aromatic esters is poor, especially in regard to polymer yield.

Conclusions

Alkoxysilanes and bulky secondary amines behave very similarly in the isotactic-specific polymerization of propene with supported Ziegler–Natta catalysts. When they are used in the presence of a solid precatalyst prepared from $TiCl_4$, $MgCl_2$, and diisobutyl phthalate, they increase

Table III[a]
Comparison between Precatalysts 1 and 2

run	precatalyst	modifier	yield, g (g of cat.)$^{-1}$ h^{-1}	I.I., %
1	1	none	1000	71
21	1	$Ph_2Si(OMe)_2$	740	95
40	1	2,2,6,6-MP	820	95
43	1	ethyl benzoate[b]	57	79
44	2	none	1170	44
45	2	$PhSi(OEt)_3$	750	80
46	2	2,2,6,6-MP	710	83
47	2	ethyl benzoate[b]	500	98

[a] See footnote *a* of Table I. [b] Aluminum/modifier molar ratio = 3.

the I.I. without depressing the catalyst productivity. With this same solid precatalyst, aromatic carboxylic esters such as ethyl benzoate only marginally increase the polymer I.I. but dramatically depress the catalyst productivity. For the solid precatalyst prepared from $TiCl_4$, $MgCl_2$, and ethyl benzoate, an inversion of effectiveness occurs between these two classes of external modifiers. The esters of aromatic carboxylic acids greatly improve polymer I.I., only marginally affecting catalyst productivity. On the contrary, alkoxysilanes and bulky secondary amines, when used in the presence of this solid precatalyst, only marginally increase the I.I. of the polymer.

It seems reasonable to conclude that, on the surface of the two kinds of solid precatalysts considered here, there are chemically different active sites that are affected by the external modifiers through at least two different mechanisms, one typical of the alkoxysilanes and secondary amines, and the other typical of the esters of the aromatic carboxylic acids. The mechanism proposed by one of us[4] for aromatic esters seems to be inadequate for alkoxysilanes and secondary amines.

The molecular shape of the modifier considerably affects the performance of the catalytic system. The addition of hydrogen causes the molecular weight of the polymer to decrease and the polymer productivity to increase. Finally, the lack of any appreciable isotope effect, when deuterium instead of hydrogen is used as a chain-transfer agent, suggests that breaking of the hydrogen molecule does not occur in a step determining the rate of either the chain transfer or the activation of the catalytic centers.

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(11) In the ^{13}C NMR spectra of the fractions of samples 48 and 49 were detected resonances due to the natural-abundance end groups. If at least 1% of the polymer chains were involved in some reaction with labeled alkoxysilanes, one would observe the relative resonance with intensity comparable to that of the natural-abundance end groups.

Registry No. $TiCl_4$, 7550-45-0; $MgCl_2$, 7786-30-3; $(Et)_3Al$, 97-93-8; $Ph(EtO)_3Si$, 780-69-8; $(Ph)_2(MeO)_2Si$, 6843-66-9; $(Me)_2(MeO)_2Si$, 1112-39-6; $MePh(EtO)_2Si$, 775-56-4; $Al(i\text{-}C_4H_9)_3$, 100-99-2; $H_2C{=}CHCH_3$ (homopolymer), 9003-07-0; $Me_2Si(OEt)_2$, 78-62-6; $Me_2Si(OPr\text{-}i)_2$, 5575-49-5; $(n\text{-}Bu)_2Si(OMe)_2$, 996-06-5; $(i\text{-}Bu)_2Si(OMe)_2$, 17980-32-4; $(i\text{-}Pr)_2Si(OMe)_2$, 18230-61-0; $Ph_2Si(OEt)_2$, 2553-19-7; $Ph_2Si(OPr\text{-}i)_2$, 18056-95-6; $PhSi(OMe)_3$, 2996-92-1; $PhSi(OPr\text{-}i)_3$, 17903-00-3; P, 110-89-4; 2,6-MP, 504-03-0; 2,2,6-MP, 4733-73-7; 2,2,6,6-MP, 768-66-1; 1,2-MP, 671-36-3; 1,2,2,6,6-MP, 79-55-0; diisobutyl phthalate, 84-69-5; ethyl benzoate, 93-89-0.