loxane blocks which are incompatible with the polystyrene matrix, may well adopt a conformation in the melt which is more compact, and hence diffuses more rapidly, than the AB copolymers.

By a comparison of the values of D actually obtained for $S_{75}D_{77}$ and $S_{129}D_{144}$ at 200 °C, it appears that approximately doubling the molecular weight leads to ca. sixfold reduction in D. (The lower limit value for $S_{40}D_{36}$, of course, provides no information on the molecular weight dependence of D; it can only be said not to be inconsistent with the other values.) As Klein and Briscoe[2] have pointed out, previous studies of polymer self-diffusion have led to quite discordant conclusions on the dependence of D on M. Their careful work with polyethylene, however, supports the conclusion that $D \propto M^{-2}$, consistant with the prediction of deGennes' "reptation" model.[5] While the present limited results suggest a slightly higher order dependence in this case, it is perhaps interesting that the difference is not larger. While the styrene segment moving through the homopolymer matrix may well undergo the motion envisioned in deGennes' model, it is not at all clear what the frictional contribution of the incompatible (and hence presumably rather compactly coiled) siloxane block will be.

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Correlation between Regio- and Syndiotactic Specificity of Soluble Vanadium-Based Catalysts for Propene Polymerization

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The syndiotactic polypropylene prepared with a vanadium-based catalyst system contains irregular linkages of propylene units arranged in head-to-head and tail-to-tail sequences. In previous papers,[1,2] the chemical structures of polypropylenes obtained with the catalyst systems, VCl_4 and alkylaluminiums, were studied by ^{13}C NMR. The sequence distribution of inverted propylene units in a polymer chain was found to follow first-order Markov statistics.[1] When propylene unit inversion is a low content, a typical propagation chain was shown to consist of short sequence blocks of "0" units and longer sequence blocks of "1" units,[1,2] as represented by

$$---11111110001111---111100001111---\mathrm{Mt} \qquad (1)$$

Here, a propylene unit is designated by a "0" when propene adds into an active metal–carbon bond by primary insertion, $-CH(CH_3)CH_2Mt$, or by a "1" when propene adds by secondary insertion, $-CH_2CH(CH_3)Mt$, and Mt indicates the metal (vanadium) atom in the catalyst site bound to a growing polymer chain. In view of the above results, we concluded that the propene orientation in the insertion is essentially attributed to the steric effects of the last propylene unit of a growing chain end.

Conversely, on the basis of ^{13}C NMR analysis on ethylene–propylene copolymers, Zambelli et al.[3-5] suggested that the syndiotactic propagation of propene occurs mainly by secondary propene insertion and is controlled by the asymmetry in the last propylene unit of a growing chain end.

In the present study, the correlation between regio- and syndiotactic specificity of the soluble vanadium-based catalyst systems for propene polymerization has been examined. The catalyst systems used in this experiment are given in Table I, together with the stereoregularities in triad fractions and molecular weights of the polypropylene samples obtained at −78 °C. The molecular weight distribution curves of polypropylene samples obtained with these soluble vanadium-based catalysts were unimodal,[6,7] and the polydispersities ($\bar{M}_w/\bar{M}_n$) were lower than 2.0, indicating that the polymerization of propene with the respective catalyst proceeds on uniform (homogeneous) catalyst sites. The stereochemical triad compositions were determined from the triad peaks of primary carbon resonance ($P_{\beta\beta}$)[8] in the ^{13}C NMR spectra of polypropylene samples. Table II shows the mole fractions of different dyads and triads of connecting propylene units in each sample. The dyad and triad fractions of propylene units, 0 and 1, were determined from the secondary and tertiary carbon resonance peak areas, respectively, in the ^{13}C NMR spectra by the same method used in our previous paper.[1] In the table, F_{00}, F_{11}, F_{01}, F_{10}, F_{000}, F_{111}, F_{001}, F_{011}, F_{100}, F_{110}, F_{101}, and F_{010} represent the mole fractions of 00, 11, 01, 10, 000, 111, 001, 011, 100, 110, 101, and 010 propylene unit sequences in a sample, respectively. Table II indicates that the regioselectivity of propene inserting into an active metal–carbon bond is mainly affected by the kind of alkylaluminium component and decreases as

$$\mathrm{AlEtCl_2} \simeq \mathrm{Al_2Et_3Cl_3} \simeq \mathrm{AlEt_2Cl} > \mathrm{AlEt_2Br} \geq \mathrm{AlEt_3} \qquad (2)$$

The relation between the syndiotactic triad fraction, $[rr]$, and the heterotactic dyad fraction of connecting propylene units, $[F_{01} + F_{10}]$, is shown in Figure 1. The syndiotactic triad fraction, $[rr]$, decreases with an increase in the amount of $[F_{01} + F_{10}]$. A good correlation between the regioselectivity of an inserting propene and the syndiotactic propylene unit composition seems to support the hypotheses that both the regio- and the syndiotactic spe-

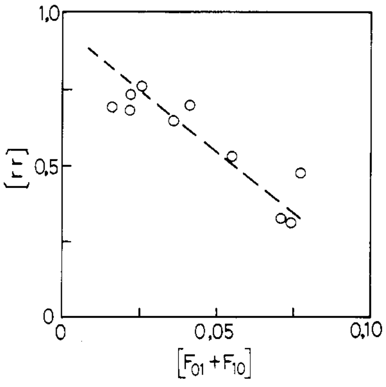

Figure 1. Relation between the syndiotactic triad fraction, $[rr]$, and the heterotactic dyad fraction of connecting propylene units, $[R_{01} + F_{10}]$, in polypropylenes obtained at −78 °C with various soluble vanadium-based catalyst systems.

Table I
Stereoregularities and Molecular Weights of Polypropylene Samples Obtained with Various Soluble Vanadium-Based Catalyst Systems at −78 °C

				stereoregularity[b]			mol wt[c]	
sample	catalyst system[a]	time, h	yield, g	[*rr*]	[*mr*]	[*mm*]	$10^{-4}\,\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1	$V(acac)_3/AlEtCl_2$	4.0	0.5	0.68	0.28	0.04	1.50	1.7
2	$V(acac)_3/Al_2Et_3Cl_3$	4.0	1.0	0.69	0.28	0.03	10.1	2.0
3	$V(acac)_3/AlEt_2Cl$	3.0	0.4	0.65	0.32	0.03	1.50	1.1
4	$V(acac)_3/AlEt_2Br$	8.5	0.3	0.48	0.38	0.14	0.81	1.2
5	$VCl_4/Al_2Et_3Cl_3$	2.5	1.5	0.70	0.26	0.04	1.50	1.7
6[d]	$VCl_4/AlEt_2Cl$	2.0	0.5	0.73	0.27	0.00	3.06	1.5
7[d]	$VCl_4/AlEt_2Cl$	7.0	2.1	0.76	0.24	0.00	4.07	1.7
8[d]	$VCl_4/AlEt_2Br$	15.0	0.2	0.53	0.25	0.22	0.27	2.0
9[d]	$VCl_4/AlEt_3$	0.5	0.3	0.31	0.38	0.31	20.4	1.7
10	$VCl_4/AlEt_3$	2.5	1.3	0.33	0.39	0.28	75.5	2.0

[a] Polymerizations were carried out at −78 °C in 100 mL of toluene (samples 1-4) or heptane (samples 5-10) solution containing 0.83 mol of propene. The amounts of catalyst components used were: $V(acac)_3$ (acac = acetyl acetonate) = 0.5 mmol and alkylaluminiums = 5.0 mmol for samples 1, 3, and 4, $V(acac)_3$ = 0.04 mmol and $Al_2Et_3Cl_3$ = 5.0 mmol for sample 2, VCl_4 = 1.0 mmol and alkylaluminiums = 5.0 mmol for samples 5-8, and VCl_4 = 0.1 mmol and $AlEt_3$ = 1.5 mmol for samples 9 and 10. [b] The values are expressed in mole fractions. [c] The number-average and weight-average molecular weight ($\overline{M}_n$, $\overline{M}_w$) of polymers were determined by GPC (Waters Associates, Model 200) with the use of five polystylene gel columns (10^7, 10^6, 10^5, 10^4, and 10^3 pore size) and with *o*-dichlorobenzene as solvent at 135 °C. [d] These samples are the same as those reported in a previous paper.[1]

Table II
Dyad and Triad Sequence Distributions of Propylene Units, 0 and 1, in Polypropylene Samples Measured by ^{13}C NMR

	dyad fractions[a]		triad fractions[b]			
sample	$F_{00}+F_{11}$	$F_{01}+F_{10}$	$F_{000}+F_{111}$	$F_{001}+F_{011}$	$F_{100}+F_{110}$	$F_{101}+F_{010}$
1	0.978	0.022	0.958	0.020	0.022	~0[c]
2	0.984	0.016	0.974	0.015	0.011	~0[c]
3	0.964	0.036	0.938	0.027	0.035	~0[c]
4	0.923	0.077	0.864	0.069	0.061	0.006
5	0.959	0.041	0.930	0.040	0.030	~0[c]
6	0.978	0.022	0.961	0.021	0.018	~0[c]
7	0.974	0.026	0.955	0.019	0.026	~0[c]
8	0.945	0.055	0.902	0.049	0.049	~0[c]
9	0.926	0.074	0.864	0.059	0.065	0.012
10	0.929	0.071	0.859	0.069	0.063	0.009

[a] Determined from secondary carbon resonance areas.
[b] Determined from tertiary carbon resonance areas.
[c] These values are less than 0.003 of experimental deviation.

cificity of soluble vanadium-based catalyst systems are controlled by the steric effects of the last propylene unit of a growing chain end. The influence of the alkylaluminium component on the regioselectivity of an inserting propene may be interpreted in terms of the difference in the distance of an active metal-carbon bond which is regulated by the alkylaluminiums involved in the active vanadium site.

Experimental Section

The polymerizations of propene were carried out at −78 °C, using the catalyst systems given in Table I. The polymerization procedure and purification of the polymers were the same as those reported previously.[6,9] ^{13}C NMR spectra of polypropylene samples were recorded at 140 °C in *o*-dichlorobenzene (15–30 w/v %), using a JEOL JNM PS-100 spectrometer equipped with PFT-100 Fourier transform system at 25.149 MHz. Instrument conditions were: $\pi/4$ pulse of 13 μs, 4–6 s repetition rate, and 4000 Hz sweep width. The number of transients accumlated were 1500–5000. ^{13}C NMR analyses were carried out following the assignments of a previous paper.[1]

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