“Living” Coordination Polymerization of Propene Initiated by the Soluble $V(acac)_3$–$Al(C_2H_5)_2Cl$ System

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ABSTRACT: The soluble $V(acac)_3$–$Al(C_2H_5)_2Cl$ system has been found to polymerize propene to give a syndiotactic “living” polymer having narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.05–1.20). A kinetic study proved that the polymerization of propene proceeds without any detectable chain termination and transfer reactions at temperatures below −65 °C. The stereoregulation energy for the syndiotactic specific chain propagation was evaluated by ^{13}C NMR analysis of the polymers produced.

An ideal living polymerization may take place only if three unusual restrictions can be achieved in a polymerization system.[1,2] The three criteria are: (1) formation of propagation centers is effectively instantaneous, or its rate constant is not slower than that of the polymerization reaction; (2) chain transfer limiting molecular weight does not occur; (3) irreversible termination with deactivation of propagation center does not take place. These limiting conditions have been achieved in the anionic polymerization of most vinyl monomers initiated by the organic derivatives of alkali metals.[3-7] The living anionic polymerization is of great utility in the preparation of monodisperse polymers and block and graft copolymers, since the chain ends remain active for long periods of time. Ziegler-type catalysts have been used to make block copolymers of α-olefins[8,9] even though there is no known example of such a catalyst meeting all the requirements for a true living polymerization. Previously, Waters et al.[10] claimed that the polymerization of ethylene initiated by the $(\pi\text{-}C_5H_5)_2Ti(C_2H_5)Cl$–$Al(C_2H_5)Cl_2$ system displayed the characteristics of living polymerization, but its polymerization activity gradually decreases during the course of polymerization, indicating the existence of an irreversible termination reaction with destruction of propagation centers.

We now find that the low-temperature polymerization of propene initiated by a combination of $V(acac)_3$ (acac = acetyl acetonate) and $Al(C_2H_5)_2Cl$ satisfies all criteria for a living polymerization and gives polymers having narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.05–1.20). The $V(acac)_3$–$Al(C_2H_5)_2Cl$ system was found originally by Natta et al.[11] to give a syndiotactic form of polypropylene. In the present study, we will discuss the nature of the living polymerization of propene initiated by the $V(acac)_3$–$Al(C_2H_5)_2Cl$ system, examining the kinetics of polymerization and the molecular weight and the stereochemical structure of polymers.

Experimental Section

Materials. $V(acac)_3$ (Alfa Division Ventron Co.) and alkylaluminums (Japan Aluminum Alkyl Co.) were used without further purification. Propene (purity 99.8%; the impurity was propane) supplied from Mistubishi Petrochemical Co. was used after passing it through columns of sodium hydroxide and phosphorus pentoxide. Nitrogen (extra pure grade) was used after passing it through a copper column reduced at 350 °C. A reagent grade of toluene was dried by refluxing it over sodium metal under a nitrogen atmosphere prior to use.

Polymerization Procedure. A three-necked glass flask equipped with a magnetic stirrer was used as a reactor. Propene was condensed into toluene in a reactor kept at the polymerization temperature (−78, −65, or −48 °C). The amount of toluene used was adjusted to be 100 mL as the total volume of the solution. Then, given amounts of alkylaluminum and $V(acac)_3$, in that order, were charged under a nitrogen stream. The beginning of the polymerization was taken as the time of addition of the $V(acac)_3$ component. The polymerization was quenched at a given time introducing 100 mL of an ethyl alcohol solution of hydrochloric acid thermostated at −78 °C. The polymers produced were washed several times with 200–300 mL of ethyl alcohol and dried in vacuo at room temperature.

Gel-Permeation Chromatogram. Gel-permeation chromatograms were recorded by using a Waters Model-200 GPC equipped with five polystyrene gel columns (10^7, 10^6, 10^5, 10^4, and 10^3 Å pore sizes) at 135 °C. The solvent was *o*-dichlorobenzene, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained on the basis of the universal calibration[12,13] with ten standard polystyrene samples (Pressure Chemical Co.) of narrow distribution of molecular weights 2100 to 2 610 000. From GPC results, the number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were obtained by standard procedures. The correction of GPC peak spreading (zone spreading) for the polydispersity parameters ($\bar{M}_w/\bar{M}_n$) was made on the basis of the method of Hamielec and Ray[14,15] using

$$\left(\frac{\bar{M}_w}{\bar{M}_n}\right)_T = \left(\frac{\bar{M}_w}{\bar{M}_n}\right)_E \exp\left(-\frac{D_2^2}{2h^2}\right) \quad (1)$$

where $(\bar{M}_w/\bar{M}_n)_T$ and $(\bar{M}_w/\bar{M}_n)_E$ are corrected and uncorrected (experimental) polydispersity parameters, D_2 is the slope of the molecular weight calibration curve, and h is the resolution factor.

^{13}C NMR Spectra. ^{13}C NMR spectra of polypropylene samples were recorded at 140 °C in *o*-dichlorobenzene (weight/volume ratio = 20–30%), using a JEOL JNM PS-100 spectrometer equipped with the PFT-100 Fourier transform system operating at 25.149 MHz. Instrument conditions were: $\pi/4$ pulse of 13 μs, 6.0-s repetition rate, and 4000 Hz sweep width. The number of transients accumulated was 5000.

Results and Discussion

Polymer Yield and Molecular Weight. The yields and the molecular weights of polymers produced in the course of polymerization between −78 and −48 °C with $V(acac)_3$–$Al(C_2H_5)_2Cl$ systems are given in Table I. All of the polymerizations were carried out in the range of a low conversion of propene monomer up to several percent. The concentration of monomer, therefore, may be regarded as a constant during the course of polymerization. The yield against time curves are almost linear through the origin at −78, −65, and −48 °C (Figure 1A), which indicates that the formation of the propagation centers is complete just after starting polymerization, and the subsequent polymerization proceeds without deactivation of the centers, i.e., without any termination reactions. The time dependence of the number-average molecular weight, $\bar{M}_n$, of polymers produced is shown in Figure 1B. Figure 1C shows the relationship between the polymerization time and the number of polymer molecules produced per vanadium atom, [N], which is calculated from the relation that [N] = polymer yield/$\bar{M}_n$. The $\bar{M}_n$ of polymers produced at −78 and −65 °C are proportional to the po-

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Table I
Yields and Molecular Weights of Polymers Obtained with the V(acac)$_3$-Al(C$_2$H$_5$)Cl System at Different Temperatures[a]

	polymerization			molecular weight			
run no.	temp, °C	time, h	yield, g	$10^{-4}\bar{M}_n$[b]	$(\bar{M}_w/\bar{M}_n)_E$[b]	$(\bar{M}_w/\bar{M}_n)_T$[c]	[N],[d] mol/mol of V
1	−78	1.0	0.11	0.604	1.16	1.11	0.036
2	−78	1.5	0.14	0.919	1.14	1.09	0.030
3	−78	2.0	0.25	1.25	1.23	1.17	0.040
4	−78	2.0	0.27	1.20	1.18	1.13	0.045
5	−78	3.0	0.38	1.50	1.15	1.10	0.051
6	−78	3.0	0.35	1.60	1.20	1.14	0.044
7	−78	4.0	0.51	2.50	1.23	1.17	0.041
8	−78	5.0	0.75	3.52	1.17	1.12	0.043
9	−78	5.0	0.70	3.18	1.21	1.15	0.044
10	−78	6.0	0.75	3.75	1.17	1.12	0.040
11	−78	8.0	1.07	4.42	1.20	1.14	0.048
12	−78	10.0	1.18	5.16	1.22	1.16	0.046
13	−78	15.0	1.76	9.13	1.24	1.18	0.039
14	−65	1.5	0.23	1.46	1.12	1.07	0.032
15	−65	2.0	0.56	3.08	1.14	1.09	0.036
16	−65	3.0	0.62	4.13	1.20	1.14	0.030
17	−65	4.0	1.02	5.43	1.18	1.13	0.038
18	−65	5.0	1.17	6.04	1.23	1.17	0.039
19	−48	0.33	0.15	1.40	1.45	1.37	0.021
20	−48	0.67	0.43	2.81	1.52	1.45	0.031
21	−48	1.33	0.82	3.22	1.47	1.40	0.051
22	−48	2.0	1.82	4.47	1.45	1.37	0.081
23	−48	2.0	1.87	4.50	1.45	1.37	0.083

[a] Polymerization conditions: [propene] = 8.3 mol·dm^{-3}, [V(acac)$_3$] = 0.005 mol·dm^{-3}, [Al(C$_2$H$_5$)$_2$Cl] = 0.05 mol·dm^{-3}; and [toluene solution] = 0.1 dm^3. [b] Calculated from GPC curves. [c] Corrected for GPC peak spreading. [d] Number of polymer molecules per vanadium atom.

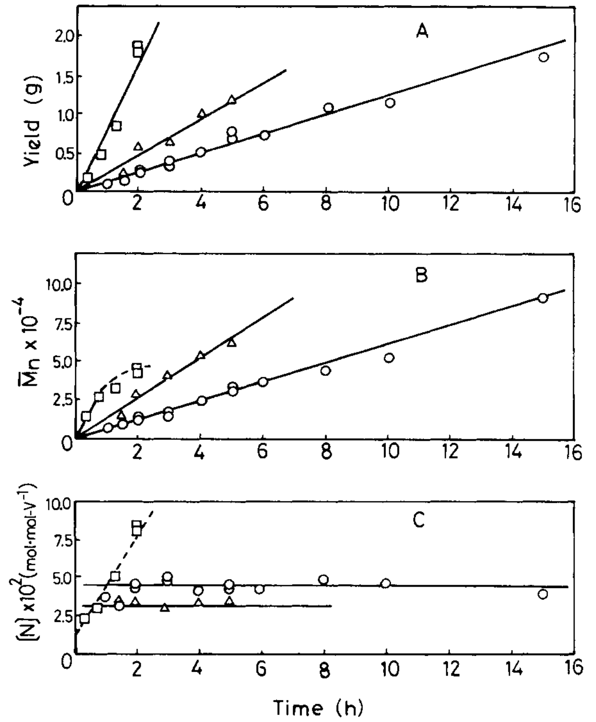

Figure 1. Time dependences of yields and number-average molecular weights, $\bar{M}_n$, of the resulting polymers and of the number of polymer molecules produced per vanadium atom, [N], in the polymerization of propene with the V(acac)$_3$-Al(C$_2$H$_5$)$_2$Cl system at −78, −65 and −48 °C: (○) at −78 °C; (△) at −65 °C; (□) at −48 °C. Polymerization conditions are given in Table I.

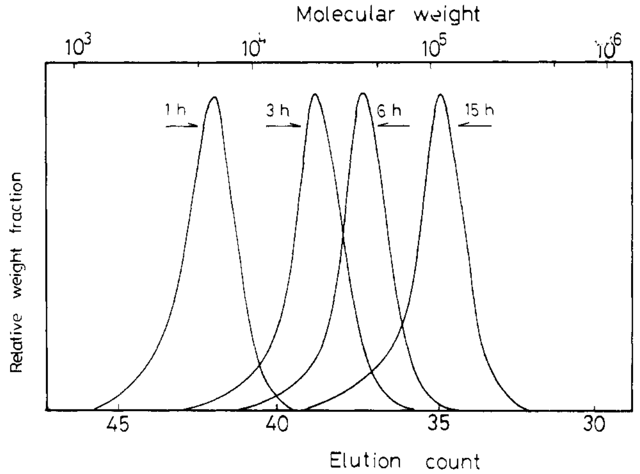

Figure 2. GPC elution (molecular weight distribution) curves of polymers obtained after different polymerization times at −78 °C in the presence of the V(acac)$_3$-Al(C$_2$H$_5$)$_2$Cl system.

lymerization time. As a result, the number of polymer molecules produced per vanadium atom remains almost constant during the course of polymerization, indicating that the polymerization precede any detectable chain transfer reactions. On the contrary, in the polymerization at −48 °C the number of polymer molecules, [N], increased with the polymerization time, i.e., with an increase of the polymer yield, which may indicate the existence of chain-transfer reactions. From these results, it may be concluded that a living polymerization of propene is achieved with the soluble V(acac)$_3$-Al(C$_2$H$_5$)$_2$Cl system at temperatures below −65 °C.

Figure 2 shows the GPC elution (molecular weight distribution) curves of polymers obtained in different polymerization times at −78 °C. The unimodal peak of the curves shifted toward low elution counts (high molecular weights) with an increase in polymerization time. The polydispersity parameters, $(\bar{M}_w/\bar{M}_n)_E$, calculated from these curves are listed in Table I, together with the values, $(\bar{M}_w/\bar{M}_n)_T$, corrected for GPC peak spreading. The corrected polydispersity parameters $(\bar{M}_w/\bar{M}_n)_T$ are 1.13 ± 0.05 in the polymerizations at −78 and −65 °C. This value is close to the theoretical value ($\bar{M}_w/\bar{M}_n = 1.0$) for an ideal living polymerization. On the other hand, the corrected polydispersity parameters $(\bar{M}_w/\bar{M}_n)_T$ of polymers produced at −48 °C are as much as 1.41 ± 0.04, as anticipated in the polymerization with chain-transfer reactions.

Table II
Values of k_p and K_m and Their Activation Energies

temp, °C	k_p, h	E_{k_p}, kJ·mol^{-1}	K_m, dm^3·mol^{-1}	E_{K_m}, kJ·mol^{-1}
−78	(1.9 ± 0.7) × 10^2	21 ± 9	0.37 ± 0.01	−1.4 ± 0.1
−65	(4.2 ± 1.9) × 10^2		0.35 ± 0.02	

Figure 3A shows the relation between the polymer yield and the concentration of propene monomer obtained in the polymerizations at −78 and −65 °C. The polymer yield was not simple first order in the monomer concentration, but it approached a constant value with increasing monomer concentration. The analogous dependence of polymer yield on the monomer concentration has been found in the polymerization of propene at −78 °C with a soluble VCl_4–$Al(C_2H_5)_2Cl$ system.[16,17] As Figure 3B shows, the number-average molecular weight, $\bar{M}_n$, of polymers increased to a constant value with an increase in the monomer concentration. Figure 3C shows the relationship between the number of polymer molecules produced per vanadium atom, [N], and the monomer concentration. The number of polymer molecules did not vary with the monomer concentration, confirming that the chain-transfer reaction with propene monomer does not exist in the present polymerization system. The yield, Y, and the

$$Y = \bar{M}_n[N] = k_p\left(\frac{K_m[M]}{1 + K_m[M]}\right)[N]t \qquad (2)$$

molecular weight, $\bar{M}_n$, of polymers produced at a given polymerization time, t, were found to be correlated with the following function of the concentration of propene monomer, [M], at temperatures below −65 °C, where [N] denotes the number of polymer molecules, and the constants K_m and k_p may represent the equilibrium constant for a propene monomer coordination to the active vanadium and the rate constant for a subsequent insertion of the coordinated monomer in a living polymer chain attached to the metal, respectively, as suggested in the polymerization of propene with the other soluble vanadium-based catalyst systems.[16,17] The values of the constants k_p and K_m, determined at −78 and −65 °C, are given in Table II, together with their activation energies.

Table III shows the results of the polymerization obtained at −78 °C with different concentrations of $Al(C_2H_5)_2Cl$, under otherwise constant conditions. As may be seen from Figure 4A, the yield of polymers produced in 3 h increased to a constant value with an increase in the concentration of $Al(C_2H_5)_2Cl$, i.e., with an increase in the Al/V ratio. In contrast, the number-average molecular weight, $\bar{M}_n$, was little dependent on the concentration of $Al(C_2H_5)_2Cl$, although a tendancy toward some increase in the $\bar{M}_n$ with the concentration may be noted (Figure 4B). The polydispersity parameters ($\bar{M}_w/\bar{M}_n$) did not increase with the concentration of $Al(C_2H_5)_2Cl$, but rather they decreased toward unity in a monodisperse polymer (Table III). These results indicate that the chain-transfer reaction with $Al(C_2H_5)_2Cl$, which has often been found in the coordination polymerization of α-olefins with the other Ziegler-type catalysts,[18] is not present in the low-temperature polymerization of propene with the $V(acac)_3$–$Al(C_2H_5)_2Cl$ system. Figure 4C shows the relation between

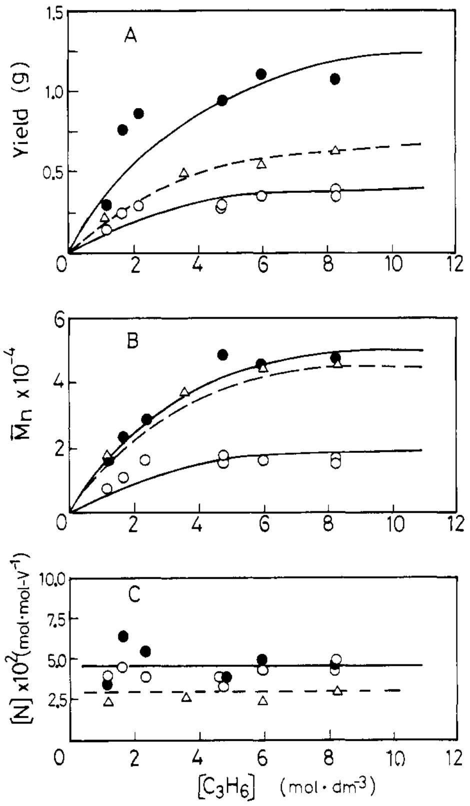

Figure 3. Effects of concentration of propene monomer on polymer yield, on number-average molecular weight, $\bar{M}_n$, and on the number of polymer molecules produced per vanadium atom, [N], at −78 and −65 °C: (○) polymers produced after 3 h at −78 °C; (●) polymers produced after 8 h at −78 °C; (△) polymers produced after 3 h at −65 °C. Polymerization conditions: $[V(acac)_3]$ = 0.005 mol·dm^{-3}, $[Al(C_2H_5)_2Cl]$ = 0.05 mol·dm^{-3}, and [toluene solution] = 0.1 dm^3.

Table III
Polymerization Data Obtained at −78 °C with Different Concentrations of $Al(C_2H_5)_2Cl$[a]

run no.	$[Al(C_2H_5)_2Cl]$, mol·dm^{-3}	yield, g	molecular weight			$[N]$,[d] mol/mol of V
			$10^{-4}\bar{M}_n$[b]	$(\bar{M}_w/\bar{M}_n)_E$[b]	$(\bar{M}_w/\bar{M}_n)_T$[c]	
38	0.02	0.05	1.87	1.19	1.13	0.005
39	0.03	0.14	1.78	1.16	1.16	0.016
5	0.05	0.38	1.50	1.15	1.10	0.051
6	0.05	0.35	1.60	1.20	1.14	0.044
40	0.07	0.44	2.32	1.11	1.06	0.038
41	0.08	0.51	2.18	1.13	1.08	0.047
42	0.10	0.55	1.70	1.12	1.07	0.065
43	0.15	0.75	2.46	1.13	1.08	0.061
44	0.20	0.63	2.41	1.11	1.06	0.052
45	0.25	0.94	2.45	1.10	1.05	0.077
46	0.25	0.93	2.40	1.11	1.06	0.078

[a] Polymerization conditions: −78° C, polymerization period = 3 h, [propene] = 8.3 mol·dm^{-3}, $[V(acac)_3]$ = 0.005 mol·dm^{-3}, and [toluene solution] = 0.1 dm^3. [b] Calculated from GPC curves. [c] Corrected for GPC peak spreading. [d] Number of polymer molecules per vanadium atom.

Table IV
Polymerization Data Obtained at −78° C with Different Concentrations of $V(acac)_3$

run no.	$[V(acac)_3]$, mol·dm^{-3}	yield, g	molecular weight: $10^{-4}\bar{M}_n$[b]	molecular weight: $(\bar{M}_w/\bar{M}_n)_E$[b]	molecular weight: $(\bar{M}_w/\bar{M}_n)_T$[c]	$[N]$,[d] mol/mol of V
47	0.0025	0.16	1.75	1.14	1.09	0.037
5	0.005	0.38	1.50	1.15	1.10	0.051
6	0.005	0.35	1.60	1.20	1.14	0.044
48	0.007	0.43	2.05	1.16	1.11	0.030
49	0.008	0.69	1.52	1.17	1.12	0.057
50	0.010	0.63	1.43	1.17	1.12	0.044

[a] Polymerization conditions: −78 °C, polymerization period = 3 h, [propene] = 8.3 mol·dm^{-3}, $[Al(C_2H_5)_2Cl]$ = 0.05 mol·dm^{-3}, and [toluene solution] = 0.1 dm^3. [b] Calculated from GPC curves. [c] Corrected for GPC peak spreading. [d] Number of polymer molecules per vanadium atom.

Table V
Stereoregularities of Polypropylenes Obtained at Different Temperatures with the $V(acac)_3$-$Al(C_2H_5)_2Cl$ System

run no.	polymerization: temp, °C	polymerization: time, h	stereoregularity, triad fractions[a]: $[rr]$	$[rm]$	$[mm]$	dyad[b] $[r]$	$4[mm][rr]/[mr]^2$
5	−78	3.0	0.652	0.324	0.024	0.814	0.60
16	−65	3.0	0.638	0.328	0.034	0.802	0.81
22	−48	2.0	0.635	0.330	0.035	0.800	0.82

[a] Determined from the methyl region of ^{13}C NMR spectra. [b] Calculated from triad fractions.

the number of polymer molecules produced per vanadium atom, [N], and the concentration of $Al(C_2H_5)_2Cl$, [A]. The number of polymer molecules increased with increasing concentration of $Al(C_2H_5)_2Cl$ and reached a constant value, as expressed by

$$[N] = \alpha\left(\frac{K[A]}{1 + K[A]}\right) \tag{3}$$

The values of the constants, α and K, at −78 °C were 0.080 mol/mol of V and 26 dm^3/mol of Al, respectively.

The results of polymerization obtained at −78 °C with different concentrations of $V(acac)_3$ are given in Table IV. The polymer yield was proportional to the concentration of $V(acac)_3$. Conversely, the $\bar{M}_n$ of polymers produced was little dependent on the concentration of $V(acac)_3$. As a result, the number of polymer molecules produced per vanadium atom did not vary with the vanadium concentration, confirming that a bimolecular reaction between propagation centers resulting in chain termination does not take place in the present polymerization system.

Molecular Weight Distribution. In the polymerization of propene initiated by the $V(acac)_3$-$Al(C_2H_5)_2Cl$ system at temperatures below −65 °C, the polymer chain ends were found to remain active for long periods of time. Flory[1] has shown that the molecular weight distribution in such a polymerization process is given by a narrow Poisson distribution, i.e., essentially a monodisperse distribution. However, the polydispersity parameters ($\bar{M}_w/\bar{M}_n$) of polymers produced were of the order of 1.1. In order to account for the deviation from the corresponding Poisson distribution, the following reasons may be considered: (a) the influence of initiation rate on the molecular weight distribution and (b) the presence of impurities which could terminate the chains. Gold[2] calculated the effect of the propagation/initiation rate ratio on the molecular weight distribution and showed that in any case the polydispersity parameters ($\bar{M}_w/\bar{M}_n$) approach unity as the molecular weight increases. In the case of the $V(acac)_3$-$Al(C_2H_5)_2Cl$ system, the polydispersity parameters of polymers did not decrease but rather increased with an increase in molecular weight. Therefore, we can exclude the effect of the initiation rate, as anticipated from the result that the initiation rate was rapid. It is most probable that small amounts of slow-reacting impurities in the polymerization system terminate the living polymer chain and cause broading of the molecular weight distribution. The impurities may be present in the propene monomer or arise from the reaction of $V(acac)_3$ with $Al(C_2H_5)_2Cl$. In any case, it was difficult to find the effect of a small-chain termination rate on the kinetic behavior of the polymerization.

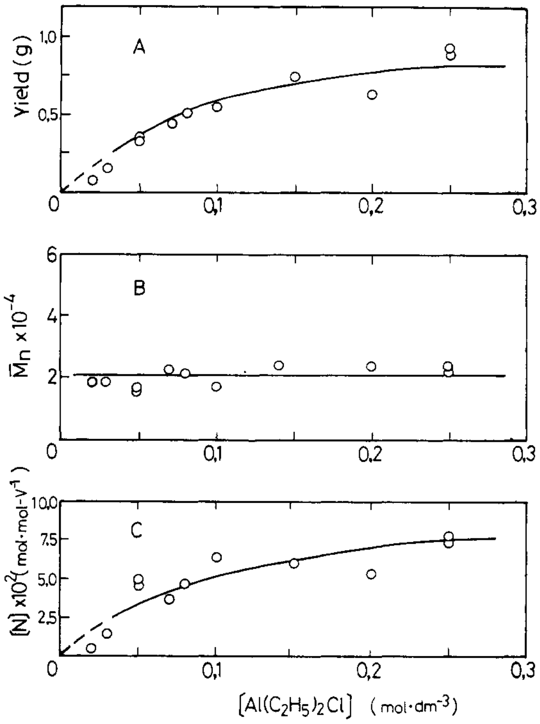

Figure 4. Dependences of concentration of $Al(C_2H_5)_2Cl$ on polymer yield, on number-average molecular weight, $\bar{M}_n$, and on the number of polymer molecules produced per vanadium atom, [N], at −78 °C. Polymerization conditions: polymerization period = 3 h, [propene] = 8.3 mol·dm^{-3}, $[V(acac)_3]$ = 0.005 mol·dm^{-3}, and [toluene solution] = 0.1 dm^3.

Stereoregularity of Polypropylene. The stereochemical configuration of polypropylenes obtained at −78,

Table VI
Polymerization of Propene Initiated with V(acac)$_3$ and Different Types of Alkylaluminum at -78 °C[a]

run no.	alkylaluminum	time, h	yield, g	molecular weight			[N],[d] mol/mol of V
				$10^{-4}\bar{M}_n$[b]	$(\bar{M}_w/\bar{M}_n)_E$[b]	$(\bar{M}_w/\bar{M}_n)_T$[c]	
51	$Al(C_2H_5)_2Br$	3.0	0.08	0.486	1.18	1.13	0.033
52	$Al(C_2H_5)_2Br$	5.0	0.14	0.548	1.20	1.14	0.051
53	$Al(C_2H_5)_2Br$	8.5	0.26	0.813	1.21	1.15	0.064
54	$Al_2(C_2H_5)_3Cl_3$	0.33	0.08	6.17	1.52	1.45	0.032
55	$Al_2(C_2H_5)_3Cl_3$	0.5	0.13	5.69	1.56	1.49	0.057
56	$Al_2(C_2H_5)_3Cl_3$	0.67	0.29	6.05	1.70	1.62	0.120
57	$Al_2(C_2H_5)_3Cl_3$	1.0	0.44	8.80	1.74	1.66	0.125
58	$Al_2(C_2H_5)_3Cl_3$	2.0	0.64	8.96	1.83	1.75	0.179
59	$Al_2(C_2H_5)_3Cl_3$	3.0	0.66	9.94	1.81	1.73	0.166
60	$Al_2(C_2H_5)_3Cl_3$	4.0	1.01	10.1	1.98	1.89	0.250
61	$Al_2(C_2H_5)_3Cl_3$	6.0	1.48	9.53	1.91	1.81	0.388
62	$Al(C_2H_5)Cl_2$	2.0	0.22	1.03	1.83	1.74	0.043
63	$Al(C_2H_5)Cl_2$	4.0	0.50	1.50	1.72	1.65	0.067
64	$Al(C_2H_5)Cl_2$	6.0	0.72	1.79	2.07	1.97	0.080
65	$Al(C_2H_5)Cl_2$	8.0	0.97	1.91	2.05	1.95	0.102
66	$Al(C_2H_5)_3$	3.0	0.00				
67	$Al(C_2H_5)_3$	7.0	0.00				
68	$Al(C_2H_5)_2H$	3.0	0.00				

[a] Polymerization conditions: -78 °C [propene] = 8.3 mol·dm^{-3}, [toluene solution] = 0.1 dm^3. V(acac)$_3$ (0.005 mol·dm^{-3}) and alkylaluminum (0.05 mol·dm^{-3}) were used in the experiments except for the system V(acac)$_3$ (4×10^{-4} mol·dm^{-3})–$Al_2(C_2H_5)_3Cl_3$ (0.05 mol·dm^{-3}). [b] Calculated from GPC curves. [c] Corrected for GPC peak spreading. [d] Number of polymer molecules per vanadium atom.

–65, and –48 °C with the soluble V(acac)$_3$–$Al(C_2H_5)_2Cl$ system was studied by using ^{13}C NMR spectroscopy. The mole fractions of steric triads, [*rr*], [*mr*], and [*mm*], are determined from the methyl carbon resonance in the ^{13}C NMR spectra[19,20] and are listed in Table V. Here, *m* and *r* are isotactic (meso) and syndiotactic (racemic) dyads, respectively. The V(acac)$_3$–$Al(C_2H_5)_2Cl$ system gives a predominantly syndiotactic form of polypropylene, as reported by Natta et al.[11] The ratio of steric triads, $4[mm][rr]/[mr]^2$, as a criterion for the symmetric Bernoullian statistics[21] is given in Table V. Although the steric triads do not strictly obey such statistics ($4[mm][rr]/[mr]^2 = 1.0$), the syndiotactic specific chain propagation appears to be controlled by the asymmetry of the last propylene unit in a living polymer chain. The difference in the activation energies for the formation of syndiotactic and isotactic dyads (i.e., the driving force for the syndiotactic control) was estimated by the following relation:

$$\ln \frac{[r]}{[m]} = \ln \frac{a_r}{a_m} + \frac{E_m - E_r}{RT} \qquad (4)$$

where E_r and E_m are the activation energies for the formation of syndiotactic and isotactic dyads, and a_r and a_m are the frequency factors. We now find that $E_m - E_r = 1.1$ kJ·mol^{-1}.

Influence of the Type of Alkylaluminum. The results of the polymerization of propene initiated by a combination of V(acac)$_3$ and a different type of alkylaluminum at –78 °C are shown in Table VI. In the case of the V(acac)$_3$–$Al(C_2H_5)_2Br$ system, both the yield and the number-average molecular weight of polymers were almost proportional to the polymerization time. This is the case of living polymerization without any detectable chain transfer and termination reactions. In fact, the molecular weight distributions of polymers were as narrow as those with the V(acac)$_3$–$Al(C_2H_5)_2Cl$ system. On the contrary, when V(acac)$_3$ is combined with $Al_2(C_2H_5)_3Cl_3$ or $Al(C_2H_5)Cl_2$, the number of polymer molecules produced per vanadium atom, [N], increased with the polymerization time, i.e., with an increase in polymer yield, which indicates the existence of chain-transfer reactions. The polydispersity parameters ($\bar{M}_w/\bar{M}_n$) of polymers increased with the polymerization time and reached the theoretical stationary-state value (2.0)[22,23] in the case of polymerization involving chain-transfer reactions. In the polymerization of propene initiated by the V(acac)$_3$–$Al_2(C_2H_5)_3Cl_3$ system, a relatively large rate of chain-transfer reaction with propene monomer has been found at –78 °C.[24] However, when V(acac)$_3$ was combined with the alkylaluminum ($Al(C_2H_5)_3$ or $Al(C_2H_5)_2H$) not containing halogen ligands, the polymerization did not take place.

The effect of different alkylaluminum halides on the polymerization was complex. The rate of chain propagation decreased in the following series of aluminum components:

$$Al_2(C_2H_5)_3Cl_3 > Al(C_2H_5)_2Cl > Al(C_2H_5)Cl_2 > Al(C_2H_5)_2Br \qquad (5)$$

In contrast, the rate of chain transfer decreased in the following way:

$$Al_2(C_2H_5)_3Cl_3 > Al(C_2H_5)Cl_2 > Al(C_2H_5)_2Cl \simeq Al(C_2H_5)_2Br \simeq 0 \qquad (6)$$

Both the chain propagation and the chain transfer were highest with $Al_2(C_2H_5)_3Cl_3$. Several binuclear complexes composed of transition metal alkyl and aluminum components have been proposed as models of the active centers in the Ziegler-type catalysts.[16,25] If these binuclear models are valid, the aluminum components must influence the electronic structure of the active carbon–vanadium bond by inductive effects. The electron-withdrawing capability of the aluminum component increases with an increase in the number of halogen ligands on aluminum. The complicated effect of different aluminum components on the kinetic behavior of polymerization may be accounted for as a result of the following cooperative or competitive effects: (a) an increase in positive charge at vanadium by inductive effects probably stabilizes an active carbon–vanadium bond[25] and results in an enhancement of the interaction with propene if σ donation from propene to vanadium is the main factor in determining a vanadium–propene interaction,[26] but excessive stability of a carbon–vanadium bond is unfavorable for an insertion of the coordinated propene into the bond; (b) the rate of β-hydrogen transfer from a living polymer chain resulting in chain transfer may increase with an increase in positive charge at vanadium, as found by Olivê et al.[27]

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Anionic Polymerization of Isoprene in Diethyl Ether

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ABSTRACT: An investigation has been made of the active centers in the anionic polymerization of isoprene in diethyl ether using model compounds. A preference for the cis configuration has been established, although some trans structure can be detected with lithium as the counterion. In this case, association can be detected at concentrations greater than 10^{-3} M. Polymerization rate measurements were made with lithium and potassium counterions. As is usual in polar solvents, the potassium-based system shows faster rates and a lower activation energy. Microstructures of the polymers formed were determined. Some factors determining polymer microstructure are discussed.

The structure of the anion pairs involved in the anionic polymerization of isoprene has been characterized in hydrocarbon solvents and in tetrahydrofuran (THF), principally using the model compound $(CH_3)_3CCH_2CHC(CH_3)CH_2$·metal. Both cis and trans forms exist,[1,2] the stable form for all alkali metals being cis in THF,[3] whereas with lithium in hydrocarbons the trans form predominates.[4,5] This phenomenon is important in the polymerization process since the reactivities of the two forms can differ, and in addition the preferential formation of one of them in the reaction with monomers can affect kinetic behavior[6] or polymer microstructure.[7] Some years ago, Sinn and co-workers[8] investigated the butyllithium-initiated polymerization of isoprene in diethyl ether, but no characterization of the active centers was made. This paper reports such a study in diethyl ether together with measurements of propagation rates for both lithium and potassium counterions.

Experimental Section

The model compound 2,5,5-trimethylhexenyl-2-lithium (I) was prepared in benzene by addition of *tert*-butyllithium to isoprene[9] or in ether from the mercury compound.[3] A trimer was produced by adding two extra molecules of isoprene to it. The corresponding potassium compound (II) was prepared in ether using diisoprenylmercury and a potassium film. NMR measurements were made on ∼10% solutions using either Varian HA-100 or XL-100 instruments. Polymer microstructure determinations were also made on the same instruments using the analysis procedure described by Essel.[10] All experiments on the alkali metal systems were carried out using high-vacuum systems. For kinetic measurements, which involve low initiator concentrations, the interior of the glassware was washed with a polydienyllithium solution followed by rinsing with solvent distilled from it.[11] Diethyl ether was washed with aqueous sodium bisulfite, dilute aqueous NaOH, and dilute aqueous H_2SO_4,[12] dried over $MgSO_4$, and finally distilled over CaH_2. It was stored over Na/K alloy. Isoprene (Phillips Research Grade) was purified as described earlier.[13]

Polymerization studies were carried out by the addition of 0.2 M monomer to low molecular weight polyisoprene salts. Polyisoprenyllithium (DP ∼ 50) was prepared in hexane using *sec*-butyllithium. The solution was distributed into fragile bulbs, the hexane being pumped-off before sealing. For the other alkali metals, monomer was left in contact with a mirror of the metal for a short time in diethyl ether to produce oligomeric active polymers. Routine measurements of active center concentrations were made using their absorption band in the near-UV: polyisoprenyllithium $\epsilon_{max} = 7600$, polyisoprenylpotassium $\epsilon_{max} = 7800$. Propagation rates were measured from the decrease in optical density at ∼240 nm where isoprene absorbs strongly. Since even the lithium compounds were not stable over the several hours required for complete polymerization but decayed at several percent per hour at room temperature, only initial rates were measured. The potassium derivatives were considerably less stable at this temperature.

Results

Compound I was prepared in hydrocarbon solvent and transferred to ether solution at −70 °C as previously described for THF.[2] Isomerization occurred on warming as determined from ^1H NMR measurements on the γ-proton

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