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"Living" Coordination Polymerization of Propene with a Highly Active Vanadium-Based Catalyst

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ABSTRACT: It is found that a soluble catalyst consisting of tris(2-methyl-1,3-butanedionato)vanadium and $Al(C_2H_5)_2Cl$ in toluene shows a very high activity for the living coordination polymerization of propene and gives a largely syndiotactic polypropylene of narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.2–1.4) at temperatures below −40 °C. The living polypropylene is soluble in toluene during the course of polymerization. Kinetic and spectroscopic results have led to the following conclusions: (1) The living polymerization involves a slow initiation reaction. (2) All of the vanadium species function as active centers for the propagation of living polypropylene. (3) Active vanadium species are in the trivalent state. (4) A limiting temperature for the living polymerization increases up to −40 °C with a decrease in the concentration of $Al(C_2H_5)_2Cl$. A well-defined diblock copolymer of polypropylene and ethylene–propylene rubber is prepared by adding ethylene monomer during the living polymerization of propene.

Introduction

Living polymerization is of practical importance in the synthesis of monodisperse polymers and tailor-made polymers such as terminally functionalized polymers and block copolymers.[1] A living polymer is formed in the polymerization system where no chain-terminating processes are present. The synthesis of living polymers was originally achieved in the anionic polymerization of styrene and butadiene initiated by the organic derivates of alkali metals.[2,3] Recently, other examples of living polymers have been found in cationic,[4] coordination,[5] and group-transfer[6] polymerization systems.

The first example of a living polyolefin with a uniform chain length was disclosed by Doi et al.,[7,8] who used a soluble Ziegler–Natta catalyst of $V(acac)_3$ (acac = acetylacetonato) and $Al(C_2H_5)_2Cl$ at temperatures below −65 °C for the polymerization of propene. The living polypropylene end of a vanadium–carbon bond was found to react with additives such as I_2 and CO to give terminally functionalized polypropylenes.[9–11] In addition, this new type of living polymerization has been applied to the synthesis of well-defined block copolymers such as polypropylene–polyethylene,[12,13] polypropylene–polystyrene,[14] polypropylene–poly(tetrahydrofuran),[15] and polypropylene–poly(methyl methacrylate).[16] However, the activity of the catalyst was relatively low for the synthesis of living polypropylene, since only several mole percent of vanadium species were active and the other vanadium species remained inactive.[7]

In this paper we report a highly active catalyst, $V(mmh)_3$ (mmh = 2-methyl-1,3-butanedionato) and $Al(C_2H_5)_2Cl$, for the living coordination polymerization of propene in which all of the vanadium species function as active centers at temperatures up to −40 °C. The features of this perfect initiator are investigated on the basis of kinetics of the living polymerization and the spectroscopic analysis of polymer and catalyst.

Experimental Section

Vanadium compounds used in this study are shown in Figure 1.

Tris(2-methyl-1,3-butanedionato)vanadium ($V(mmh)_3$). The preparation of $V(mmh)_3$ was carried out with the use of Schlenk techniques under nitrogen according to the method of Holm et al.[17] An aqueous solution of (2-methyl-1,3-butanedionato)sodium (7.0 g, 57 mmol) was treated with a solution of vanadium trichloride (3.0 g, 19 mmol) in 60 cm³ of water, resulting in an immediate formation of brown precipitate. After 1 h of stirring, the brown precipitate was washed 10 times with water and dried under vacuum at room temperature. Anal. Calcd for $C_{15}H_{21}O_6V$: C, 51.73; H, 6.08. Found: C, 51.38; H, 6.17.

Tris(2,4-pentanedionato)vanadium ($V(acac)_3$). $V(acac)_3$ (from Alfa Division, Ventron Co.) was purified by repeated dissolution in toluene followed by reprecipitation in heptane.

Polymerization. $Al(C_5H_5)_2Cl$ (from Toyo Stauffer Chemical Co.) was used without further purification. Propene (from Mitsubishi Petrochemical Co.) and ethylene (from Toa Nenryo Kogyo Co.) were purified by passing them through columns of NaOH and P_2O_5. Reagent grade toluene was dried by refluxing it over sodium metal under nitrogen prior to use. The polymerization of propene was carried out in a glass reactor (ca. 300 cm³) or a steel autoclave (ca. 200 cm³) with a stirrer. Propene was condensed into toluene in the reactor kept at polymerization temperature. Then prescribed amounts of $Al(C_2H_5)_2Cl$ and vanadium compound were charged at the start of polymerization. For a block copolymerization, a small amount of ethylene was admitted into the reactor during the course of propene polymerization. The polymerization was quenched at a given time by adding a methanol solution of hydrochloric acid kept at −78 °C. The resulting polymer was washed several times with methanol and dried under vacuum at room temperature.

Analysis. Gel permeation chromatograms (GPC) of polymers were recorded on a Shodex LCHT-3 gel permeation chromatograph using a Shodex 80 M column and *o*-dichlorobenzene as solvent at 140 °C. From GPC data, the number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were calculated by standard procedures based on a molecular weight calibration curve of polypropylene. The ^{13}C NMR spectra of polymers were recorded at 100 °C in *o*-dichlorobenzene on a JEOL FX-200 spectrometer operating at 50 MHz under proton decoupling in the Fourier transform (FT) mode. The ESR and UV–vis spectra of vanadium catalysts were recorded at different temperatures in toluene on a JEOL FEIX spectrometer and a Hitachi EPS-3T spectrometer, respectively.

Results and Discussion

Time Dependence. Figure 2 shows the result of propene polymerization at −78 °C with a soluble $V(mmh)_3$–$Al(C_2H_5)_2Cl$ catalyst. The polymer yield increases with the polymerization time after an induction period of several hours. In contrast, the $\bar{M}_n$ of polypropylene is almost proportional to time. As a result, the number of polymer chains produced per vanadium atom [N], calculated from yield/$\bar{M}_n$, increases with time to approach a constant value. The polydispersity ($\bar{M}_w/\bar{M}_n$) of polypropylene is as narrow as 1.4 ± 0.1.

These results can be interpreted in terms of a living polymerization involving a slow initiation reaction as schematically represented by

$$V(mmh)_3 + Al(C_2H_5)_2Cl \xrightarrow{k_i} V^*\text{–}C_2H_5 \tag{1}$$

$$V^*\text{–}[CH(CH_3)CH_2]_n\text{–}C_2H_5 + C_3H_6 \xrightarrow{k_p} V^*\text{–}[CH(CH_3)CH_2]_{n+1}\text{–}C_2H_5 \tag{2}$$

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Table I
Rate Constants for Initiation and Propagation Reactions in the Living Polymerization of Propene with $V(mmh)_3$-$Al(C_2H_5)_2Cl$ Catalyst

polym temp, °C	$[Al(C_2H_5)_2Cl]$, mol/dm^3	k_i, h^{-1}	E_i, kcal/mol	k_p, h^{-1}	E_p, kcal/mol	C_0*, mol/(mol of V)
-78	0.05	0.024	14.1	85.0	6.8	1.0
-70	0.05	0.16		160		1.0
-70	0.20	0.80		165		1.0
-60	0.05	0.50		400		1.0

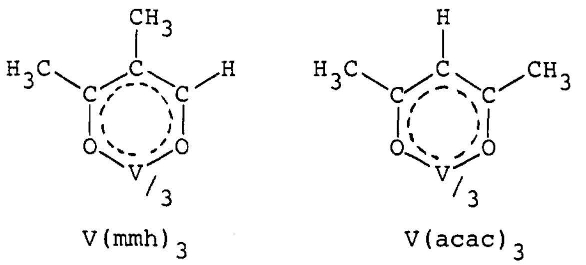

Figure 1. Vanadium compounds used in this study.

where V* represents an active vanadium center and k_i and k_p are the pseudo-first-order rate constants for initiation and chain propagation reactions; note that k_i and k_p contain the concentrations of $Al(C_2H_5)_2Cl$ and propene monomer, respectively. In a previous paper[9] the chain propagation of living polypropylene with a soluble $V(acac)_3$-$Al(C_2H_5)_2Cl$ catalyst was reported to take place via secondary insertion of a propene molecule into a vanadium-polymer bond. Assuming a slow formation of active center, we can represent the time dependence of the number of active centers [C*], polymer yield in moles per mole of vanadium, and $\bar{M}_n$ by the following relations:

$$[C^*] = C_0^*(1 - \exp(-k_i t)) = [N] \tag{3}$$

$$\text{yield} = \int_0^t k_p[C^*]\, dt = k_p \int_0^t C_0^*(1 - \exp(-k_i t))\, dt = k_p C_0^* \left[t + \frac{1}{k_i}(\exp(-k_i t) - 1) \right] \tag{4}$$

$$\bar{M}_n = 42\frac{\text{yield}}{[C^*]} = 42k_p\left(\frac{t}{1 - \exp(-k_i t)} - \frac{1}{k_i}\right) \tag{5}$$

where C_0^* is the concentration of total vanadium compound and t is polymerization time. In a living polymerization the number of active centers [C*] is consistent with the number of polymer chains [N]. Assuming that C_0^* = 1.0 mol/(mol of V), we determined the values of k_i and k_p from the time dependences of [N] and polymer yield in Figure 2, using relations 3 and 4. The values of k_i and k_p at -78 °C are given in Table I. The solid lines in Figure 2 are those calculated by relations 3-5 with the values of k_i and k_p in Table I. The calculated values of [N], yield, and $\bar{M}_n$ are in good agreement with the observed values, confirming that the soluble $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst initiates a living polymerization of propene at a slow rate at -78 °C.

To accelerate the initiation reaction, polymerizations of propene were performed at -70 and -60 °C. The results are shown in Figure 3, together with the result of polymerization with $V(acac)_3$-$Al(C_2H_5)_2Cl$ catalyst at -70 °C for comparison. The rate of increase in the number of polymer chains [N] (i.e., the rate of initiation reaction) is dependent upon both concentration of $Al(C_2H_5)_2Cl$ and polymerization temperature. The value of [N] attains a constant value (1.0 ± 0.1 mol/(mol of V)) within a few hours. Here, it is noted that all of the vanadium species function as active centers, since the value of [N] is almost unity during the polymerization. The polydispersities ($\bar{M}_w/\bar{M}_n$) of polypropylenes are as narrow as 1.25 ± 0.05. Thus, the living polymerization of propene has been achieved at a relatively fast rate of initiation reaction at -70 and -60 °C. As can be seen in Figure 3, the polymerization activity of $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst is higher by 1 order of magnitude than that of $V(acac)_3$-$Al(C_2H_5)_2Cl$ catalyst at comparable conditions. The increase in polymerization activity is mainly due to an increase in the number of active centers.

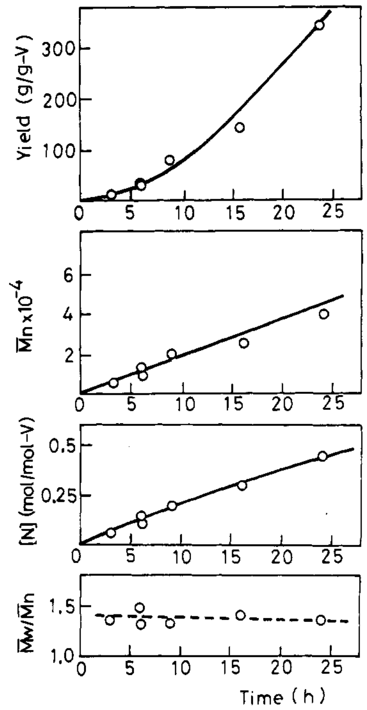

Figure 2. Time dependence of yield, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ of polypropylene and of the number of polymer chains produced per vanadium atom [N] in the polymerization of propene at -78 °C with a $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst. Polymerization conditions: [propene] = 8.3 mol/dm^3; $[V(mmh)_3]$ = 0.005 mol/dm^3; $[Al(C_2H_5)_2Cl]$ = 0.05 mol/dm^3; toluene solution = 0.1 dm^3.

The values of rate constants k_i and k_p at different conditions were determined from the time dependences of [N] and polymer yield in Figure 3 by using kinetic relations 3 and 4. The result is listed in Table I. The lines in Figure 3 are those calculated by relations 3-5 with the values of k_i and k_p in Table I. The value of k_p in Table I is independent of the concentration of $Al(C_2H_5)_2Cl$. The apparent activation energy of k_p is determined as 6.8 kcal/mol. As anticipated, the value of k_i increases with the concentration of $Al(C_2H_5)_2Cl$ and may be expressed by the relation $k_i = k_i'[Al(C_2H_5)_2Cl]$. The activation energy of its rate constant k_i' is as large as 14 kcal/mol.

Figure 4 shows the relation between polymer yield and concentration of propene monomer observed in the polymerization at -70 °C. The polymer yield is not simply

Table II
Temperature Effects of Propene Polymerization at Different $[Al(C_2H_5)_2Cl]/[V(mmh)_3]$ Mole Ratios[a]

temp, °C	[Al]/[V], mol/mol	polymer yield, g/(g of V)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	[N],[b] mol/(mol of V)
-70	20	12	1.30	1.48	0.05
-60	20	275	3.77	1.38	0.37
-50	20	753	6.05	1.38	0.64
-40	20	2070	10.5	1.39	1.01
-20	20	1310	2.42	1.60	2.76
0	20	686	0.97	1.68	3.61
-78	100	8	0.67	1.36	0.06
-70	100	114	1.12	1.30	0.52
-65	100	235	2.01	1.26	0.60
-60	100	561	3.55	1.25	0.81
-60	100	616	2.98	1.22	1.05
-55	100	1540	3.70	1.24	2.12
-50	100	2310	6.41	1.47	1.83
-40	100	2370	4.18	1.75	2.89
-20	100	1440	1.71	1.79	4.29
0	100	361	0.86	1.71	2.14
-78	400	43	0.84	1.36	0.26
-70	400	306	1.65	1.24	0.95
-65	400	635	1.96	1.25	1.65
-60	400	1220	1.89	1.92	3.29
-38	400	1460	1.59	1.75	4.68
-20	400	1290	0.72	1.75	9.17
0	400	706	0.39	1.57	9.23

[a] Polymerization conditions: polymerization time = 3 h; [propene] = 8.3 mol/dm^3; $[V(mmh)_3]$ = 0.5 mmol/dm^3; toluene solution = 0.1 dm^3. [b] Number of polymer chains produced per vanadium atom.

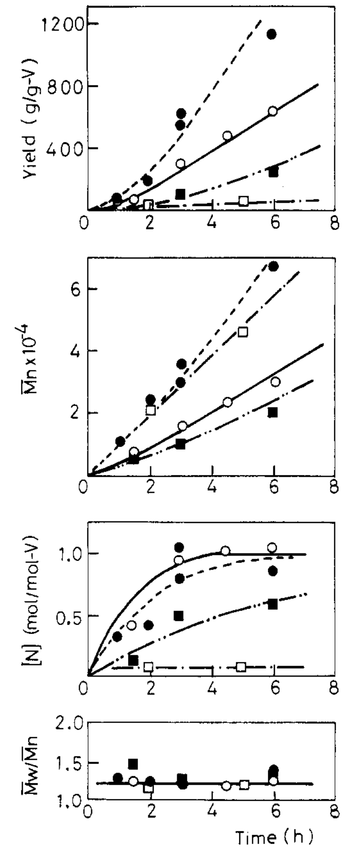

Figure 3. Time dependences of yield, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ of polypropylene and of the number of polymer chains produced per vanadium atom [N] in the polymerization of propene at -70 and -60 °C with different catalysts: (●) $[V(mmh)_3]$ = 0.0005 mol/dm^3, $[Al(C_2H_5)_2Cl]$ = 0.05 mol/dm^3 at -60 °C; (○) $[V(mmh)_3]$ = 0.0005 mol/dm^3, $[Al(C_2H_5)_2Cl]$ = 0.2 mol/dm^3 at -70 °C; (■) $[V(mmh)_3]$ = 0.0005 mol/dm^3, $[Al(C_2H_5)_2Cl]$ = 0.05 mol/dm^3 at -70 °C; (□) $[V(acac)_3]$ = 0.005 mol/dm^3, $[Al(C_5H_5)_2Cl]$ = 0.05 mol/dm^3 at -70 °C. Polymerization conditions: [propene] = 8.3 mol/dm^3; toluene solution = 0.1 dm^3.

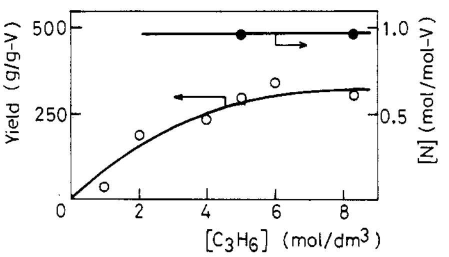

Figure 4. Effect of monomer concentration on propene polymerization with a $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst at -70 °C. Polymerization conditions: $[V(mmh)_3]$ = 0.0005 mol/dm^3; $[Al(C_2H_5)_2Cl]$ = 0.2 mol/dm^3; toluene solution = 0.1 dm^3.

first order in the monomer concentration but approaches a constant value with an increase in monomer concentration. The analogous dependence of polymer yield on the monomer concentration has been found in the living polymerization of propene with $V(acac)_3$-$Al(C_2H_5)_2Cl$ catalyst.[7] The polymer yield may be expressed by

$$\text{yield} = k_p \int_0^t [C^*]\,dt = k_s \frac{K_M[M]}{1 + K_M[M]} \int_0^t [C^*]\,dt \qquad (6)$$

where [M] denotes a concentration of propene monomer which is assumed to remain constant during the polymerization. The constants K_M and k_s may represent the equilibrium constant for a propene monomer coordinating to an active vanadium center and the rate constant for a subsequent insertion of the coordinated monomer into a vanadium-polymer bond, respectively. The values of k_s and K_M at -70 °C were estimated as 170 h^{-1} and 0.24 dm^3/mol, respectively.

Temperature Dependence. The polymerization of propene was carried out in the temperature range -78 to 0 °C at different concentrations of $Al(C_2H_5)_2Cl$ in the presence of $V(mmh)_3$. The results are summarized in Table II.

The polymer yield produced at 3 h increases with increasing temperature, followed by a gradual decrease at temperatures above -40 °C. Maximum values of polymer yield were observed at around -40 °C, independent of $Al(C_2H_5)_2Cl$ concentration. These results indicate that an irreversible deactivation of active vanadium centers occurs at temperatures above -40 °C. In fact, a change in the

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

polym temp, °C	stereoregularity: triad fractions[a] [rr]	[mr]	[mm]	diad[b] [r]
-78	0.632	0.305	0.063	0.785
-50	0.622	0.321	0.057	0.783
-38	0.603	0.341	0.056	0.774
-20	0.583	0.358	0.059	0.762
0	0.592	0.349	0.059	0.767

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

color of the polymerization solution was observed around -40 °C. The toluene solution of $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst exhibited a red color, characteristic of V^{3+} species, at temperatures below -40 °C. At temperatures above -40 °C the color of the toluene solution changed from orange to yellow with increasing temperature. When the toluene solution of $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst was heated to 20 °C, electronic absorption bands appeared at 1150, 730, and 473 nm, which may be assigned to spin-allowed ligand-field transitions of V^{2+} species. A change in the oxidation state of the vanadium ion has also been suggested in the ESR measurement of $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst at various temperatures. At temperatures below -40 °C no ESR signals could be detected, which suggests that all vanadium ions exist in the trivalent state. A broad ESR signal ($\Delta H \simeq 20$ mT) appeared at $g = 1.98$ at temperatures above -30 °C, and its intensity increased with temperature to reach a constant value at 20 °C, indicating that the concentration of V^{2+} species increases with temperature. Thus, these spectral data indicate that the vanadium species active for propene polymerization are in the trivalent state.

The temperature dependence of $\bar{M}_n$ is shown in Figure 5, together with the temperature dependence of propagation rate constant k_p. The $\bar{M}_n$ of polypropylene produced at 3 h shows maximum values at different temperatures, depending on the concentration of $Al(C_2H_5)_2Cl$, i.e., the mole ratio of $Al(C_2H_5)_2Cl$ to $V(mmh)_3$. The temperature of the maximum value of $\bar{M}_n$ increases with a decrease in the mole ratio of [Al]/[V]: -40 °C at [Al]/[V] = 20; -50 °C at [Al]/[V] = 100; and -65 °C at [Al]/[V] = 400. At low temperatures where the value of $\bar{M}_n$ increases with temperature, the polydispersities of polymers are relatively narrow ($\bar{M}_w/\bar{M}_n$ = 1.2-1.4; see Table II), indicating that a living polymerization of propene takes place. Thus, the limiting temperature for the living polymerization increases with a decrease in the mole ratio of [Al]/[V]. It is noted in Table II that a very high yield (2 kg/(g of V)) of living polypropylene is achieved at -40 °C at [Al]/[V] = 20. At high temperatures where the value of $\bar{M}_n$ decreases with temperature, a chain-transfer reaction with $Al(C_2H_5)_2Cl$ takes place together with an irreversible deactivation of active centers due to the reduction of active V^{3+} to inactive V^{2+} species, resulting in a broadening of molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.6-2.0) and an increase in the number of polymer chains ([N] > 1.0).

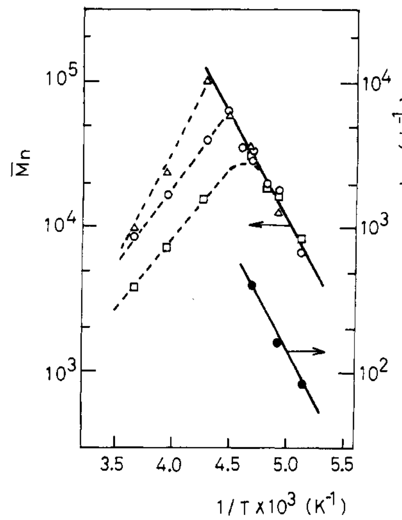

Figure 5. Temperature dependences of $\bar{M}_n$ and k_p in the propene polymerization with a $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst: (△) [Al]/[V] = 20 mol/mol; (○) [Al]/[V] = 100 mol/mol; (□) [Al]/[V] = 400 mol/mol. Polymerization conditions are given in Table II. (●) k_p values in Table I.

The stereoregularities of polypropylenes obtained at different temperatures were examined by using ^{13}C NMR spectroscopy. The steric triad fractions [rr], [mr], and [mm] were determined from the methyl carbon resonance of ^{13}C NMR spectra. As shown in Table III, the $V(mmh)_3$-$Al(C_2H_5)_2Cl$ catalyst gives a syndiotactic polypropylene at temperatures of -78 to 0 °C. The difference in activation energies for the formation of syndiotactic and isotactic diads (i.e., the driving force for syndiotactic control) was estimated by the relation

$$\ln \frac{[r]}{[m]} = \ln \frac{a_r}{a_m} + \frac{E_m - E_r}{RT} \tag{7}$$

where E_r and E_m are the activation energies for the formation of syndiotactic and isotactic diad units, and a_r and a_m are the frequency factors. It is found that $E_m - E_r$ = 1.2 kcal/mol. The value of 1.2 kcal/mol is almost consistent with the value of 1.1 kcal/mol in a syndiotactic-specific polymerization of propene with $V(acac)_3$-$Al(C_2H_5)_2Cl$ catalyst.[7]

Block Copolymerization. Well-defined diblock copolymers consisting of syndiotactic polypropylene block (P) and ethylene-propylene random copolymer block (R) were prepared by adding a small amount of ethylene monomer during the living polymerization of propene at -70 and -60 °C. As shown in Table IV, the addition of ethylene results in rapid increases in both the yield and the $\bar{M}_n$ of polymers. The formation of R block in the

Table IV
Results of Block Copolymerization of Propene and Ethylene with the $V(mmh)_3$-$Al(C_2H_5)_2Cl$ Catalyst[a]

run	temp, °C	[Al]/[V], mol/mol	time,[b] min	time,[c] min	polymer yield, g/(g of V)	$\bar{M}_n \times 10^{-4}$ [d]	$\bar{M}_w/\bar{M}_n$ [d]
1	-70	400	180	0	305	1.65	1.24
2[e]	-70	400	180	10	1540	7.34	1.09
3	-60	100	360	0	1120	6.73	1.39
4[f]	-60	100	360	10	2670	9.42	1.32

[a] Polymerization conditions: [propene] = 8.3 mol/dm^3; [$V(mmh)_3$] = 0.5 mmol/dm^3; toluene solution = 0.1 dm^3. [b] Polymerization time of propene homopolymerization. [c] Polymerization time after the addition of ethylene. [d] Calculated from GPC data based on the molecular weight calibration curve of polypropylene. [e] Ethylene (42 mmol) was added. [f] Ethylene (17 mmol) was added.

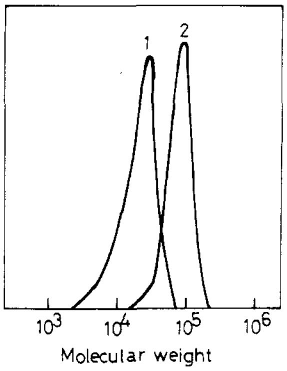

Figure 6. Molecular weight distributions of polymers obtained in runs 1 and 2 in Table IV: (1) homopolypropylene at 180 min (run 1); (2) P–R diblock copolymer at 180 + 10 min (run 2).

resulting polymers was confirmed in the ^{13}C NMR spectra.[12]

Figure 6 shows molecular weight distributions (MWD) of the resulting polymers at −70 °C. Curves 1 and 2 correspond to the MWD of polypropylene at the first stage (run 1; t = 180 min) and the MWD of the P–R diblock copolymer at the second state (run 2; t = 180 + 10 min), respectively. The MWD of the P–R diblock copolymer is clearly shifted toward higher molecular weights and remains a narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.09), indicative of the formation of a block copolymer free of homopolymer impurities. Thus, the living polymerization of α-olefin in the presence of V(mmh)$_3$–Al(C$_2$H$_5$)$_2$Cl catalyst is also supported by the result of block copolymerization.

Registry No. Al(C$_2$H$_5$)$_2$Cl, 96-10-6; V(mmh)$_3$, 16521-95-2; polypropylene, 9003-07-0; (propene)(ethylene) (copolymer), 9010-79-1; propene, 115-07-1.

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Preparation of (*p*-Vinylbenzyl)poly(2-vinylpyridine) Macromers

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ABSTRACT: Styrene-terminated poly(2-vinylpyridine) macromers, i.e., α-(*p*-vinylbenzyl)- and α,ω-bis(*p*-vinylbenzyl)poly(2-vinylpyridines), were prepared by reaction of α-lithio- and α,ω-dilithiopoly(2-vinylpyridines) with *p*-vinylbenzyl chloride, respectively. In this reaction, the α-pyridyl carbanion does not attack the vinyl group of *p*-vinylbenzyl chloride but exclusively reacts with its chloromethyl group. This selectivity leads to macromers with very high functionality (>96%) even in the case of the preparation of α,ω-bis(*p*-vinylbenzyl)poly(2-vinylpyridine). A method for determining the functionality of the macromers was employed that involves copolymerization with methyl methacrylate followed by GPC analysis. The values determined by the method were confirmed by ^{1}H NMR spectroscopy and radical homopolymerization.

Introduction

Poly(2-vinylpyridine) (PVP) is a versatile polymer that is easily and reversibly quaternized to form quaternized water-soluble PVP that behaves as a polyelectrolyte. It is of interest with such a polymer to endow it with polymerizable group(s), i.e., to prepare PVP macromers. This macromer can be used for the preparation of well-defined types of branched polymers such as star and graft copolymers, which are expected to be useful as emulsifiers, surface modifiers, compatibilizers, etc.

Two types of PVP macromers containing *p*-isopropenylbenzyl and methacryloyl groups as polymerizable groups, respectively, were synthesized previously by Rempp et al.[1] The former type, however, is not readily subject to radical polymerization, and its numerical functionalities were not reported.

In order to equip PVP with a styrene-type functional group that is suitable for various polymerization methods, we carried out the reaction of living PVP with *p*-vinylbenzyl chloride (*p*-VBC) in the same way[2] as in the preparation of (*p*-vinylbenzyl)polystyrene macromer. It was confirmed that the carbanions of living PVP do not attack the vinyl group of *p*-VBC, facilitating the synthesis of a pure telechelic macromer. Thus, α,ω-bis(*p*-vinylbenzyl)poly(2-vinylpyridine) macromer (α,ω-BVB-PVP) became possible as well. This telechelic macromer would be useful as a novel hydrophilic polymeric cross-linking reagent.

In this paper, the preparation of the PVP macromers will be described, and the results of their polymerization

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