

Stereochemistry in “living” coordination polymerization of propene initiated by vanadium-based catalytic systems

Yoshiharu Doi*, Tetsuya Koyama, Kazuo Soga

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Tetsuo Asakura

Department of Biopolymer Engineering, Faculty of Technology,
Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo 184, Japan

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SUMMARY:

Soluble catalysts of $V(acac)_3$ and AlR_2X ($R = C_2H_5$, $n-C_3H_7$, $i-C_4H_9$; $X = Cl, Br$) initiate a living polymerization of propene at $-78^\circ C$ to afford monodisperse polymers of syndiotactic structure. The stereochemistry of the living polymerization was investigated by examining the structures of monodisperse polypropylenes and of propylene-ethylene block copolymers by means of ^{13}C NMR spectroscopy. It was found that syndiotactic- and regio-specificities of the soluble vanadium-based catalysts are not influenced by the sequence length of the living polymer chain.

Introduction

In previous papers^{1,2}, we have reported that the soluble Ziegler catalysts composed of $V(acac)_3$ ($acac =$ acetyl acetonate) and dialkylaluminium halides initiate a living polymerization of propene at $-78^\circ C$ to afford syndiotactic polypropylenes with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.05$ to 1.20). A kinetic study³ has proved that the living polymerization proceeds via a coordination polymerization mechanism involving a sequence of two successive reactions, represented by propene coordination to the active vanadium and a subsequent insertion. This new type of living polymerization has been recently applied to the syntheses of well-defined block copolymers of propylene-ethylene^{4,5}, of propylene-styrene⁶, and of propylene-tetrahydrofuran⁷. In this communication we discuss the stereochemistry in the living coordination polymerization of propene, examining the structures of monodisperse polypropylenes and propylene-ethylene block copolymers by means of ^{13}C NMR spectroscopy.

Results and discussion

Tab. 1 summarizes the results of polymerization of propene initiated by various catalytic systems composed of $V(acac)_3$ and dialkylaluminium halides at $-78^\circ C$. All the polymerization runs give monodisperse polypropylenes ($\bar{M}_w/\bar{M}_n = 1.1 - 1.2$), indicating the propagation of all chains is initiated quasi-simultaneously and both

Tab. 1. Structures of monodisperse polypropylenes obtained at -78°C with $\text{V}(\text{acac})_3$ and different types of alkylaluminiums^{a)}

Run	Alkylaluminium	Time in h	Yield in g	Molecular weight ^{b)}		Stereoregularity ^{c)}			Tail-to-tail unit mole fraction ^{d)} [$-\text{CH}_2-\text{CH}_2-$]/[$-\text{CH}_2-\text{CH}_2-$]
				$10^{-4} \cdot \bar{M}_n$	\bar{M}_w/\bar{M}_n	[rr]	[rm]	[mm]	
1	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	1,5	0,39	0,70	1,2	0,66	0,31	0,03	0,01
2	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	6,0	1,90	2,9	1,2	0,65	0,32	0,03	0,01
3	$\text{Al}(n\text{-C}_3\text{H}_7)_2\text{Cl}$	2,0	0,21	0,76	1,1	0,63	0,33	0,04	0,02
4	$\text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$	7,0	0,37	3,4	1,2	0,53	0,38	0,09	0,02
5	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}$	8,5	0,26	0,81	1,2	0,48	0,38	0,14	0,03

a) Polymerization conditions: $\text{V}(\text{acac})_3 = 0,5$ mmol, alkylaluminium = 5,0 mmol, propene = 830 mmol, toluene = 25 cm^3 .

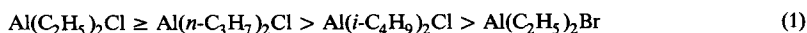
b) Obtained from GPC data.

c) Steric triad fractions determined from ^{13}C NMR spectra of primary carbon.

d) Determined from ^{13}C NMR spectra of tertiary carbons.

chain transfer and termination are virtually absent. Furthermore, the formation of monodisperse polymers indicates that the polymerization of propene with the respective catalyst proceeds with one kind of active sites.

The stereoregularities of monodisperse polypropylenes were determined from the triad intensities of primary carbon resonance ($P_{\beta\beta}$) in the ^{13}C NMR spectra. As can be seen from Tab. 1, the syndiotactic triad fraction, $[\text{rr}]$, of monodisperse polypropylene is influenced by the kind of alkylaluminum component and decreases in the series:



The results offer direct evidence for the bimetallic structure of active sites. From the comparison of the results in runs 1 and 2, the stereoregularity seems to remain unchanged during the living polymerization of propene, indicating that the syndiotactic regulation is not influenced by the sequence length of a living polymer chain.

The amount of the irregular linkage of two propylene units consisting of a tail-to-tail sequence, $[-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_2-\text{CH}(\text{CH}_3)-]$, was determined from the ^{13}C NMR spectra by the same method as used in a previous paper⁸⁾. The result is given in Tab. 1. The monodisperse polypropylenes contain 1 to 3 mol-% of tail-to-tail units.

In order to elucidate the stereochemistry of the living polymerization of propene, we prepared polypropylene (PP)-ethylene/propylene rubber (EPR) block copolymers by adding a small amount of ethylene (0,9 to 1,7 mmol) during the living polymerization of propene at -78°C and analyzed the sequence structures of ethylene and propylene units in the EPR blocks by means of ^{13}C NMR spectroscopy. The results are given in Tab. 2. As reported in a previous paper⁴⁾, a random copolymerization of

Tab. 2. Effects of the addition of ethylene during the living polymerization of propene^{a)}

Run	Alkylaluminum	Polymerization time in h	Time ^{b)} in h	Polymer yield in g	Ethylene content ^{c)} in mol-%	$\frac{[-\text{CH}_2-\text{CH}_2-]_2}{[-\text{CH}_2-\text{CH}_2-]_3}$ ^{d)}	$\frac{\bar{M}_w}{\bar{M}_n}$ ^{e)}
6	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	1,0	0	0,35	12	6	1,2
7	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	1,0	0,5	0,35	12	5	1,2
8	$\text{Al}(n\text{-C}_3\text{H}_7)_2\text{Cl}$	2,0	0	0,35	21	5	1,2
9	$\text{Al}(n\text{-C}_3\text{H}_7)_2\text{Cl}$	2,0	1,0	0,37	20	5	1,2
10	$\text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$	6,0	3,0	0,40	14	6	—

^{a)} Polymerization conditions: $\text{V}(\text{acac})_3 = 0,5$ mmol, alkylaluminum = 5,0 mmol, propene = 830 mmol, ethylene = 0,9 to 1,7 mmol, toluene = 25 cm^3 , -78°C .

^{b)} Moment of ethylene addition after the start of polymerization.

^{c)} Determined by Eq. (4) using the peak areas of secondary carbons.

^{d)} Determined by Eq. (5) using the peak areas of secondary carbons.

^{e)} Obtained from GPC data.

ethylene with propene proceeds rapidly upon adding ethylene, resulting in the formation of an EPR sequence block. Then, two types of block copolymers, EPR-PP and

PP-EPR-PP, can be prepared when ethylene is added in the starting and middle stages of the living polymerization, respectively.

Fig. 1 shows the ^{13}C NMR spectrum (b) of a PP-EPR-PP triblock copolymer (run 9) obtained with the system $\text{V}(\text{acac})_3/\text{Al}(n\text{-C}_3\text{H}_7)_2\text{Cl}$, together with the spectrum (a) of monodisperse polypropylene (run 3). In spectrum (b), the secondary carbon

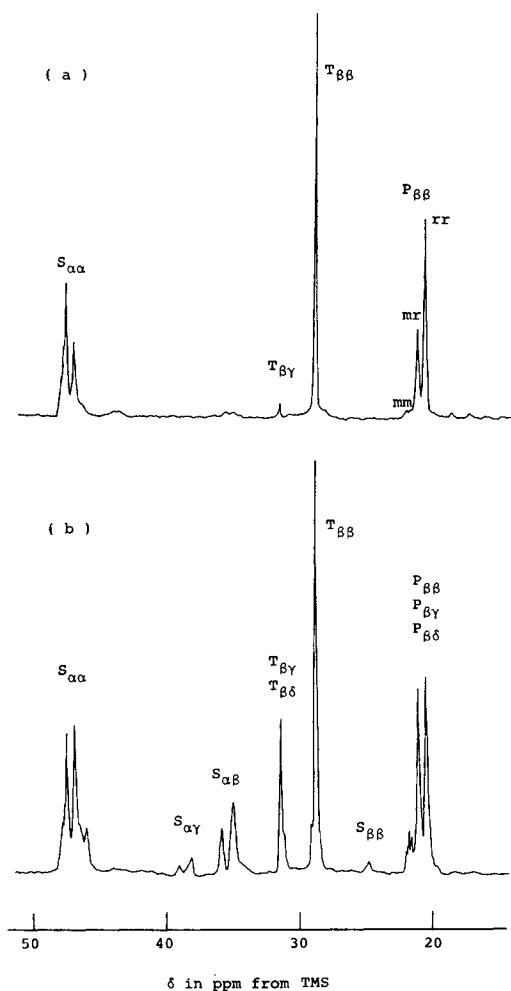
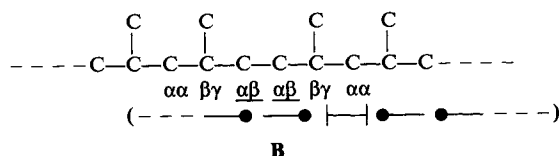
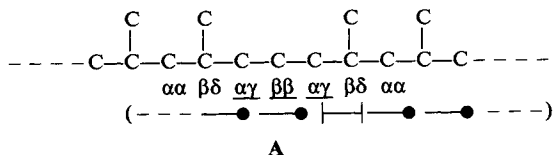


Fig. 1. ^{13}C NMR spectra of monodisperse polypropylene ((a): run 3) and PP-EPR-PP triblock copolymer ((b): run 9) obtained with $\text{V}(\text{acac})_3/\text{Al}(n\text{-C}_3\text{H}_7)_2\text{Cl}$ system

resonances ($S_{\alpha\gamma}$, $S_{\alpha\beta}$, and $S_{\beta\beta}$) are observed due to the following two types of isolated ethylene units (structures **A** and **B**) in the sequence of propylene units:



Here, —● and ●— indicate the propylene units in the orientation $\text{+CH}_2\text{—CH(CH}_3\text{)+}$ and $\text{+CH(CH}_3\text{)—CH}_2\text{+}$, respectively, and |—| represents an ethylene unit. In Fig. 1, tertiary and secondary carbons are denoted as T and S, respectively, with two Greek subscripts indicating the position relative to the nearest tertiary carbon in both directions along the polymer chain, as used by Carman et al.⁹⁾ Each primary carbon is designated by P with Greek subscripts defined as those of the tertiary carbons. The secondary carbon resonances $S_{\alpha\gamma}$ and $S_{\alpha\beta}$ are split into two peaks due to different stereochemical environments¹⁰⁾. The tertiary carbon resonances $T_{\beta\gamma}$ and $T_{\beta\delta}$ are indistinguishable spectroscopically.

The mole fraction of ethylene units in the polymer was determined from the secondary carbon resonance intensities by relation (4), since any sequences of ethylene units were not detected in the ^{13}C NMR spectra.

$$[\text{C}_2\text{H}_4] = \frac{1}{2} \left(S_{\alpha\beta} + \frac{1}{2} S_{\alpha\gamma} + S_{\beta\beta} \right) \quad (2)$$

$$[\text{C}_3\text{H}_6] = S_{\alpha\alpha} + \frac{1}{2} S_{\alpha\gamma} \quad (3)$$

$$\frac{[\text{C}_2\text{H}_4]}{[\text{C}_2\text{H}_4] + [\text{C}_3\text{H}_6]} = \frac{\frac{1}{2} \left(S_{\alpha\beta} + \frac{1}{2} S_{\alpha\gamma} + S_{\beta\beta} \right)}{\left(S_{\alpha\alpha} + \frac{3}{4} S_{\alpha\gamma} + \frac{1}{2} S_{\alpha\beta} + \frac{1}{2} S_{\beta\beta} \right)} \quad (4)$$

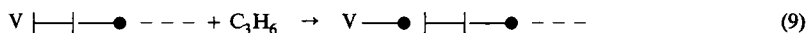
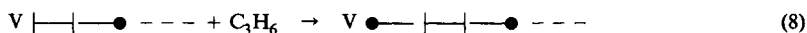
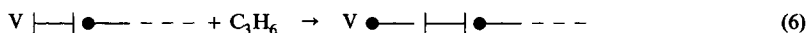
In the above determination the presence of tail-to-tail sequences (—●—●—) of two propylene units is neglected, since the intensities of $S_{\alpha\beta}$ resonance in monodisperse polypropylenes were very small relative to the intensities in copolymers (see Fig. 1). The amounts of ethylene units in the copolymers determined by Eq. (4) are given in Tab. 2, and their values were almost consistent with the amounts of ethylene monomer added during polymerization, confirming the above assumption.

The mole ratio of $\text{-(CH}_2\text{)}_2$ sequence to $\text{-(CH}_2\text{)}_3$ sequence, i.e., the relation of structures **B** to **A**, was determined from the secondary carbon resonance intensities by relation (5).

$$\frac{[\text{-(CH}_2\text{)}_2]}{[\text{-(CH}_2\text{)}_3]} = \frac{\frac{1}{2} S_{\alpha\beta}}{\frac{1}{3} (S_{\alpha\gamma} + S_{\beta\beta})} \quad (5)$$

The results are given in Tab. 2. The mole ratios of $\text{-(CH}_2\text{)}_2$ sequence to $\text{-(CH}_2\text{)}_3$ sequence were determined to be 5 to 6, independently of both the type of alkylaluminum and the stage at which ethylene was added the living system. The constancy of the $[\text{-(CH}_2\text{)}_2]/[\text{-(CH}_2\text{)}_3]$ ratio indicates that the sequence structure of ethylene and propylene units is not influenced by the sequence length of a living polymer chain.

The formation of isolated ethylene units in the structures **A** and **B** can be understood by a copolymerization involving the following propagation steps.



The $\text{-(CH}_2\text{)}_2$ sequence is formed via propagation step (7), whereas the $\text{-(CH}_2\text{)}_3$ sequence is formed via propagation step (6) or (9). The absence of $\text{-(CH}_2\text{)}_4$ sequence in the copolymers indicates that the propagation step (8) does not occur in the present polymerization. The predominant occurrence of $\text{-(CH}_2\text{)}_2$ sequence over $\text{-(CH}_2\text{)}_3$ sequence indicates that step (7) is a major propagation reaction among four steps, i.e., a primary insertion of propene into a vanadium-carbon bond takes place predominantly after ethylene insertion. In addition, the propagation step (7) suggests that the syndiotactic sequence of propylene units is mainly formed via a secondary insertion of propene. The same conclusion has been reached by Zambelli et al.¹⁰⁾ who made a careful analysis of ^{13}C NMR spectra of random copolymers of propylene with ^{13}C -enriched ethylene obtained with the catalyst $\text{VCl}_4/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.

In summary, we have demonstrated that syndiotactic- and regio-specificities of the soluble vanadium-based catalysts are not influenced by the sequence length of a living polymer chain.

Experimental part

A three-necked glass flask (300 cm³) with a magnetic stirrer was used as a reactor. Propene (830 mmol) was condensed into toluene (25 cm³) in the reactor, kept at -78°C with methanol/dry ice. Then, 5.0 mmol of alkylaluminum and 0.5 mmol of $\text{V}(\text{acac})_3$ were charged for the start of the polymerization. When required, a small amount of ethylene (0.9 to 1.7 mmol) was admitted into the reactor during the course of the polymerization of propene at

-78°C . The polymerization was quenched at a given time by adding 100 cm^3 of a methanol solution of hydrochloric acid kept at -78°C . The polymers produced were washed several times with 500 cm^3 of methanol and dried i. vac. at room temperature.

Gel permeation chromatograms (GPC) of the polymers were recorded on a Shodex LCHT-3 gel permeation chromatograph using Shodex 80 M columns and *o*-dichlorobenzene as solvent at 140°C . From GPC results, the number-average and weight-average molecular weights (\bar{M}_n and \bar{M}_w) were calculated by standard procedures based on the molecular weight calibration curve of polypropylene. The ^{13}C NMR spectra of polymers were recorded on a JEOL FX-100 spectrometer operating at 25,14 MHz under proton decoupling in the Fourier Transform (FT) mode. Instrument conditions were: $\pi/4$ pulse of $9,0\text{ }\mu\text{s}$, 7,0 s repetition rate, and 5000 Hz sweep width. Solutions of polymers were made up in trichlorobenzene to $300\text{ mg per } 2\text{ cm}^3$ without degassing, and temperature for measurement was 120°C . The chemical shift is presented in p.p.m. downfield from tetramethylsilane (TMS) as internal standard.

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