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Articles

Copolymerization of Atactic Polypropene Macromonomer with Propene by an Isospecific Metallocene Catalyst

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ABSTRACT: Atactic polypropene macromonomer (PPM) with a number-average polymerization degree of ca. 20 was synthesized by bis(pentamethylcyclopentadienyl)zirconium dichloride−methylaluminoxane and its structure was analyzed by ^{1}H and ^{13}C NMR spectroscopies. Copolymerization of propene and PPM was conducted with isospecific *rac*-dimethylsilylenebis(2-methylbenz[*e*]indenyl)zirconium dichloride using methylaluminoxane as a cocatalyst. The detailed analyses of resulting copolymers by GPC, DSC, and ^{13}C NMR proved that PPM was copolymerized with propene to give poly(propene-*co*-PPM). PPM content in the copolymer was found to be controlled by the amount of PPM in feed.

Introduction

Around 40 years after the discovery of Ziegler−Natta catalysts, we are observing rapid development of new polyolefin materials based on the epoch-making discovery of homogeneous metallocene catalysts by Kaminsky and Sinn.[1] In contrast to conventional heterogeneous multicenter Ziegler−Natta catalysts, polymerization by a metallocene catalyst occurs principally at a single type of metal center. Metallocene catalysts can polymerize cycloolefins and diolefins as well as common α-olefins such as ethene and propene. These characteristics make it possible to produce a variety of uniform polyolefins. Actually, metallocene catalysts now commercially produce several ethene-based copolymers.[2]

Another merit of metallocene catalysts is the precise control of stereoregularity of poly(α-olefin)s.[3] The finding of isospecific polymerization by *ansa*-type chiral C_2-symmetric metallocenes has opened the way to new stereoregular polypropenes (PPs) such as highly syndiotactic PP and stereoblock PP, although the stereoregularity and the molecular weight of the initial isospecific metallocenes were not enough to meet the requirements of industrial processes.

The drawbacks of isospecific metallocene catalysts have been overcome successfully by intensive synthetic work of organometallic chemists. For example, Brintzinger et al.[4] discovered that both benzannelation and 2-methyl substitution of indenyl ligands in *rac*-$Me_2Si(Ind)_2ZrCl_2$ significantly improved isotacticity together with the molecular weights of PP obtained. They also reported that the same zirconocene compound *rac*-Me_2Si(2-MeBenz[*e*]Ind)$_2ZrCl_2$ showed better activity than *rac*-$Me_2Si(Ind)_2ZrCl_2$ for the polymerization of sterically hindered α-olefins branched at the γ-position, such as 3-methyl-1-butene or 3-methyl-1-pentene.

Besides the control of stereochemistry and molecular weight, control of comonomer incorporation represents a key feature of metallocene-catalyzed polymerization. In this context, Mülhaupt et al. studied the influence of the substituent of the indenyl ligand on copolymerization of propene and 1-octene and found that the benzannelation and 2-methyl substitution of *rac*-$Me_2Si(Ind)_2ZrCl_2$ also enhanced the comonomer incorporation.[5]

As described above, zirconocene catalysts for isotactic PP have improved to give polymers comparable to those obtained by commercial heterogeneous catalysts. Metallocene catalysts show their characteristics especially in copolymerization just as it is shown in the commercial production of linear low-density polyethene. The isospecific metallocene catalysts are also expected to develop isotactic polypropene-based copolymers.

We have previously investigated copolymerization of ethene with vinyl-terminated atactic PP synthesized by bis(pentamethylcyclopentadienyl)zirconium dichloride ($Cp^*_2ZrCl_2$)/methylaluminoxane (MAO) and found that (*tert*-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dichloride (CGC−Ti) combined with MAO effectively gave polyethene grafted with atactic polypropene.[6] The aim of this work was to synthesize isotactic PP with an atactic side chain by copolymerization of propene and an atactic PP macromonomer. The objective polymer has hard and soft segments in the main and side chains, respectively, which probably show some interesting properties especially in rheology. Since *rac*-Me_2Si(2-MeBenz[*e*]Ind)$_2ZrCl_2$ is one of the best catalysts at present for isospecific polymerization of propene with respect to molecular weight, isotacticity, and comonomer incorporation,[4,5,7] *rac*-Me_2Si(2-MeBenz[*e*]Ind)$_2$-$ZrCl_2$/MAO was used to synthesize the objective copolymer.

Experimental Section

Materials. Propene of research grade purity (Mitsubishi Chemical Co.) was further purified by passing it through

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columns of $CaCl_2$, P_2O_5, and molecular sieves (3 Å). $Cp^*{}_2ZrCl_2$ was prepared according to the literature method.[8,9] *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$ and MAO were donated from Mitsubishi Chemical Co. and Tosoh-Akzo Co., respectively. The other chemicals of research grade were commercially purchased and used without further purification.

Synthesis of Atactic Polypropene Macromonomer (PPM). PPM was prepared by $Cp^*{}_2ZrCl_2$/MAO according to the analogous procedure as reported in the literature.[6,10] $Cp^*{}_2ZrCl_2$/MAO predominantly gives a slightly syndiotactic-rich polypropene with a terminal allyl group.[10] Propene polymerization was conducted with a 100-mL stainless steel autoclave equipped with a magnetic stirrer. After measured amounts of MAO (9 mmol of Al), toluene (100 mL), and the Zr compound (6 μmol) were added into the reactor under nitrogen atmosphere, 20 L of propene gas at STP was condensed into the reactor at liquid nitrogen temperature. Polymerization was carried out at room temperature for 12 h. The polymerization was quenched by adding a dilute solution of hydrochloric acid in methanol. The toluene layer was adequately washed with plenty of water. After the solvent was evaporated, the product was dried under vacuum at 60 °C for 8 h. The yield was 25.9 g (conversion = ca. 80%). The number average molecular weight (M_n) by gel permeation chromatography (GPC) as polystyrene = 630 (M_w/M_n = 2.4).

Polymerization and Analytical Procedures. Polymerization was conducted in a 200-mL glass reactor equipped with a magnetic stirrer under atmospheric pressure of propene. After measured amounts of toluene, PPM, and *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$ were added into the reactor under nitrogen atmosphere, propene was introduced at polymerization temperature until the toluene was saturated with propene. Polymerization was started by adding the toluene solution of MAO. The polymerization was quenched by adding a small amount of a dilute solution of hydrochloric acid in methanol. The polymerization mixture was then poured into 600 mL of methanol and stirred overnight. The precipitated copolymers were separated by filtration and then dried under vacuum at 60 °C for 6 h.

To remove the residual PPM in the copolymer, the dried copolymer (2 g) was dissolved in *o*-dichlorobenzene (ODCB) (10 mL) at 120 °C and reprecipitated at room temperature by adding ether (20 mL) and separated by filtration. The purified copolymer was dried under vacuum at 60 °C for 6 h.

M_n and M_w/M_n values of copolymers were measured by GPC (Waters 150C) using ODCB as solvent. The calibration curve was made with standard polystyrene samples.

The melting point (T_m) and the heat of fusion (ΔH) were measured with a Seiko SSC/5200 DSC calorimeter. A polymer sample (ca. 3 mg) was encapsulated in an aluminum pan, preheated at 200 °C for 5 min, cooled to room temperature, and scanned at a heating rate of 10 °C/min. ^1H and ^{13}C NMR spectra of polymers were recorded on a JEOL GX-500 spectrometer operated at 500.00 and 125.65 MHz in the pulse Fourier transform (FT) mode. The solvents were chloroform-*d* for PPM, and tetrachloroethane-d_2 for isotactic PP and copolymers. The spectra were obtained at room temperature for PPM and at 120 °C for isotactic PP and copolymers. The internal standard for ^1H NMR measurements was chloroform (7.24 ppm) or tetrachloroethane (5.90 ppm). The center peak of chloroform-*d* (77.0 ppm) or tetrachloroethane-d_2 (74.47 ppm) was used as an internal standard for ^{13}C NMR measurements. In the ^1H NMR measurements, the pulse angle was 45° and 100−1000 scans were accumulated in 10 s of pulse repetition. In the ^{13}C NMR measurements, broad band decoupling was used to remove $^{13}C-{}^1H$ couplings. The pulse angle was 45°, and 5000−10000 scans were accumulated in 8 s of pulse repetition.

Results and Discussion

Structure of PPM. PPM was synthesized with $Cp^*{}_2ZrCl_2$/MAO according to the method described in the Experimental Section. The ^1H NMR spectrum of PPM is displayed in Figure 1a. Besides the strong resonances of aliphatic protons in the main chain, the resonances of vinyl protons are observed at 5.0 and 5.8 ppm. The resonance assignable to the vinylidene protons is observed around 4.8 ppm with a very weak intensity. The relative intensity between the vinyl and vinylidene protons indicates that the majority of unsaturated chain ends in a vinyl group (ca. 80 mol %).

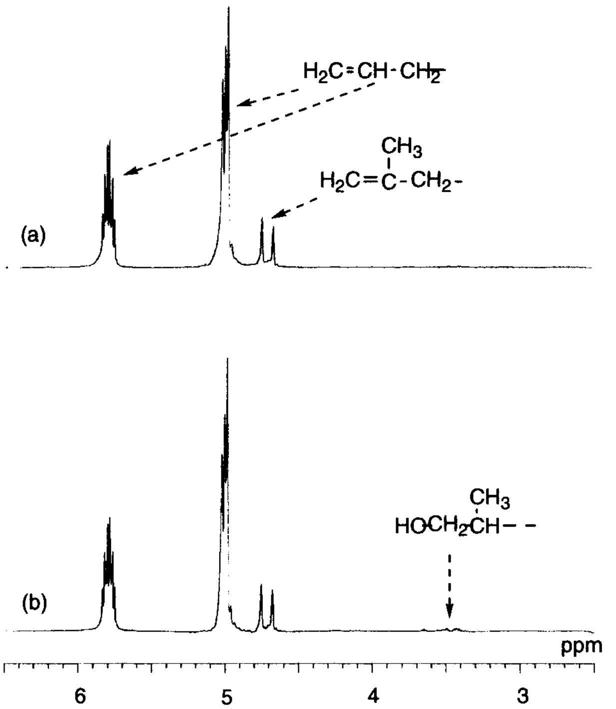


Figure 1. ^1H NMR spectra of PPM: (a) quenched by H^+/MeOH and (b) quenched by O_2.

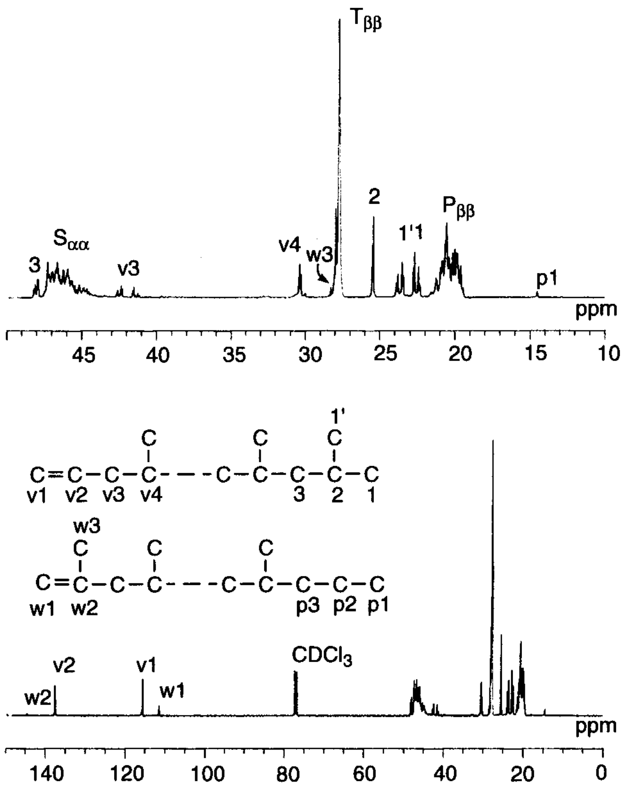
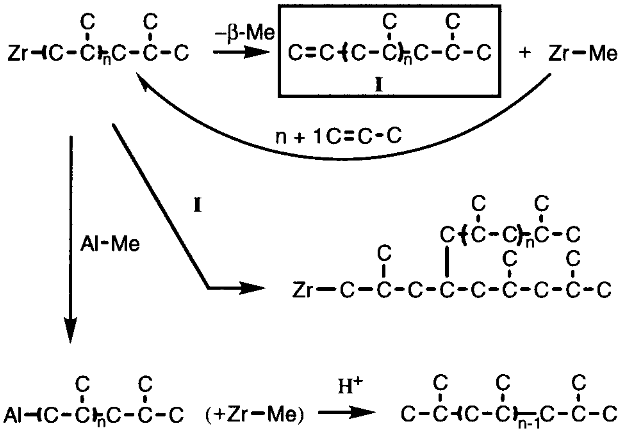


Figure 2. ^{13}C NMR spectrum of PPM.

The ^{13}C NMR spectrum of PPM is shown in Figure 2 to investigate the structure of PPM in more details.

Scheme 1



Strong resonances at around 20, 28, and 46 ppm are resulting from methyl ($P_{\beta\beta}$), methine ($T_{\beta\beta}$), and methylene ($S_{\alpha\alpha}$) carbons in the main chain. The methyl resonance indicates that PPM is atactic. Aside from the resonances of the main chain carbons, the spectrum displays several weak resonances at around 22.5, 24.5, 25.7, 30.8, 41.5, 42.5, 115.2, and 138.9 ppm, which are assignable to the 2-methyl propyl and 2-methyl-4-pentenyl end groups as shown in Figure 2. Some of the resonances split into several peaks because of the diastereomeric structures of the chain end, because PPM is atactic.

Much weaker resonances are observed at around 14.5, 28.2, and 112.0 ppm with almost the same intensities. These resonances are assigned to *n*-propyl and vinylidene end groups, which formed by β-hydrogen transfer in a pair.

Any resonance assignable to the other chain end structure is not observed. It can be concluded, therefore, that β-methyl elimination predominates under the present polymerization conditions, which is in accord with the previous reports.[6,10] The intensity of the 2-methylpropyl group was about 2 times stronger than that of the 2-methyl-4-pentenyl group, albeit these groups should be formed in a pair by β-methyl transfer.

There are two possibilities in the formation of a higher amount of 2-methylpropyl in PPM, as shown in Scheme 1. One is the chain transfer by MAO or $AlMe_3$ in MAO, which forms a 2-methylpropyl group at the termination end after hydrolysis. The other is the copolymerization of produced PPM with propene resulting from the high conversion of propene in the PPM synthesis, which gives the pendent 2-methylpropyl group.

To investigate the reasons for the discrepancy, PPM was again synthesized under the same conditions and the polymerization mixture was separated into three parts before quenching. One part was quenched by H^+/MeOH as usual. The second part was contacted with oxygen before quenching. The third part was quenched by $^2HCl/MeO^2H$.

The ^1H NMR spectrum of the O_2-quenched part is illustrated in Figure 1b. In the spectrum, the resonance of the hydroxymethylene protons was observed around 3.5 ppm; however, their intensity was negligibly weak compared with that of the vinyl and vinylidene protons. These results suggest that the amount of Al-terminated chain end was very small.

The absence of Al-terminated chain end was also checked by quenching the polymerization with $^2HCl/MeO^2H$. The ^{13}C NMR spectra of MeOH-quenched and MeO^2H-quenched polymers were totally the same, regardless of the quenching methods. The result also supports that the 2-methylpropyl end group was not formed by the hydrolysis of Al-terminated chain end.

Table 1. Copolymerization of Propene with PPM Using *rac*-Me_2Si(2-MeBenz[*e*]Ind)$_2ZrCl_2$/MAO[a]

run	polym temp (°C)	PPM[b] in feed (mmol)	consumed propene (mmol)	activity[c] (kg/mmol of Zr·h)
H-15	50	0.0	283.3	11.9
C-10	50	2.3	104.9	4.4
C-11	50	4.6	48.3	2.0
C-24	50	6.9	107.4	4.5
C-17	40	2.3	93.8	3.9
C-20	40	4.6	64.8	2.7
C-18	20	2.3	32.2	1.3
C-21	20	4.6	20.7	0.87
C-19	0	2.3	18.6	0.78

[a] Polymerization conditions: 200-mL round bottom flask; total volume of toluene = 100 mL; Zr = 0.5 μmol; MAO = 7.9 mmol; [Al]:[Zr] = 15 800; polymerization time = 2 h. [b] PPM denotes atactic polypropene macromonomer. [c] Calculated from the amount of consumed propene.

The NMR analyses proved that copolymerization of produced PPM with propene occurred during the PPM synthesis, probably due to the high conversion (80%) of propene to PPM. The chain-end analysis by NMR indicates that the resultant PPM has one side-chain branch in average. The number-average polymerization degrees determined by ^1H and ^{13}C NMR were 19 and 20, which are in good agreement each other.

Copolymerization of PPM with Propene. Polymerization of propene was conducted at 50 °C under atmospheric pressure of propene in the presence or absence of PPM by *rac*-Me_2Si(2-MeBenz[*e*]Ind)$_2ZrCl_2$/MAO. The results are summarized in Table 1. Addition of PPM decreased the rate of propene consumption, although the rate was scattered to some extent. Copolymerization of propene and PPM was also conducted at 40, 20, and 0 °C. The results obtained at 40 and 20 °C indicate that the rate was decreased with augmenting the amount of PPM added. Arnold et al.[11] investigated the copolymerization of propene with 1-octene or 4-methyl-1-pentene, and found that addition of 1-octene enhanced the catalyst productivity while addition of 4-methyl-1-pentene, even a small amount, significantly decreased the productivity.

Rate enhancements in ethene and propene polymerization have been observed in heterogeneous and homogeneous catalysts.[12] Such rate enhancement is ascribed to an increase in solubility and/or a decrease in crystallinity of the produced polymer, which enhances diffusion of monomer to an active center. We have previously reported the copolymerization of ethene and PPM with CGC−Ti/MAO and observed the rate enhancement at 40 °C but not at 90 °C.[6]

For comparison, we have also conducted the copolymerization of propene and 4-methyl-1-pentene, which has the same vinyl structure as PPM, under the same condition of propene and PPM copolymerization. Contrary to the observation by Arnold et al., the rate of propene consumption was enhanced by the addition of 4-methyl-1-pentene. Although the reason of this discrepancy is not clear at present, our result indicates that the suppression of propene consumption in the copolymerization of propene and PPM is not due to the structure of the 4-methyl-1-pentene end group. The suppression of propene consumption might be due to the

Table 2. Properties of Poly(propene-*co*-PPM) Obtained with *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$/MAO

run	PPM in feed (mmol)	M_n[a] ($\times 10^{-4}$)	M_w/M_n[a]	T_m[b] (°C)	ΔH[b] (J/g)	PPM content (mol %)	PPM conversion[c] (%)
H-15	0	3.5	1.9	146.3	106.2		
C-10	2.3	4.8	1.8	142.4	88.3	1.0	46
C-11	4.6	4.5	1.7	132.4	73.7	1.3	14
C-24	6.9	4.5	1.7	123.7	59.9	2.0	32
C-17	2.3	7.8	1.8	141.1	84.1	0.7	29
C-20	4.6	8.4	1.7	132.5	73.6	1.4	20
C-18	2.3	19.0	2.4	145.5	77.9	0.9	13
C-21	4.6	21.3	2.5	135.1	42.7	3.8	18
C-19	2.3	32.7	3.2	149.5	89.5	1.5	12

[a] Measured by GPC. [b] Melting temperature measured by DSC. [c] Calculated from the amount of consumed propene and the PPM content in copolymer.

increase in viscosity of the liquid phase or impurities in PPM, because PPM is a sticky material.

In Table 2 are summarized the properties of the produced polymers. Molecular weight and polydispersity were measured by GPC. The GPC chromatograms of the crude copolymers had shown bimodal distributions, one of which was attributed to PPM. The produced polymers were, therefore, purified by dissolving in ODCB and reprecipitated in diethyl ether. After the purification, the PPM peak disappeared in the GPC chromatograms. The value of polydispersity is almost 2, which indicates that the copolymerization proceeded homogeneously.

The thermal properties of produced polymers were, then, measured by differential scanning calorimetry. The T_m and ΔH values of the polymers obtained in the presence of PPM were lower than that obtained without PPM and decreased with an increase of PPM added. The molecular weight was slightly increased by the addition of PPM.

The incorporation of PPM was then investigated in more detail by ^{13}C NMR. Here the ^{13}C NMR of the copolymer obtained in the highest PPM concentration (Run C-24) is categorically discussed. The ^{13}C NMR spectrum of the copolymer is illustrated in Figure 3 together with those of homo-PP and PPM. The strong resonances of methylene, methine, and methyl carbons of PP are observed at around 46, 28, and 21 ppm. The resonance of the methyl group splits into several peaks according to the stereoregularity of polypropene. In the spectrum of homo-PP, steric defects attributed to mrrm, mmrr, and mmmr are observed with the strong resonance of mmmm. The relative intensity of these defects is about 1:2:2, which indicates that highly isotactic PP was produced by an enantiomorphic site controlled mechanism. On the other hand, the methyl region of the copolymer contains more stereoirregular sequences that come from the PPM chains.

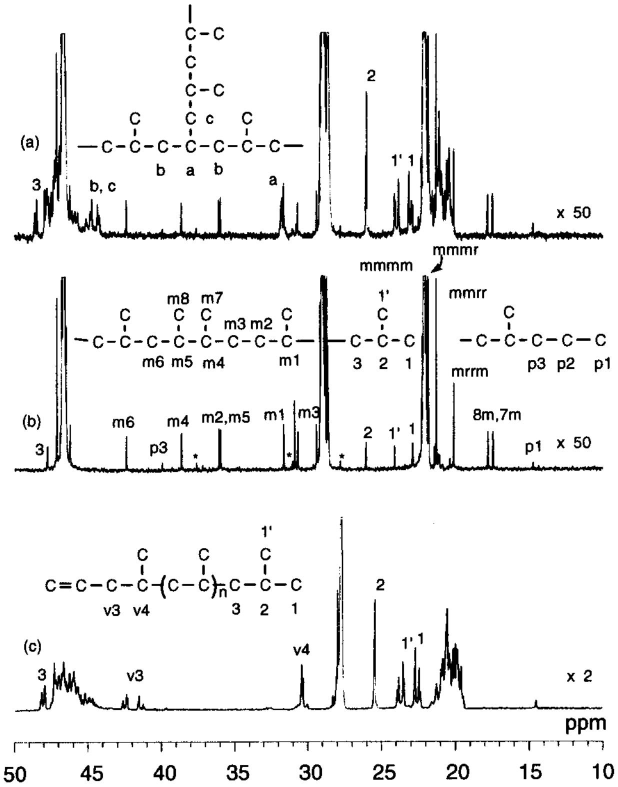
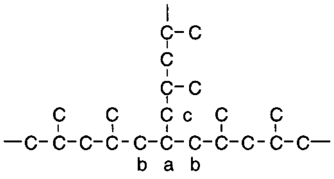


Figure 3. ^{13}C NMR spectra of poly(propene-*co*-PPM) and homo-PPs: (a) run C-24, (b) run H-15, and (c) PPM.

Table 3. Observed and Calculated Chemical Shifts of the Conjunction Carbons in Poly(propene-*co*-PPM)



carbon	chemical shift in ppm calculated	chemical shift in ppm observed
a	30.84	31.73
b	42.17	44.24−44.84
c	42.17	44.24−44.84

In the spectrum of the copolymer, the carbons of the 2-methylpropyl end group of PPM (1, 1′, 2, and 3) appear at around 22.5, 23.5, 25.5, and 48.2 ppm, whereas those of 4-methyl-2-pentenyl group (v3 and v4) disappear. On the other hand, new resonances are observed at around 32 and 44 ppm, which probably come from the conjunction carbons of PPM in the copolymer. The chemical shifts of the conjunction carbons were calculated according to the increment rule of Lindeman−Adams.[13] A plausible structure and the calculated values are shown in Table 3. The observed values roughly agree with the calculated ones. The methylene carbons of conjunction parts split into several peaks, which is probably ascribed to the stereoirregularity of the PPM chain end. These results strongly indicate that PPM was copolymerized with propene to give an isotactic PP with a pendant atactic polypropene. The assignments of the conjunction carbons were confirmed by investigating the copolymers obtained in the various PPM concentrations at 50 °C (Figure 4). In the spectra, the intensities of resonances at around 32.7 and 44.5 ppm assigned to the

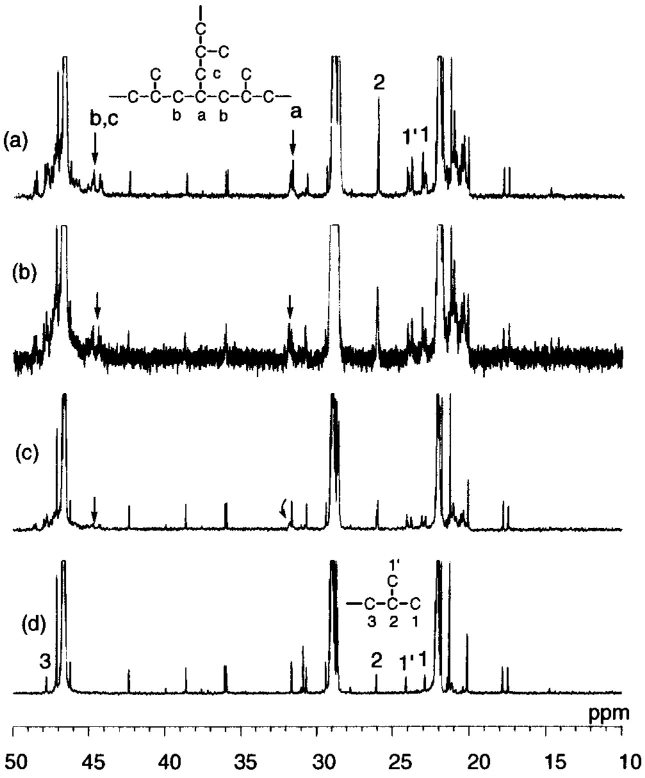


Figure 4. ^{13}C NMR spectra of poly(propene-*co*-PPM) and homo-PP: (a) run C-24, (b) run C-11, (c) run C-10, and (d) run H-15.

conjunction carbons decreased together with a decrease in the intensities of the 2-methylpropyl end group of PPM. The result supports the validity of the assignments.

In all the spectra, several weak resonances are observed, regardless of PPM content. These resonances can be assigned to a 2,1-inserted propene unit in isotactic 1,2-inserted propene sequences as indicated in Figure 3b.[14] The resonances of the 1,3-inserted propene unit, which are indicated by an asterisk (*), are also observed although the intensity is very weak.

The other weak resonances in the homo-PP can be assigned to the 2-methylpropyl end group. The resonances are very sharp compared with those of PPM because of the high stereoregularity of methyl group. In the spectrum, the resonances of the *n*-propyl end group are observed; however, their intensities are very weak compared with those of the 2-methylpropyl groups. It can be concluded, therefore, that chain transfer to MAO or $AlMe_3$ in MAO was predominant over β-hydrogen transfer under the present polymerization conditions. The result is in good agreement with the kinetic study by Brintzinger et al., which indicated that monomer transfer was strongly suppressed in propene polymerization with this catalyst.[4]

Since the structures of the copolymers have been clarified by ^{13}C NMR, comonomer contents can be determined from the relative intensities of the chain end-methyl carbons of PPM and those of main chains. The results are summarized in Table 2. The PPM contents in copolymer are from 1 to 2 mol %, the intensities depending on the PPM concentration in the feed. Considering the number-average polymerization degree of PPM, the PPM content are about 20−30% in weight.

An atmospheric pressure of propene was continuously supplied during the copolymerization, while PPM was added only at the beginning. The conversion of PPM was, therefore, calculated from the amount of consumed propene and the PPM content in the copolymer. The results are shown in Table 2. The conversions of PPM are scattered by polymerization conditions and in the range from ca. 10 to 50%.

In conclusion, it was demonstrated that atactic polypropene macromonomer (PPM) was copolymerized with propene by the isospecific zirconocene catalyst using MAO as cocatalyst to produce isotactic PP with atactic long chain branching.

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