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Copolymerization of Propene and Nonconjugated Diene Involving Intramolecular Cyclization with Metallocene/Methylaluminoxane

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ABSTRACT: Copolymerizations of propene with 1,5-hexadiene and 1,7-octadiene were carried out with isospecific *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (**1**) and syndiospecific diphenylmethylene-(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (**2**) combined with methylaluminoxane. Microstructures of the copolymers were determined by ^{1}H NMR, ^{13}C NMR, and DEPT (distortionless enhancement of polarization transfer) spectroscopies. Incorporation of nonconjugated dienes in the copolymer was higher with **2** than with **1**. Intramolecular cycloaddition of the nonconjugated dienes proceeded regardless of the catalysts. Stereoselectivity in cycloaddition of 1,5-hexadiene was investigated based on the structures of isolated methylene-1,3-cyclopentane units. It was found that 1,5-hexadiene was inserted stereospecifically by enantiomorphic site control with both catalysts. The diastereoselectivity of the cyclization step of 1,2-inserted 1,5-hexadiene was, however, found to be independent of stereospecificity of the catalyst. The cyclization selectivity of 1,5-hexadiene copolymerization was higher than that of 1,7-octadiene copolymerization. **1** gave the copolymers with higher selective in cyclization than **2** in the propene/1,5-hexadiene copolymerization, while the opposite tendency was observed in the propene/1,7-octadiene copolymerization. Decrease of cyclization selectivity was observed with the increases of 1,5-hexadiene and 1,7-octadiene concentration in both copolymerizations. Propene insertion could disturb the cyclization of 1,2-inserted dienes, which declined the cyclization selectivity of the copolymers, except propene/1,5-hexadiene copolymerization with **2**.

Introduction

In comparison to conventional heterogeneous Ziegler−Natta catalysts, metallocene catalysts are suitable for homo- and copolymerization of cycloolefins and diolefins. Polyolefins with cyclic groups are excellent materials with high glass transition temperature and high transparency. The properties of these polyolefins can be widely controlled by designing the structures of cyclic groups. From such a point of view, much effort has been focused on copolymerizations and terpolymerizations of olefins with cycloolefins by metallocene catalysts, especially on ethene/cycloolefin copolymers and ethene/propene/cycloolefin terpolymers.[1] Copolymerizations of propene with cycloolefins and dienes with metallocene catalysts have been also conducted.[2] Köller et al. investigated the copolymerization of propene and cyclopentene.[2a] Moreover, Henschke et al. carried out the copolymerization of propene and norbornene with an isospecific metallocene catalyst and synthesized the polyolefin with high glass transition temperature.[2b]

A disadvantage in homo- and copolymerization of cycloolefins is low productivity, which restricts the synthesis of polyolefins with cyclic groups. Recently, a new method to synthesize the cycloolefin polymers, namely, cyclopolymerization of diolefins, was reported. Waymouth et al. performed detailed investigations on the cyclopolymerization of nonconjugated dienes, in particular 1,5-hexadiene, with metallocene catalysts.[3] They succeeded in the synthesis of optically active poly(methylene-1,3-cyclopentane) by enantioselective cyclopolymerization of 1,5-hexadiene with optically active zirconocenes.[4]

Marques et al. and Luft et al. conducted the ethene/1,5-hexadiene copolymerization with metallocene catalysts.[5] Mülhaupt et al. investigated ethene/1,5-hexadiene copolymerization and ethene/styrene/1,5-hexadiene terpolymerization with CGC (constrained geometry catalyst).[6] Copolymerizations of propene and nonconjugated dienes with stereospecific metallocene catalysts seem to be useful method to synthesize polypropene with cyclic groups and to study the mechanism of stereoselectivity in the insertion and cyclization of dienes.

In this study, we reported propene/1,5-hexadiene and propene/1,7-octadiene copolymerizations with stereospecific metallocene catalysts of dimethylsilylenebis(indenyl)zirconium dichloride (*rac*-$Me_2Si(Ind)_2ZrCl_2$, **1**) and diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride ($Ph_2C(Cp)(Flu)ZrCl_2$, **2**). Furthermore, we studied microstructures of the resulting copolymers in detail to confirm the mechanism of propene/nonconjugated diene copolymerization.

Results and Discussion

Copolymerization of Propene and 1,5-Hexadiene. Copolymerization of propene and 1,5-hexadiene was conducted at 40 °C with the isospecific zirconocene **1** and the syndiospecific zirconocene **2**. The results are summarized in Tables 1 and 2. The rate of polymerization (R_p) decreased with an increase of 1,5-hexadiene in the monomer in both systems. The molecular weight of copolymer obtained with **2** decreased with the increase of 1,5-hexadiene in the monomer; besides, no clear tendency was found in the case of using **1**.

1,5-Hexadiene content in the copolymers was determined by ^{1}H NMR spectroscopy according to the literature.[7] Copolymerization diagrams of propene/1,5-hexadiene with **1** and **2** are shown in Figure 1. A consistently higher incorporation of 1,5-hexadiene was observed with **2** than with **1**. This tendency is in good agreement with

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Table 1. Results of Propene/1,5-Hexadiene (HD) Copolymerization with *rac*-$Me_2Si(Ind)_2ZrCl_2$ (1)−MAO[a]

no.	propene (mol/L)	HD (mol/L)	HD in monomer (mol %)	t^b (min)	yield (g)	$R_p{}^c$	HD in polymer[d] (mol %)	[C][e] (%)	*cis*[f] (%)	Δ[C][g] (%)	$T_g{}^h$ (°C)	$M_n{}^i$ ($\times 10^{-4}$)	$M_w/M_n{}^i$
1			0	30	8.7	8700	0				−18.7	1.9	2.6
2	0.568	0.042	6.9	30	6.5	6500	3.1	95.5	35.1		−9.6	2.1	2.6
3	0.567	0.084	12.9	30	4.2	4200	4.9	94.7	35.7		−8.4	2.0	3.0
4	0.561	0.211	27.5	30	2.3	2300	15.6	94.6	33.6	3.7	−6.9	1.9	2.9
5	0.553	0.421	43.2	60	4.3	2000	26.4	93.1	35.4	4.0	−3.1	2.6	3.9
6	0.535	0.842	61.1	60	1.7	860	43.3	91.7	37.8	5.1	−1.0	1.9	3.1
7	0.484	2.106	81.3	60	1.2	600	64.8	88.6	37.7	4.2	1.0	2.9	3.0
8[j]		0.842	100	30	8.4	8400	100	96.8	29.5		24.6		

[a] Polymerization conditions: Zr = 2.0 μmol, molar ratio of (MAO)Al/Zr = 3000, 1,5-hexadiene + toluene = 200 mL, propene = 1 atm, polymerization temperature = 40 °C. [b] Polymerization time. [c] Rate of polymerization (kg of polymer/(mol of Zr h)). [d] Determined by ^{13}C NMR spectroscopy. [e] Cyclization selectivity determined by ^1H NMR spectroscopy. [f] Content of *cis* units in cyclic units. [g] Δ[C] = (cyclization selectivity in homopolymerization of 1,5-hexadiene) − (cyclization selectivity in copolymerization, [C]). [h] Glass transition temperature. [i] Determined by GPC using polystyrene standards. [j] 1,5-Hexadiene (20 mL) + toluene (180 mL).

Table 2. Results of Propene/1,5-Hexadiene (HD) Copolymerization with $Ph_2C(Cp)(Flu)ZrCl_2$ (2)−MAO[a]

no.	propene (mol/L)	HD (mol/L)	HD in monomer (mol %)	t^b (min)	yield (g)	$R_p{}^c$	HD in polymer[d] (mol %)	[C][e] (%)	*cis*[f] (%)	Δ[C][g] (%)	$T_g{}^h$ (°C)	$M_n{}^i$ ($\times 10^{-4}$)	$M_w/M_n{}^i$
9			0	60	4.0	2000	0				−2.0	13.6	2.7
10	0.568	0.042	6.9	30	1.1	1100	5.8	98.8	35.1		−3.3	8.2	2.7
11	0.567	0.084	12.9	30	0.83	830	11.3	98.6	35.7		−2.2	5.8	2.6
12	0.561	0.211	27.5	60	1.2	580	25.5	98.2	33.6	0.2	−1.2	4.2	2.8
13	0.553	0.421	43.2	60	1.0	500	33.8	98.1	35.4	−0.1	1.8	3.5	2.6
14	0.535	0.842	61.1	60	0.90	450	50.3	96.3	37.8	0.6	−1.9	1.7	2.8
15	0.484	2.106	81.3	60	0.40	200	72.5	93.8	37.7	−0.1	5.2	2.2	2.0
16[j]		0.842	100	60	0.41	210	100	96.9	29.5		1.8	1.8	3.3

[a] Polymerization conditions: Zr = 2.0 μmol, molar ratio of (MAO)Al/Zr = 3000, 1,5-hexadiene + toluene = 200 mL, propene = 1 atm, polymerization temperature = 40 °C. [b] Polymerization time. [c] Rate of polymerization (kg of polymer/(mol of Zr h)). [d] Determined by ^{13}C NMR spectroscopy. [e] Cyclization selectivity determined by ^1H NMR spectroscopy. [f] Content of *cis* units in cyclic units. [g] Δ[C] = (cyclization selectivity in homopolymerization of 1,5-hexadiene) − (cyclization selectivity in copolymerization, [C]). [h] Glass transition temperature. [i] Determined by GPC using polystyrene standards. [j] 1,5-Hexadiene (20 mL) + toluene (180 mL).

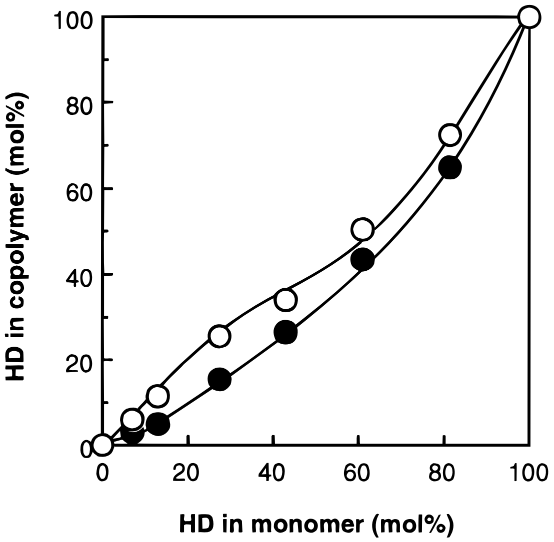


Figure 1. Copolymerization diagrams of propene/1,5-hexadiene with **1** (●) and **2** (○).

the results of propene/1-hexene copolymerization, which was conducted with specific catalysts by Soga et al.[8]

^{13}C NMR and DEPT (distortionless enhancement by polarization transfer) (135°) spectra of the copolymer obtained with **1** in run 5 are shown in Figure 2, a and b, respectively. Scheme 1 shows the corresponding structures and chemical shifts in the ^{13}C NMR spectroscopy of propene/1,5-hexadiene copolymer. The resonances of 20.0−22.2, 28.9, 30.2, 31.4, 45.1, and 46.6 ppm are assigned to propene units in the copolymer. The resonances at 32.4−33.0, 33.6−34.2, 37.0, 38.4, 39.8, 40.4, 41.7, 44.3, and 45.1 ppm are assignable to cyclic units of methylene-1,3-cyclopentane (MCP) derived from the intramolecular cyclization of 1,5-hexadiene.[9] ^{13}C NMR and DEPT (135°) spectra of the copolymer obtained with **2** in run 13 are shown in Figure 3, a and b, respectively. The resonances can be assigned according to the method described above.

To characterize the microstructures of propene/1,5-hexadiene copolymers more precisely, we investigated ^{13}C NMR spectroscopy of the copolymers with different 1,5-hexadiene contents. The microstructures of propene/1,5-hexadiene copolymer obtained with **1** and **2** are summarized also in Tables 1 and 2, respectively. The average [*cis*]/[*trans*] molar ratios of MCP units in these copolymers are 35.8/64.2 with **1** and 31.7/68.3 with **2**. Waymouth et al. reported the effect of metallocene structures on the diastereoselectivity (selectivity of *cis*-cyclization or *trans*-cyclization) in the 1,5-hexadiene polymerization with various zirconocene catalysts.[4d] They concluded that diastereoselectivity in cyclopolymerization of 1,5-hexadiene was affected by the bulkiness of ligand and bite angle associated with the zirconocene catalyst precursors rather than by the symmetry of the zirconocene precursors. Moreover, Cavallo et al. carried out conformational calculations about the diastereoselectivity and reported a good agreement with the polymerization results.[3d] The results of propene/1,5-hexadiene copolymerization with **1** (C_2 symmetrical) and **2** (C_s symmetrical) described above agree with their studies.

Conformational structures of isolated MCP units give important information about the enantioselectivity of propene and 1,5-hexadiene insertion mechanism. Figures 4 and 5 show ^{13}C NMR spectra of the copolymers with low 1,5-hexadiene content prepared by **1** (run 3)

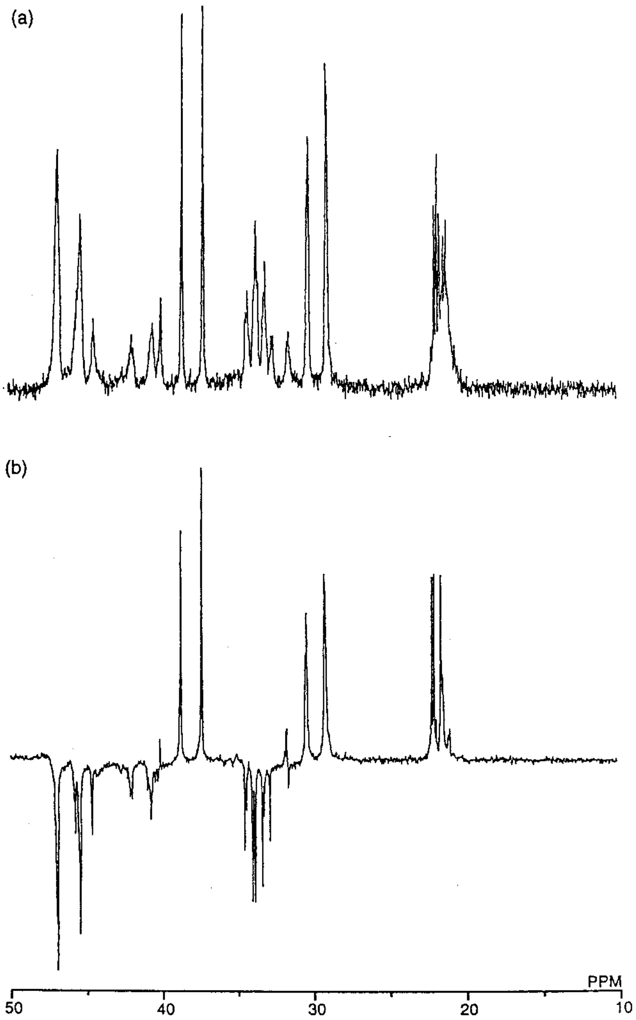


Figure 2. ^{13}C NMR spectrum (a) and DEPT spectrum (b) of propene/1,5-hexadiene copolymer obtained with **1** (run 5).

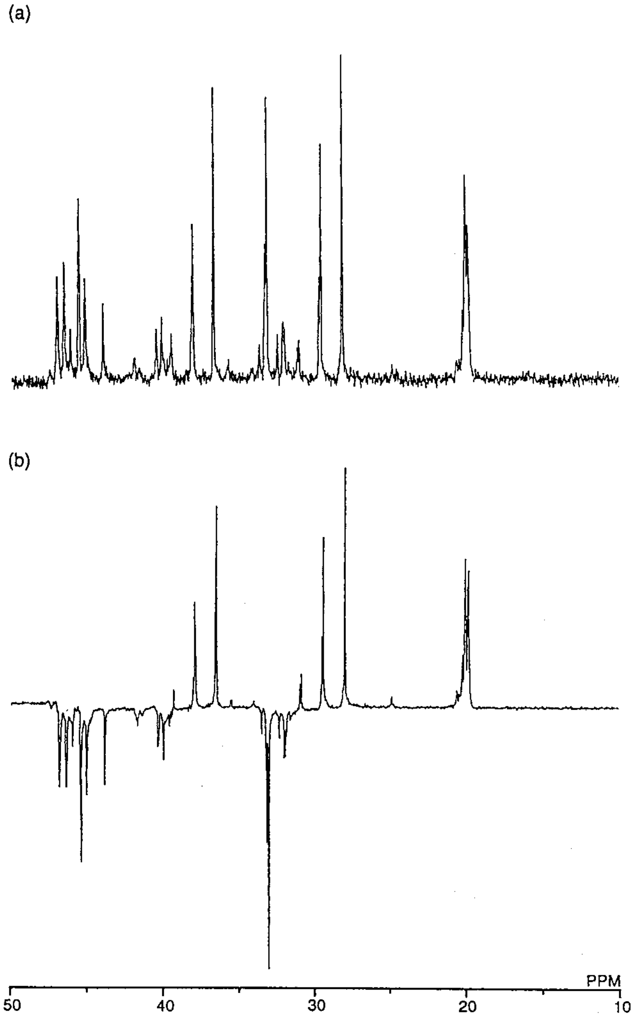
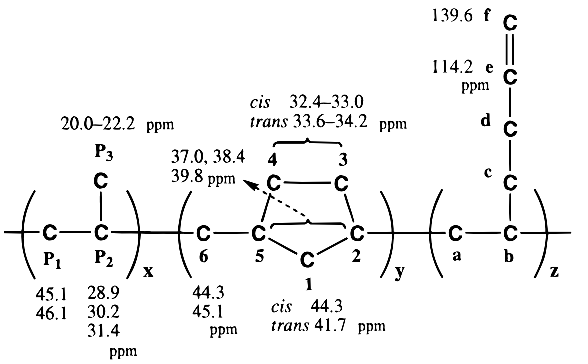


Figure 3. ^{13}C NMR spectrum (a) and DEPT spectrum (b) of propene/1,5-hexadiene copolymer obtained with **2** (run 13).

Scheme 1



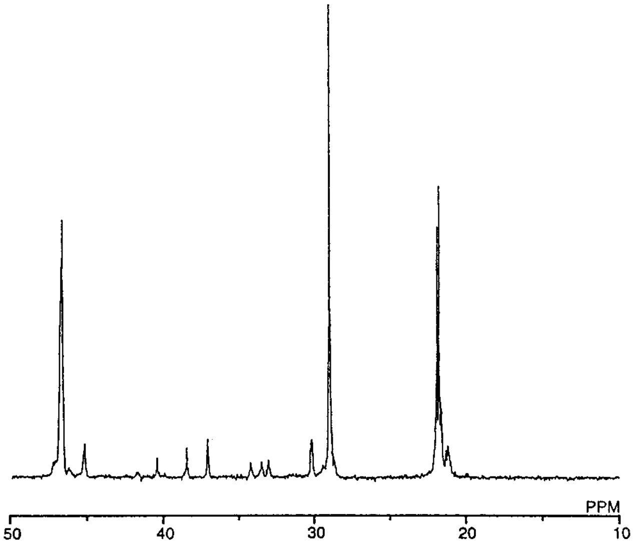


Figure 4. ^{13}C NMR spectrum of propene/1,5-hexadiene copolymer obtained with **1** (run 3).

and **2** (run 11), respectively. In these figures, the absence of a resonance at around 44.3 ppm, which is observed when the cyclic 1,5-hexadiene units are adjacent to one another, indicates that all of the 1,5-hexadiene units are separated by propene units in the copolymers. No resonance is observed at 31.4 ppm in either Figure 4 or 5, and the resonances at 28.9 and 30.2 ppm could be assigned to the P_2 carbons of italic propene units as Pr—*Pr*—Pr and Pr—*Pr*—MCP sequence (Pr = propene), respectively. The resonances at 37.0, 38.4, and 39.8 ppm, which are observed in Figures 2 and 3, are assingnable to i-*trans*, i-*cis* + s-*trans*, and s-*cis* of 2,5 carbons (i = isolation, s = sequence) in the MCP units. There are three resonances at 33.0, 33.4, and 34.2 ppm derived from 3,4 carbons of MCP units in Figure 4, while, there are four resonances derived from the corresponding carbons at 32.4, 32.8, 33.5, and 34.0 ppm in Figure 5.[9]

We define stereoregulations of 3,4 carbons in the isolated MCP units next to propene units as *cis*-m, *cis*-

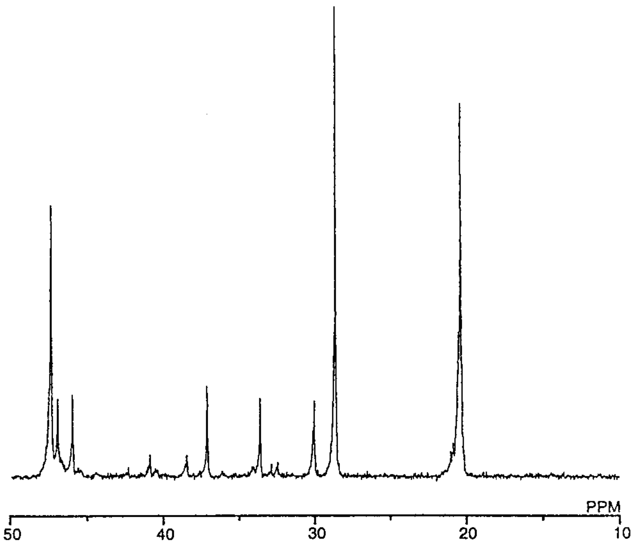
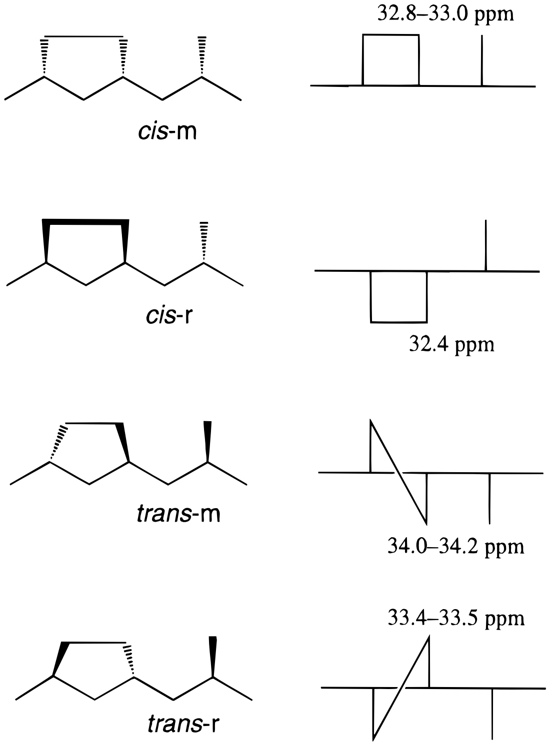


Figure 5. ^{13}C NMR spectrum of propene/1,5-hexadiene copolymer obtained with **2** (run 11).

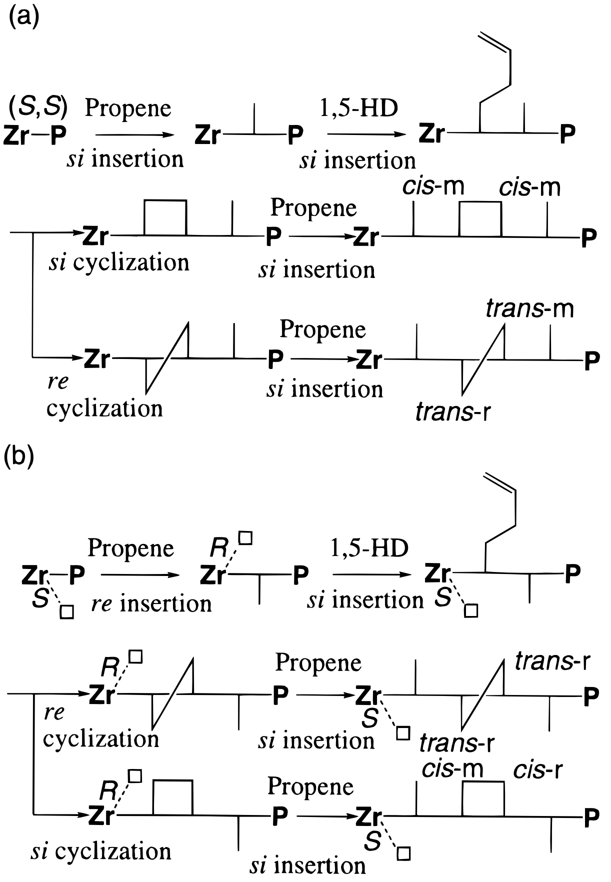
Scheme 2



r, *trans*-m, and *trans*-r as shown in Scheme 2. Assuming that the enantiomorphic site control of propene insertion and 1,2-insertion of 1,5-hexadiene proceeds with **1** as shown in Scheme 3a (*si* insertion of (*s*,*s*)-**1** is applied), *cis*-m, *trans*-m, and *trans*-r can be formed with the same intensity of *trans*-m and *trans*-r. In the same way, the copolymerization with **2** proceeds syndiospecifically as shown in Scheme 3b; *cis*-m and *cis*-r units can be formed together with *trans*-r units.

Judging from the chemical shifts and intensities of resonances in Figures 4 and 5, the resonances of 32.4, 32.8−33.0, 33.4−33.5, and 34.0−34.2 were assigned to isolated 3,4 carbons of *cis*-r, *cis*-m, *trans*-r, and *trans*-m units, respectively. In the case of using isospecific catalyst **1**, all of *cis* units are m type, and the molar ratio of *trans*-m to *trans*-r is almost 1 as shown in Figure

Scheme 3



4. These results indicate that the enantiomorphic site control of propene insertion and 1,2-insertion of 1,5-hexadiene proceeded as shown in Scheme 3a with **1**. If the propene insertion and 1,2-insertion of 1,5-hexadiene are perfectly controlled through the syndiospecific polymerization with **2**, no *trans*-m unit should be observed, and ratio of *cis*-m to *cis*-r should be 1 in the copolymer (Scheme 3b). The molar ratio of [*cis*-m]/[*cis*-r] is 46/54 and [*trans*-m]/[*trans*-r] is 8/92 in the copolymer obtained with **2** as shown in Figure 5. The [r] dyad in the syndiotactic polypropene with **2** (run 9) is 98%. We can suggest two mechanisms for the less stereoselectivity of 3,4 carbons in the isolated MCP units in the copolymer. One is that a propene insertion after the MCP units is less enantioselective in the copolymerization with **2**. The other is the chain migration of propagating chain end at MCP units to the another vacant site of **2** without a propene insertion.

The effect of 1,5-hexadiene concentration on the cyclization selectivity was discussed. Figure 6 shows the relationship between the cyclization selectivity ([C] = mole percent of cyclic units in the incorporated 1,5-hexadiene) and the 1,5-hexadiene concentration in the monomer. The results of 1,5-hexadiene homopolymerization with **1** and **2** are also plotted for references.[10] The cyclization selectivity decreased with an increase of the 1,5-hexadiene concentration in both 1,5-hexadiene homopolymerization and propene/1,5-hexadiene copolymerization. It is quite reasonable that insertion of another 1,5-hexadiene monomer is preferred to the cyclization of the 1,2-inserted unit under the high 1,5-hexadiene concentration. Mülhaupt et al. reported the same phenomenon in the 1,5-hexadiene polymerization with CGC.[6] Δ[C] values, which are summarized in Tables 1

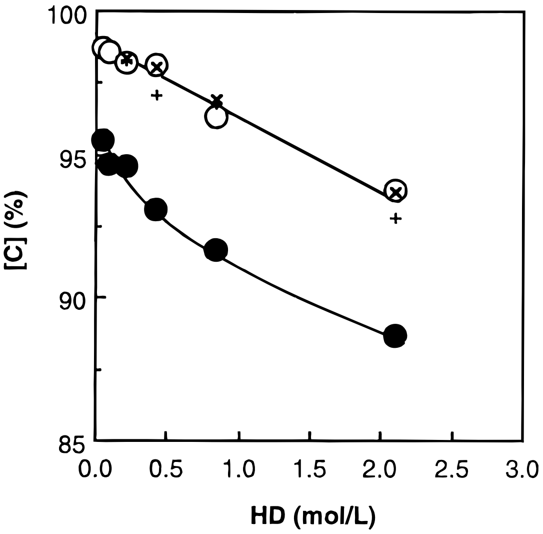


Figure 6. Plots of [C] (mole percent of cyclic units) against 1,5-hexadiene concentration of the propenen/1,5-hexadiene copolymerization (and 1,5-hexadiene homopolymerization) with **1** and **2**: copolymerization with **1** (●) and **2** (○), homopolymerization with **1** (+) and **2** (×).

and 2, mean the differences of cyclization selectivity between homopolymerization[10] and copolymerization at the same 1,5-hexadiene concentration in the monomer. No difference in the cyclization selectivity was observed between homopolymerization and copolymerization with **2**. On the other hand, the cyclization selectivities in the copolymerization with **1** are lower than those of in homopolymerization ($\Delta[C] = 3.7-5.1$ mol %). This result indicates that propene insertion could disturb the cyclization of the 1,2-inserted 1,5-hexadiene in the copolymerization with **1**.

Copolymerization of Propene and 1,7-Octadiene. Copolymerization of propene and 1,7-octadiene was conducted with **1** and **2** at 40 °C. The results are summarized in Tables 3 and 4, respectively. The rate of polymerization (R_p) and the molecular weight of resulting copolymer decreased with an increase of 1,7-octadiene concentration in the monomer. Copolymerization diagrams of propene/1,7-octadiene with **1** and **2** are shown in Figure 7, which indicates that **2** could incorporate more 1,7-octadiene than **1**.

^{13}C NMR and DEPT (135°) spectra of copolymers obtained with **1** in run 20 are shown in Figure 8, a and b, respectively. Scheme 4 illustrates plausible structures of the copolymer with nomenclature and chemical shift in the ^{13}C NMR spectroscopy of each carbon. The resonances of 21.0−22.1, 28.8, 44.1, and 46.5−47.5 ppm are assigned to P_3, P_2, and P_1 carbons of propene units in the copolymer. The resonances at 26.7, 36.8, 37.1, 42.2, 47.4−47.6, and 48.6 ppm are assignable to the cyclic units of methylene−cycloheptane as shown in Scheme 4. Furthermore, the resonances of 26.7, 30.0, 33.9, 34.0, 36.0, 42.4−42.6, 44.1, 114.5, and 139.5 ppm are assigned to 1,2-addition units of 1,7-octadiene without cyclization.[11] ^{13}C NMR and DEPT (135°) spectra of copolymer obtained with **2** in run 27 are shown in Figure 9, a and b, respectively. The resonances can be assigned according to the assignments in the copolymer obtained with **1**.

The effect of 1,7-octadiene concentration on the cyclization selectivity was discussed. The microstructures of 1,7-octadiene units were determined by ^{1}H NMR spectroscopy. We could detect a small amount of vinylene groups (less than 5% among the inserted 1,7-octadiene units) in the copolymers obtained with **1**, and this structure can be explained by the hydrogen elimination after a 2,1-addition of 1,7-octadiene, whose mechanism was observed in the polymerization of 1,7-octadiene with a vanadium-based catalyst.[7] The internal double bond in olefin polymerization could be formed through a chain-transfer mechanism, which was suggested in propene polymerization with zirconocene catalyst: Zr−CH=CHR (R = side chain of olefin) formed by vinylic C−H activation of olefin gives internal olefins by following monomer insertion.[12] Figure 10 shows plots of cyclization selectivity ([C] = mole percent of cyclic units in the incorporated 1,7-octadiene) against the 1,7-octadiene concentration in the monomer. The data of 1,7-octadiene homopolymerization with **1** and **2** are plotted for references.[13] Cyclization selectivity decreased with the increase of 1,7-octadiene concentration in both 1,7-octadiene homopolymerization and propene/1,7-octadiene copolymerization. **1** gave the poly(propene-*co*-1,7-octadiene)s with higher cyclization selectivity than that with **2**. This difference could be explained by conformational models in the transition state of cyclization. Assuming that both the initial insertion and the cyclization are enantiofacially selected, homofacial cyclization (*cis*-cyclization from *re*-insertion followed by *re*-cyclization or *si*-insertion followed by *si*-cyclization) with **1** and heterofacial cyclization (*trans*-cyclization from *re*-insertion followed by *si*-cyclization or *si*-insertion followed by *re*-cyclization) with **2** could proceed preferentially. The heterofacial cyclization with **2** hardly occurs because of the steric hindrance of the fluorenyl ligand, and the insertion of another monomer could be preferable to cyclization. More detailed conformational studies have been discussed in 1,7-octadiene homopolymerization and will be reported elsewhere.[13]

Δ[C] values, which are summarized in Tables 3 and 4, mean the differences of cyclization selectivity between homopolymerization[13] and copolymerization at the same 1,7-hexadiene concentration. The cyclization selectivity in the copolymerization is lower than that in the homopolymerization regardless of the catalysts. The values of Δ[C] in 1,7-octadiene polymerization were larger than those in the 1,5-hexadiene polymerization. These results indicate that propene insertion could occur frequently before the cyclization of the 1,2-inserted 1,7-octadiene at the propagating chain end. The values of Δ[C] in 1,7-octadiene polymerization were almost the same between these two catalysts at the same monomer concentration. This result suggests that the rate constants of propene insertion to the propagating chain ends with 1,2-inserted 1,7-octadiene are not so different between these catalysts.

Conclusion

Copolymers of propene and nonconjugated dienes with stereospecific metallocene catalysts give important information on the cyclization reaction of the incorporated dienes. The microstructures of propene/1,5-hexadiene copolymers proved clearly that 1,2-insertion of 1,5-hexadiene with isospecific and syndiospecific metallocene catalysts proceeded in enantiomorphic site control. On the other hand, diastereoselectivity of the cyclization reaction was independent of the stereospecificity of metallocene catalysts. Propene insertion disturbed the cyclization of 1,2-inserted 1,5-hexadiene in the copolymerization with **1**.

Table 3. Results of Propene/1,7-Octadiene (OD) Copolymerization with *rac*-$Me_2Si(Ind)_2ZrCl_2$ (1)−MAO[a]

no.	propene (mol/L)	OD (mol/L)	OD in monomer (mol %)	t^b (min)	yield (g)	R_p[c]	OD in polymer[d] (mol %)	[C][e] (%)	Δ[C][f] (%)	T_g[g] (°C)	M_n[h] ($\times10^{-4}$)	M_w/M_n[h]
17	0.572	0.034	5.6	30	2.1	2100	3.6	100.0		−5.0	1.9	2.7
18	0.569	0.068	10.6	30	0.93	930	6.7	83.7		−8.4	1.6	2.6
19	0.568	0.169	23.0	60	0.81	410	16.8	77.5	18.9	−2.1	1.1	2.5
20	0.566	0.339	37.4	120	0.68	170	25.0	72.9	22.0	2.8	0.93	2.5
21	0.562	0.677	54.7	120	0.47	120	38.4	70.3	14.2	5.0	0.68	2.4
22	0.549	1.692	75.7	180	0.16	27	60.6	62.7	12.3	20.5	0.69	2.3
23[i]		0.677	100	180	0.34	57	100	84.5		34.3	0.68	2.5

[a] Polymerization conditions: Zr = 2.0 μmol, molar ratio of (MAO)Al/Zr = 3000, 1,7-octadiene + toluene = 200 mL, propene = 1 atm, polymerization temperature = 40 °C. [b] Polymerization time. [c] Rate of polymerization (kg of polymer/(mol of Zr h)). [d] Determined by ^1H NMR spectroscopy. [e] Cyclization selectivity. [f] Δ[C] = (cyclization selectivity in homopolymerization of 1,7-octadiene) − (cyclization selectivity in copolymerization, [C]). [g] Glass transition temperature. [h] Determined by GPC using polystyrene standards. [i] 1,7-Octadiene (20 mL) + toluene (180 mL).

Table 4. Results of Propene/1,7-Octadiene (OD) Copolymerization with $Ph_2C(Cp)(Flu)ZrCl_2$ (2)−MAO[a]

no.	propene (mol/L)	OD (mol/L)	OD in monomer (mol %)	t^b (min)	yield (g)	R_p[c]	OD in polymer[d] (mol %)	[C][e] (%)	Δ[C][f] (%)	T_g[g] (°C)	M_n[h] ($\times10^{-4}$)	M_w/M_n[h]
24	0.572	0.034	5.6	30	0.50	500	4.7	69.7		1.0	5.4	2.9
25	0.569	0.068	10.6	60	0.45	230	10.0	66.7		7.9	3.4	3.2
26	0.568	0.169	23.0	60	0.29	140	20.5	58.9	18.9	13.4	1.8	3.1
27	0.566	0.339	37.4	120	0.31	77	35.9	53.9	22.0	8.9	1.5	2.4
28	0.562	0.677	54.7	120	0.17	43	46.0	44.3	14.2	−5.2	1.4	2.3
29	0.549	1.692	75.7	360	0.08	13	74.8	36.4	12.3		1.2	2.6
30[i]		0.677	100	360	0.10	8.3	100			2.2	0.75	2.4

[a] Polymerization conditions: Zr = 2.0 μmol, molar ratio of (MAO)Al/Zr = 3000, 1,7-octadiene + toluene = 200 mL, propene = 1 atm, polymerization temperature = 40 °C. [b] Polymerization time. [c] Rate of polymerization (kg of polymer/(mol of Zr h)). [d] Determined by ^1H NMR spectroscopy. [e] Cyclization selectivity. [f] Δ[C] = (cyclization selectivity in homopolymerization of 1,7-octadiene) − (cyclization selectivity in copolymerization, [C]). [g] Glass transition temperature. [h] Determined by GPC using polystyrene standards. [i] 1,7-Octadiene (20 mL) + toluene (180 mL).

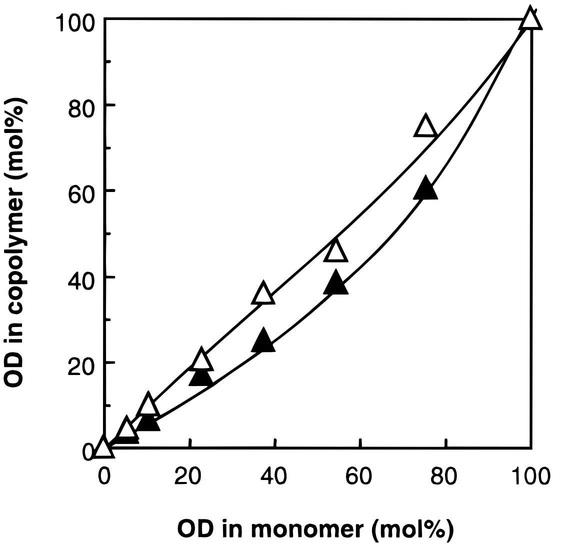


Figure 7. Copolymerization diagrams of propene/1,7-octadiene with **1** (▲) and **2** (△).

In propene/1,7-octadiene copolymerization, although the stereoselectivity of incorporated 1,7-octadiene could not be determined by ^{13}C NMR spectroscopy, there were some interesting results about the cyclization selectivity of 1,7-octadiene. The higher cyclization selectivity was observed in the copolymerization with **1** than with **2**. This result was opposite to that in the propene/1,5-hexadiene copolymerization (higher cyclization selectivity was observed with **2**). We considered the conformation of the transition state in the cyclization and suggested the possibility of enantioselective cyclization of the 1-hexenyl side chain by chiral catalytic sites. Propene insertion could occur frequently before the cyclization of 1,2-inserted 1,7-octadiene at the propagating chain end in the copolymerization with both **1** and **2**.

Copolymerization of propene and nonconjugated diene involving intramolecular cyclization with stereospecific metallocene catalysts could be one of the useful methods to synthesize the stereoregular polypropene with cyclic group. The decrease in polymerization activity was not so drastic compared to that of propene/cycloolefin copolymerization. The cyclization selectivity, namely, content of cyclic groups and pendent vinyl groups, could be controlled by the diene concentration in the monomer. In addition, the remained vinyl side chains could be transferred to functional groups or used for cross-linking reaction.

Experimental Part

Materials. Zirconocene complexes **1** and **2** were purchased from Witco Co., Ltd., and Boulder Science Co., Ltd., respectively, and used without further purification. Methylaluminoxane (MAO) was donated from Tosoh Akzo Co., Ltd., and used without further purification. Propene (from Mitsubishi Petrochemical Co., Ltd.) was purified by passing it through columns of NaOH, P_2O_5, and molecular sieves 3A. 1,5-Hexadiene, 1,7-octadiene, and toluene were commercially obtained and dried with CaH_2.

Copolymerizations of Propene and Nonconjugated Dienes. Copolymerizations of propene and dienes (1,5-hexadiene, 1,7-octadiene) were conducted in a 300 mL glass reactor equipped with a magnetic stirrer. Toluene and a diene (toluene + diene = 190 mL) were added to the reactor. Propene was introduced at 40 °C under 1 atm until the solvent was saturated with propene. The amount of dissolved propene was monitored by a gas flow meter to determine the propene concentration in the reaction medium. Toluene solution of MAO (6 mmol of [Al] in 10 mL of solution) and a metallocene catalyst were premixed in a 100 mL glass flask at 25 °C for 5

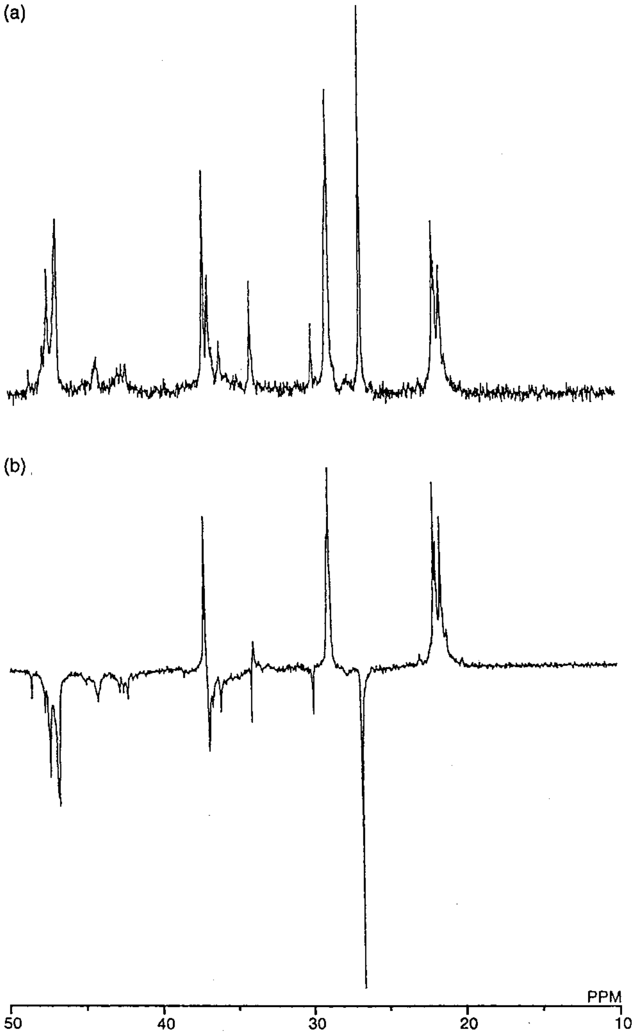


Figure 8. ^{13}C NMR spectrum (a) and DEPT spectrum (b) of propene/1,7-octadiene copolymer obtained with **1** (run 20).

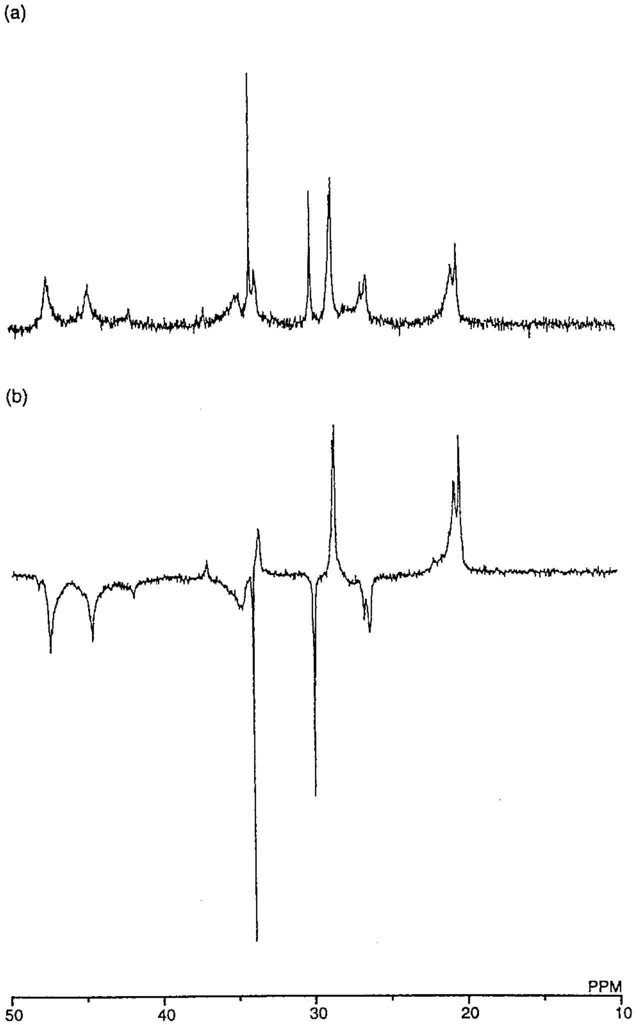
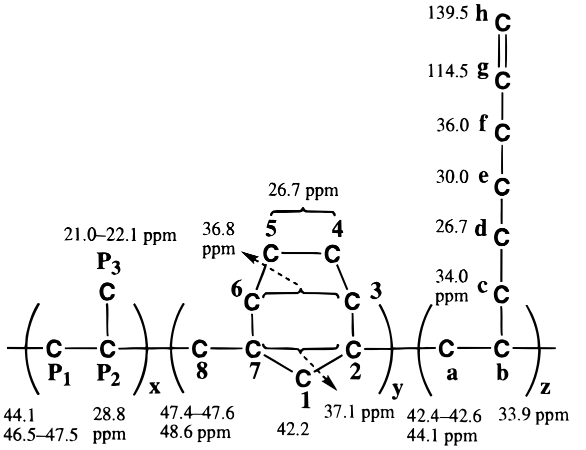


Figure 9. ^{13}C NMR spectrum (a) and DEPT spectrum (b) of propene/1,7-octadiene copolymer obtained with **2** (run 27).

Scheme 4



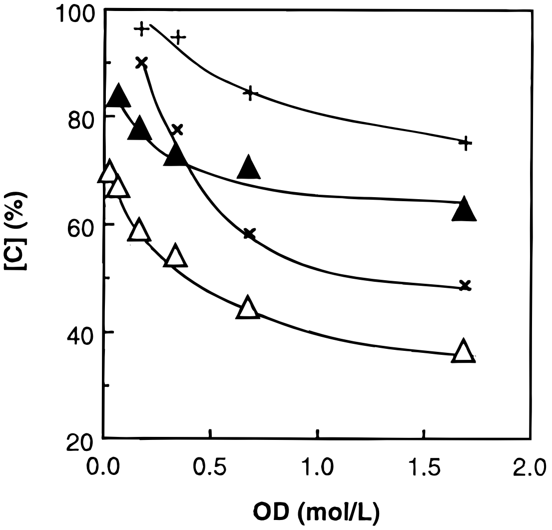


Figure 10. Plots of [C] (mole percent of cyclic units) against 1,7-octadiene concentration of the propenen/1,7-octadiene copolymerization (and 1,7-octadiene homopolymerization) with **1** and **2**: copolymerization with **1** (▲) and **2** (△), homopolymerization with **1** (+) and **2** (×).

min. Polymerization was started by introducing the premixed catalyst solution into the reactor. Polymerization was terminated by adding a small amount of methanol. The reaction medium was filtered to remove the catalyst residues. The resulting polymer was obtained by evaporation of filtrate and dried in vacuo at 60 °C for 6 h.

Analytical Procedure. Molecular weight and molecular weight distribution of the produced polymers were measured at 140 °C by means of gel permeation chromatography (GPC, Waters 150C) using *o*-dichlorobenzene as a solvent and calibrated with standard polystyrene samples. ^{1}H NMR, ^{13}C NMR, and DEPT spectra were recorded at 130 °C using a JEOL EX-400 NMR spectrometer in the pulse Fourier transfer (FT) mode. Polymers were dissolved in 1,1,2,2-tetrachloroethane-d_2 (2 wt % for ^{1}H NMR and up to 10 wt % for ^{13}C NMR and DEPT). In the ^{1}H NMR measurements, the pulse angle was 45°, and 50−100 scans were accumulated in 7 s of pulse repetition. In the ^{13}C NMR measurements, the pulse angle was 45°, and 1000−1500 scans were accumulated in 5.4 s of pulse repetition. In the DEPT measurements, the pulse angle was 135°, and 1000−1500 scans were accumulated in 5.4 s of pulse repetition. Differential scanning calorimetry (DSC) measurements were made on a Seiko DSC-220 (Seiko Instruments Inc., Tokyo) at a heating rate of 10 °C/min after previous heating to 200 °C and cooling to −50 °C by 10 °C/min.

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(9) The resonances in the ^{13}C NMR spectra of poly(propene-*co*-1,5-hexadiene)s were assigned as described below. We can recognize from the chemical shifts of polypropenes that the resonances at 20−22.2, 28.9 (with **1**), 28.6 (with **2**), and 46.6 ppm were derived from P_3, P_2 (m), P_2 (r), and P_1 of the homosequential units, respectively. Moreover, from the chemical shifts of poly(MCP) homopolymer, the resonances of 32.4, 33.4, 38.4, 39.8, 40.4, 41.7, and 44.3 ppm were assigned to *cis*-3,4, *trans*-3,4, *trans*-2,5, *cis*-2,5, *trans*-1, *cis*-1, and 6 in the homosequential units, respectively.[3,4,10] The primary, secondary, and tertiary carbons could be distinguished by the DEPT spectra of the copolymers. In the ^{13}C NMR spectra of copolymers with low content of HD, the resonances at 30.2 and 45.1 ppm were observed and assignable to P_2 and CH_2 (P_1 and 6) of Pr−MCP sequences. Besides, the resonances of 32.4, 32.8−33.0, 33.4−33.5, and 34.0−34.2 were assigned to isolated-3,4 of *cis*-r, *cis*-m, *trans*-r, and *trans*-m, respectively, as described in the Results and Discussion. The resonances of tertiary carbon 37.0 and 38.4 ppm were observed at almost the same intensity of isolated *trans*-3,4 and *cis*-3,4, and we assigned those resonances to isolated *trans*-2,5 and *cis*-2,5, respectively. In the ^{13}C spectra of the copolymers with high content of HD, the resonance of 31.4 ppm from tertiary carbon was found and assigned to the P_2 of the MCP−Pr−MCP sequence.

(10) Homopolymerization of 1,5-hexadiene with **1** and **2** was carried out under the same conditions of propene/1,5-hexadiene copolymerization (without propene) in the half scale.

(11) The resonances in the ^{13}C NMR spectra of poly(propene-*co*-1,7-octadiene)s were assigned form the chemical shifts of polypropene, poly(1,7-octadiene) with and without an intramolecular cyclization.[7,13]

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(13) Homopolymerization of 1,7-octadiene with **1** and **2** was carried out under the same conditions of propene/1,7-octadiene copolymerization (without propene) in the half scale. The detailed data were submitted for publication.

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