Polymerization of Isoprene with Ni(acac)₂–Methylaluminoxane Catalyst

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ABSTRACT: The polymerization of isoprene (IP) with transition metals (MtX) and methylaluminoxane (MAO) catalysts was carried out. Nickel(II) acetylacetonate [Ni(acac)₂] in combination with MAO revealed high catalytic activity. The microstructure of the polymers obtained with the Ni(acac)₂–MAO catalyst was mainly *cis*-1,4-units, and but no 1,2-units were observed, indicating that the polymerization of IP with the Ni(acac)₂–MAO catalyst proceeds through a mainly 4,1-addition mode. From the copolymerization of styrene (St) and IP with the Ni(acac)₂ and MAO catalyst, monomer-reactivity ratios were estimated to be $r_{\text{St}} = 1.18$ and $r_{\text{IP}} = 0.88$, indicating an ideal copolymerization to proceed to give a random copolymer. The IP units in the copolymers consist of mainly *cis*-1,4-microstructure.

KEY WORDS: Polymerization / Isoprene / Nickel(II) Acetylacetonate / Methylaluminoxane / Ideal Copolymerization / Styrene /

Many studies have been reported on polymerizations of olefins with group IV metallocene in combination with methylaluminoxane (MAO).^{1–13} Group VIII metal compounds were found to be effective catalysts for the polymerization of ethylene and α -olefins.^{14–16} On the other hand, the polymerizations of dienes with transition metals (MtX) and MAO catalysts have not been given much attention, although some works on the polymerizations of dienes have been reported.^{17–19} The polymerization of IP with nickel(II) acetylacetonate [Ni(acac)₂] in combination with MAO gives *cis*-1,4-poly(IP), but the detailed microstructure and kinetics of polymerization with the Ni(acac)₂–MAO catalyst were not investigated.¹⁸

Previously, we reported that the Ni(acac)₂–MAO catalyst showed high catalytic activity for the polymerization of methyl methacrylate,²⁰ styrene (St),²¹ and butadiene (BD).²² Thus, it is interesting to know whether the Ni(acac)₂–MAO catalyst is effective for the polymerization of isoprene (IP) and produces high *cis*-1,4 polymers as well as the polymerization of BD.²² In this article, we investigate the polymerization of IP with MtX–MAO catalysts, especially Ni(acac)₂–MAO catalyst.

When copolymerizations of St and IP with anionic catalysts such as alkylolithiums were carried out, random copolymers were not produced, and IP units were incorporated predominantly into the copolymers.^{23,24} Copolymerizations of St and IP with CpTiCl₃–MAO catalyst have been reported to produce fairly random copolymers,^{25,26} but the Ni(acac)₂–MAO catalyst was not examined. In a previous paper,²¹ we assumed that the polymerization of St with Ni(acac)₂–MAO catalyst may involve a homolytic scission of nickel-carbon bonds. Thus, it should be possible to obtain random copolymers in the copolymerization of St and IP with Ni(acac)₂–MAO catalyst. To check this point, we examined the copolymerization of St and IP with the Ni(acac)₂–MAO catalyst.

EXPERIMENTAL

Materials

IP and St were purified by distillation over calcium hydride before use. Ni(acac)₂ was used after sublimation. Other transition metal compounds purchased from Dojin Chem. Co. were used without further purification. MAO supplied from Tosoh-Akzo Co. was used as toluene solution as received, and its molecular weight was about 1100 in toluene. Solvents and other reagents were used after purification by conventional methods.

Polymerization

Polymerization and copolymerization were carried out in a sealed glass tube with a rubber septum with a connection to a vacuum system. The required amounts of reagents were charged by syringe through the septum. After polymerizations, the tube was opened, and the contents in the tube were poured into a large amount of methanol containing a few percent hydrochloric acid to precipitate the polymers formed. After washing in excess of methanol, the polymers were dried under vacuum. Polymer and copolymer yields were determined by gravimetry.

Characterization of Polymers

The number- and weight-average molecular weights (M_n and M_w , respectively) were determined by gel-permeation chromatography (GPC) using a Tosoh GPC-8000 series instrument in THF at 38°C (calibrated with standard polystyrenes). The microstructures of polymers and the copolymer composition were determined by ¹H and ¹³C NMR spectra recorded on JEOL A-400 NMR spectrometer in *d*-chloroform at 25°C as described previously.^{21,27}

RESULTS AND DISCUSSION

Polymerization of IP with Mt(acac)_x–MAO Catalyst

The results of the polymerization of IP with transition metal acetylacetonates [Mt(acac)_x] in combination with MAO are shown in Table I. The polymerization rate of IP was found to depend on Mt(acac)_x used, and the

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Table I. Polymerization of IP with $\text{Mt}(\text{acac})_x$ -MAO catalysts in toluene at 0°C^a

$\text{Mt}(\text{acac})_x$	Time	Yield	$M_n \times 10^{-4}$	M_w/M_n	Microstructure/%			
	h	%			<i>cis</i> -1,4-	<i>trans</i> -1,4-	3,4-	1,2-
$\text{Ni}(\text{acac})_2$	48	7.0	1.3	1.96	86	7	7	0
$\text{Cr}(\text{acac})_3$	48	8.3	0.2	1.29	80	13	7	0
$\text{V}(\text{acac})_3$	48	12.4	5.0	4.25	75	17	8	0
$\text{Fe}(\text{acac})_3$	48	6.9	1.5	1.94	83	10	7	0
$\text{Co}(\text{acac})_3$	48	0.2	1.0	1.47	85	9	6	0
$\text{Mn}(\text{acac})_3$	48	0	—	—	—	—	—	—

^a $[\text{IP}] = 4.0 \text{ mol L}^{-1}$; $[\text{Mt}(\text{acac})_x] = 0.5 \times 10^{-3} \text{ mol L}^{-1}$; $[\text{MAO}]/[\text{Mt}(\text{acac})_x] = 100$.

Figure 1. Relationships between electronegativity of the transition metal and microstructure of poly(IP) obtained with the $\text{Mt}(\text{acac})_x$ -MAO catalysts. For polymerization conditions see the footnote to Table I.

catalytic activities of these catalysts for the polymerization of IP were lower than those for the polymerization of BD.²²

The microstructures of the polymers of IP determined by their ^1H NMR spectra are also listed in Table I. The $\text{Ni}(\text{acac})_2$ -MAO catalyst gave the highest *cis*-1,4 content (*cis*-1,4 = 85.8%), although other catalysts also afforded polymers consisting of high *cis*-1,4-unit. High *cis*-1,4-poly(IP) was also obtained with MAO-containing catalysts as reported previously.^{18,19} The polymers obtained with the $\text{Ni}(\text{acac})_2$ -MAO catalyst have no 1,2-units, indicating that propagating chain ends attack at the terminal carbon of the vinylene group in IP monomer. The GPC elution curves of the polymers obtained with the $\text{Ni}(\text{acac})_2$ -MAO catalyst were a monomodal, and M_n of the polymer was more than 10^4 and M_w/M_n was 1.96. This suggests that the polymerization of IP with the $\text{Ni}(\text{acac})_2$ -MAO catalyst took place at a single active site. Since no polymers were obtained with any catalyst component, binary components are necessary to form an active site for the polymerization of IP.

Figure 1 shows the relationship between electronegativity of the center metal and microstructure of poly(IP) obtained with the $\text{Mt}(\text{acac})_x$ -MAO catalysts. The contents of *cis*-1,4 units in the polymers increased with electronegativity of the metal determined by Allred-Rochow.²⁸

It is also interesting that polymers having high *cis*-1,4-units were obtained regardless of the transition metal when MAO was used as a cocatalyst. This is in contrast to the previously reported results,^{19,29} e.g., the polymerization of IP with $\text{V}(\text{acac})_3$ - AlEt_3 catalyst²⁹ produce polymers with 90% 3,4-content. A similar uniqueness of MAO in giving high *cis*-1,4-unit content was also observed in the polymerization of BD.²² Accordingly, MAO plays an important role to determine microstructures of polymers of conjugated dienes.

Polymerization of IP with the $\text{Ni}(\text{acac})_2$ -MAO Catalyst

Since the $\text{Ni}(\text{acac})_2$ -MAO catalyst revealed catalytic activity for the polymerization of IP and gave the high *cis*-1,4-polymers, the polymerization of IP with the $\text{Ni}(\text{acac})_2$ -MAO catalyst was examined in detail. The effects of ligand in the NiX_2 on the polymerization of IP with the $\text{Ni}(\text{acac})_2$ -MAO catalyst were examined. The results are shown in Table II. Stereoregularity and catalytic reactivity of polymerizations of olefins with transition metal-alkylaluminum catalysts are influenced by the ligands of the transition metals. However, the effects of ligand in NiX_2 on both microstructure and polymerization rate were not observed significantly; i.e., the transition metal and MAO are factors for producing catalytic activity and determining the microstructure of the polymers.

The effects of the polymerization temperature (0, 30, and 40°C) of IP with the $\text{Ni}(\text{acac})_2$ -MAO catalyst were checked. The results are listed in Table III. The contents of *cis*-1,4-units and M_n of the polymers did not change significantly by varying temperature.

The time-polymer yields curves for the polymerization of IP with the $\text{Ni}(\text{acac})_2$ -MAO catalyst are shown in Figure 2. The polymerization rate (R_p) increased with polymerization temperature. From the initial slope of these lines, Arrhenius plots were obtained as depicted in Figure 3. Since $\ln R_p$ and $1/T$ gave a straight line, the overall activation energy for the polymerization of IP with the $\text{Ni}(\text{acac})_2$ -MAO catalyst was determined to be 24.0 kJ mol^{-1} from the slope.

The dependence of monomer concentration on the polymerization of IP with the $\text{Ni}(\text{acac})_2$ -MAO catalyst was examined. The catalyst concentration was kept constant ($[\text{Ni}(\text{acac})_2] = 6.4 \times 10^{-3}$, $[\text{MAO}]/[\text{Ni}(\text{acac})_2] = 100$), and the results are depicted in Figure 4. A linear relationship between R_p and monomer concentration was observed. From the slope of the line, R_p was found to be proportional to the 1.8 power of the monomer concentration.

The effects of catalyst concentration on R_p for the

Table II. Effects of ligand of NiX₂ on the polymerization of IP with NiX₂-MAO catalyst in toluene at 0°C for 48 h^a

NiX ₂	Yield	M_n $\times 10^{-4}$	M_w/M_n	Microstructure/%			
	%			<i>cis</i> -1,4-	<i>trans</i> -1,4-	3,4-	1,2-
Ni(acac) ₂	7.0	1.3	1.96	86	7	7	0
Ni(C ₆ H ₅ COO) ₂	4.8	1.4	2.07	81	11	8	0
Ni(HCOO) ₂	0.5	0.9	3.40	—	—	—	—

^a [IP] = 4.0 mol L⁻¹; [NiX₂] = 0.5 × 10⁻³ mol L⁻¹; [MAO]/[NiX₂] = 100.**Table III.** Polymerization of IP with the Ni(acac)₂-MAO catalyst in toluene^a

Temp.	Time	Yield	M_n $\times 10^{-3}$	M_w/M_n	Microstructure/%			
		%			<i>cis</i> -1,4-	<i>trans</i> -1,4-	3,4-	1,2-
40	1	2.0	3.69	2.61	80	12	8	0
30	1	1.8	3.42	2.11	81	12	7	0
0	4	2.1	2.40	1.24	83	10	7	0

^a [Bd] = 3.0 mol L⁻¹; [Ni(acac)₂] = 7.0 × 10⁻³ mol L⁻¹; [MAO]/[Ni(acac)₂] = 100. **Figure 2.** Time-polymer yield curves for polymerization of IP with the Ni(acac)₂-MAO catalyst in toluene at 0°C (□), 30°C (Δ), and 40°C (○): [IP] = 3.0 mol L⁻¹; [Ni(acac)₂] = 7.0 × 10⁻³ mol L⁻¹; [MAO]/[Ni] = 100. **Figure 4.** Dependence of IP concentration on R_p for polymerization of IP with Ni(acac)₂-MAO catalyst in toluene at 0°C: [Ni(acac)₂] = 6.4 × 10⁻³ mol L⁻¹; [MAO]/[Ni(acac)₂] = 100. **Figure 3.** Arrhenius plots for the polymerization of IP with the Ni(acac)₂-MAO catalyst. For polymerization conditions see the footnote to Figure 2. **Figure 5.** Dependence of catalyst concentration on R_p for polymerization of IP with Ni(acac)₂-MAO catalyst in toluene at 0°C: IP = 2.0 mol L⁻¹; [MAO]/[Ni(acac)₂] = 100.

polymerization of IP with the Ni(acac)₂-MAO catalyst were examined at constant monomer concentration and MAO/Ni(acac)₂ mole ratio. The results are shown in Figure 5. From the slope of the straight line, the kinetic order of the catalyst concentration on R_p was estimated to be 0.7. Based on these results, R_p of the polymerization of IP with the Ni(acac)₂-MAO catalyst can be expressed as follows:

$$R_p = k[\text{IP}]^{1.8}[\text{Ni(acac)}_2\text{-MAO}]^{0.7}$$

where k is the overall polymerization rate constant.

This rate equation indicates that the polymerization mechanism of IP is similar to that obtained in the polymerization of BD with the Ni(acac)₂-MAO catalyst.²² The polymerization of IP proceeds through a coordination between nickel complexes and IP and bimolecular termination takes place.

Copolymerization of IP and St

Copolymerizations of St and IP with Mt(acac)_x in combination with MAO were carried out, and the results are shown in Table IV. The Ni(acac)₂-MAO catalyst revealed high catalytic activity for copolymerization. Since only the Ni(acac)₂-MAO catalyst showed high catalytic activity for the homopolymerization of St as reported previously,²¹ catalytic activity with respect to the Mt(acac)_x for the copolymerizations of St and IP appears to depend on the catalytic activity for the homopolymerization of St.

The copolymerization of St (M_1) and IP (M_2) with the Ni(acac)₂-MAO catalyst was carried out at different comonomer feed compositions. The results are shown in Table V. The copolymerization of St and IP was

compared with homopolymerizations of St and IP under similar conditions (run no. 1, 5, and 9). The copolymerization rate was faster than that of homopolymerization of IP, but was slower than that of St. Similar results are reported for the copolymerizations of St and IP with CpTiCl₃-MAO catalyst.^{25,26}

The microstructure of a IP unit estimated by analysis of ¹H and ¹³C NMR spectra of the polymers is rich in *cis*-1,4 contents, and no 1,2-units in the IP units were observed from the NMR spectra of the polymers, indicating that the propagating chain end attacks at the terminal carbon in the vinylene group of IP.²³ The GPC elution curves monitored by refractive index (RI) and UV detectors revealed the same unimodal distribution (Figure 6). The M_w/M_n of the polymers was around 2.0, suggesting the copolymerization to take place at a single active site, without the formation of a homopolymer.

From the copolymerization of St and IP with the Ni(acac)₂-MAO catalyst, a copolymer composition curve was obtained, and is shown in Figure 7, in which the reported curve obtained by radical copolymerization with benzoyl peroxide (BPO)³⁰ is indicated for comparison. The curve obtained with the Ni(acac)₂-MAO catalyst is very close to that obtained with radical copolymerization initiated by BPO.

Monomer-reactivity ratios determined by a nonlinear least-squares method based on a differentiation equation³¹ were $r_1 = 1.18$ and $r_2 = 0.88$ for the copolymerization of St and IP with the Ni(acac)₂-MAO catalyst. The product of $r_1 \times r_2$ was almost equal to 1. This indicates that ideal copolymerization of St with IP proceeds with the Ni(acac)₂-MAO catalyst to give perfectly random copolymers.

The contents of *cis*-1,4 IP units in the copolymers decreased with increasing St units in the comonomer feed, but 3,4-IP units were not influenced significantly by St units in the copolymers. The microstructure of IP seems related to the St unit incorporated. Similar behavior was found in the polymerization of St and BD.³²

From a kinetic study of the polymerization of IP and copolymerization of St and IP, we presumed that the polymerization involves coordination between nickel complex and IP and homolytic scission of nickel-carbon bonds. However, other explanations may be possible, e.g., a coordinated anionic mechanism. Since the detail

Table IV. Copolymerization of St and IP with Mt(acac)_x-MAO catalysts in toluene at 0°C for 48 h^a

Mt(acac) _x	Yield	[St] in copolymer
	%	mol%
Ni(acac) ₂ ^b	24.2	50.5
Co(acac) ₂	0.6	45.0
V(acac) ₃	2.8	11.0

^a [St] = [IP] = 2.0 mol L⁻¹; [Mt(acac)_x] = 2.0 × 10⁻³ mol L⁻¹; [MAO]/[Mt(acac)₂] = 100. ^b [Ni(acac)₂] = 5.0 × 10⁻⁴ mol L⁻¹.

Table V. Copolymerization of St (M_1) and IP (M_2) with Ni(acac)₂-MAO catalysts in toluene at 30°C for 1 h^a

Run no.	[M] in comonomer	Copolymer							
		Yield	[St]	M_n × 10 ⁻³	M_w/M_n	Microstructure of IP/%			
	mol%	%	mol%			<i>cis</i> -1,4	<i>trans</i> -1,4	3,4	1,2
1	0.0 ^b	7.0	—	13.0	2.0	85.8	7.2	7.0	0.0
2	20.0	2.6	22.0	4.8	2.0	83.2	10.5	6.3	0.0
3	40.0	3.3	44.1	5.0	2.0	81.3	13.5	5.2	0.0
4	50.0	5.7	53.8	5.3	1.9	79.1	16.4	4.5	0.0
5	50.0 ^b	24.2	50.4	15.2	2.0	80.7	13.0	6.3	0.0
6	60.0	7.7	62.8	5.6	2.0	76.5	19.2	4.3	0.0
7	80.0	16.7	82.9	6.9	2.2	70.5	23.5	6.0	0.0
8	100.0 ^c	35.8	100	31.7	2.1	—	—	—	—

^a ([St] + [IP]) = 4.0 mol L⁻¹; [Ni(acac)₂] = 5.0 × 10⁻⁴ mol L⁻¹; [MAO]/[Ni(acac)₂] = 100. ^b Polymerized at 0°C for 48 h. ^c Polymerized at 0°C for 1.0 h.

Figure 6. GPC elution curves for the copolymer obtained from copolymerization of St and IP with the Ni(acac)₂-MAO catalyst: —, intensity of RI detector; ---, intensity of UV (254 nm) detector.

Figure 7. Copolymer composition curves for copolymerizations of St (M_1) and IP (M_2) obtained with (1) Ni(acac)₂-MAO catalyst at 30°C ($r_1 = 1.18$; $r_2 = 0.88$) and (2) BPO at 80°C ($r_1 = 1.92$; $r_2 = 0.54$).

mechanism is not clear now, we are investigating the mechanisms for the polymerizations of conjugated monomers with nickel(II)-MAO catalysts.

CONCLUSIONS

Mt(acac)_x-MAO catalysts were found to be effective for the polymerization of IP. The Ni(acac)₂-MAO catalyst showed the highest catalytic activities for the polymerization of IP. The polymerization rate of IP was slower than those of BD and St, and polymerization of IP took place at a single active site. The microstructures of the polymers were mainly *cis*-1,4-units. From a kinetic

study, the polymerizations of IP with the Ni(acac)₂-MAO catalyst appears to proceed through a successive insertion of nickel-carbon bond after coordination of the diolefins to the nickel. Copolymerization parameters for the copolymerization of IP and St indicate ideal copolymerization to take place.

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