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Synthesis of stereodiblock polyisoprene consisting of *cis*-1,4 and *trans*-1,4 sequences by using a neodymium catalyst: change of the stereospecificity triggered by an aluminum compound†

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The first example of the synthesis of stereodiblock polyisoprene which consists of *cis*-1,4 and *trans*-1,4 sequences was achieved by using a neodymium catalyst. The stereospecificity was controlled by the ratio of Bu$_2$Mg and modified methylaluminoxane (MMAO), and by sequential addition of Bu$_2$Mg and MMAO, a geometrically well-defined stereodiblock polymer was obtained.

A stereoblock polymer, which contains multiple different stereosequences in one polymer chain, changes its physical properties from the original stereoregular polymer. One strategy to synthesize such a polymer is exchanging a propagating chain between two different metal species by equilibrium. Sita applied activated cationic zirconium for the isospecific propylene polymerization and unactivated neutral zirconium species for the racemization of stereocenters which are in equilibrium, giving an isotactic–atactic stereomultiblock polypropylene.[1] This stereomultiblock polypropylene shows elastomeric properties, whereas isotactic polypropylene shows crystallinity. More simply, mixing two different polymerization catalysts with a chain transfer reagent can also afford the isotactic-capped syndiotactic polystyrene[2] and isotactic–syndiotactic stereomultiblock polypropylene.[3] Sometimes a isostructural catalyst performs as an equilibrium of two kinds of catalysts with different symmetries by occasional flipping of the polymer chain or the rotation of the ligand during propylene polymerization, resulting in the formation of isotactic and atactic polypropylene blocks.[4,5]

Another way to synthesize stereoblock polymers is using a living polymerization system and changing the selectivity by external stimuli during polymerization (Scheme 1). In this synthetic strategy, the lengths of each block can be controlled precisely by the polymerization time. We have previously reported the synthesis of di- or triblock polypropylene which consists of

Stimulus
(Pressure, solvent, *etc.*)

Monomer + Cat.

t_1 t_2

t_2 t_1

stereodiblock polymer

Scheme 1 Synthetic strategy of stereodiblock polymers by changing the stereospecificity of living polymerization with an external stimulus.

syndiotactic and atactic sequences by changing the reaction temperature,[6] solvent[7] or monomer concentration.[8] However, none of them have control over two different high stereoregularities. Namely, they just control stereospecific polymerization and non-stereospecific polymerization.

Additives are among the most fundamental tools to control the selectivity of the metal-catalyzed reaction. In the coordination polymerization of olefins, the stereospecificity strongly depends on the symmetry of the catalyst and therefore it is difficult to control with additives. However, in the polymerization of conjugated dienes, a small amount of additives sometimes dramatically change the stereospecificities. For example, a *cis*/*trans*- or 1,4/1,2-specificity of butadiene polymerization can be controlled by the ratio of phosphine and metal precursors such as Ni(tfa)$_2$[9] and CoCl$_2$[10,11] activated by methylaluminoxane (MAO). In addition, main group metal alkyls, which can coordinate to transition metal with σ-bond bridges, are also applied as additives. The *cis*/*trans*-1,4 specificity of the isoprene polymerization catalyzed by Nd(BH$_4$)$_3$(thf)$_3$[12–14] or Y(allyl)$_2$Cl(MgCl$_2$)$_2$(thf)$_4$[15] is varied with activators such as Bu$_2$Mg, Ph$_3$CB(C$_6$F$_5$)$_4$, ^{i}Bu$_3$Al and MAO. Switching 3,4- and *cis*-1,4 specificities by the addition of Me$_3$Al to the yttrium amidinate catalyst is also reported.[16] The application of these

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additive effects to living polymerization systems would open up the way to the synthesis of stereodiblock polymers. As the first example, we were motivated to investigate the synthesis of geometrically well-defined stereodiblock[17] polyisoprene using a neodymium catalyst activated by Bu₂Mg, controlling cis-1,4 and trans-1,4 specificities in the living manner.

Nd(BH₄)₃(thf)₃ activated by Bu₂Mg can promote the trans-1,4 specific isoprene polymerization in a living manner (Table 1, run 1). For the synthesis of stereodiblock polyisoprene, the trans-1,4 specificity should be shifted to cis-1,4 in a living manner. Therefore, we first investigated the effect of several aluminum additives on the stereospecificity of isoprene polymerization. The 1,4/3,4 specificity was determined by ¹H NMR and the cis/trans specificity was determined by ¹³C NMR.[18]

An excess amount of modified methylaluminoxane (MMAO), which was prepared by the partial hydrolysis of ⁱBu₃Al and Me₃Al greatly increased the cis-1,4 specificity and activity so that the reaction proceeded at room temperature. The cis-1,4 ratio increased according to the Al/Mg ratio, whereas the 3,4-selectivity remained unchanged (runs 1–5). The molecular weight distribution became narrower and the cis-1,4 specificity was improved by the addition of ⁱBuCl, although the polymerization rate was decreased (run 6). The addition of Me₂SiCl₂ to dried MMAO (dMMAO) also gave a narrow molecular weight polymer (run 8). The use of ⁱBu₃Al gave small molecular weight poly(cis-1,4-isoprene), which is because of the frequent chain transfer between neodymium and aluminium (run 8). Such a tendency was also observed when Cp*La(BH₄)₂(thf)₂ was used as a catalyst precursor, although the change of selectivity from trans to cis did not take place.[19] Using MAO, which contains 30 mol% of Me₃Al (run 9), instead of MMAO decreased the activity probably because small Me₃Al can suppress the polymerization by coordinating to the cationic neodymium active species. MMAO alone did not promote the polymerization, indicating that cationic neodymium-alkyl species was not generated only by MMAO (run 10).

The ¹³C NMR spectrum of polyisoprene obtained by using the Nd–Mg/Al system (Table 1, run 4, cis : trans = 59 : 37) in the region of carbon at the 1-position (31–41 ppm) is shown in Fig. 1. Four peaks are observed corresponding to the tactic dyads, which are assigned to cis–trans (23%), trans–trans (16%), cis–cis (38%), and trans–cis (23%). The integral ratios of all the four peaks follow the statistical probability, showing that the cis–trans unit is randomly distributed in this polyisoprene.

In general, the cis/trans stereospecificity in the coordination polymerization of isoprene is determined as follows: when isoprene coordinates to the metal center in a cis-η⁴-manner, the following insertion gives anti-π-allyl species. Normally, the syn-π-allyl configuration which gives the trans-1,4 sequence is more stable than the anti-π-allyl configuration which gives the

Fig. 1 A part of the ¹³C NMR spectrum of polyisoprene synthesized by using the Nd–Mg/Al catalyst system (125 MHz, in CDCl₃, Table 1, run 4).

Table 1 Effect of aluminum compounds on the polymerization of isoprene using the Nd(BH₄)₃(thf)₃−Bu₂Mg system[a]

Nd(BH₄)₃(thf)₃ / Bu₂Mg / **Al source**
toluene, 60 min

Run	Nd (μmol)	Al source	Al/Mg	Toluene (mL)	Temp. (°C)	Yield (%)	M_n[b] (10³)	PDI[b]	Cis/trans/3,4[c] (mol%)
1	38	None	—	1.3	40	15	11	1.1	5 : 93 : 2
2	25	MMAO	10	1.4	r.t.	Trace	n.d.[d]	n.d.[d]	n.d.[d]
3[e]	25	MMAO	20	1.7	r.t.	97	78	1.6	48 : 48 : 4
4	25	MMAO	40	1.2	r.t.	89	121	1.5	59 : 37 : 4
5	18	MMAO	100	3.1	r.t.	49	55	1.7	85 : 11 : 4
6[f]	33	MMAO	100	3.4	40	25	24	1.4	90 : 8 : 2
7[g]	50	dMMAO	100	2.9	r.t.	22	34	1.4	84 : 11 : 5
8	50	ⁱBu₃Al	100	2.3	r.t.	43	3	1.3	72 : 24 : 4
9	45	MAO	100	2.9	r.t.	4	10	1.5	n.d.[d]
10[h]	25	MMAO	100	1.8	r.t.	0	n.d.[d]	n.d.[d]	n.d.[d]

[a] Reaction conditions: [isoprene]/[Nd] = 625, [Bu₂Mg]/[Nd] = 1, time = 60 min, and solvent = toluene. [b] Determined by GPC calibrated with the polystyrene standard. [c] Determined by ¹H and ¹³C NMR. [d] Not determined. [e] The amount of Bu₂Mg was 2 equiv. of Nd. [f] 1 equiv. of ⁱBuCl was added and the time was 10 h. [g] 0.25 equiv. of Me₂SiCl₂ was added. [h] Bu₂Mg was not added.

cis-1,4 sequence because of the steric hindrance of the polymer chain. Therefore, the *trans*-1,4 sequence is obtained when the *anti–syn* configurational equilibrium is fast enough compared with the propagation. The *cis*-1,4 sequence is obtained when the propagation is faster than the *anti–syn* equilibrium, namely, as a kinetic product. When isoprene coordinates in a *trans*-η^4-manner, the *syn*-π-allyl intermediate, which gives the *trans*-1,4 sequence, would be obtained regardless of the rate of the *anti–syn* equilibrium.[20]
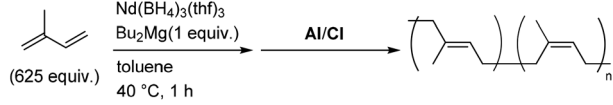
Alkylmagnesium is considered as an alkylating reagent and the NMR investigation implies that Nd–Mg bimetallic species is formed in the previously reported Nd–Bu$_2$Mg system.[12,21] Taube reported *trans*-1,4 specific polymerization of butadiene using (C$_3$H$_5$)$_3$Nd and the stereospecificity is because of the steric hindrance of the propagating chain forcing the butadiene monomer to bind in a *trans*-η^4 or η^2 manner.[22] The *trans*-specificity of Nd(BH$_4$)$_3$(thf)$_3$–Bu$_2$Mg can also be derived by following this mechanism: the isoprene coordinates to the neutral neodymium species in a *trans*-η^4 or η^2 manner because of the steric hindrance of alkylmagnesium, and the following *syn*-π-allyl intermediate would give the *trans*-1,4 sequence.

On the other hand, a cationic neodymium catalyst from Nd(BH$_4$)$_3$(thf)$_3$[23] or neutral dialkyl neodymium (C$_3$H$_5$)$_2$NdCl[24] can promote the *cis*-1,4 specific polymerization of conjugated dienes. Excess alkylaluminum can form a dimer with magnesium and a naked neodymium is generated, which can derive the enhancement of the propagation rate and allow isoprene to coordinate in a *cis*-η^4 manner. As a result, a kinetic *cis*-1,4 product would be obtained. In our mixed cocatalyst system, a fast equilibrium between Nd–Mg bimetallic species and Mg–Al multimetallic species would propagate the *cis/trans* random sequences (Fig. 2). The relatively broad molecular weight distribution when MMAO is applied is probably because of the deactivation of the unstable naked cationic active species. The addition of chloride would prevent the deactivation by coordinating to the neodymium center.[25,26]

The synthesis of stereodiblock polymers by the sequential addition of Bu$_2$Mg and MMAO/^{t}BuCl or dMMAO/Me$_2$SiCl$_2$ was performed (Table 2). In both systems, a polymer with a narrow molecular weight distribution was obtained in high yield. The GPC trace of the obtained polymer shifted to higher molecular weight from the prepolymer obtained using the Nd–Bu$_2$Mg system with a narrow molecular weight distribution (Fig. 3). This result strongly suggested that the polymer was obtained in a living manner. The integral ratios of *cis–cis* and *trans–trans* dyads from ^{13}C NMR were much higher than the others, indicating the formation of a stereodiblock polymer which consists of *cis*- and *trans*-polyisoprene sequences (Fig. 4).

The synthesized *cis–trans* stereodiblock polyisoprene in Table 2, run 2 showed a melting point (T_m) at 33 °C, which was almost the same value with *trans*-1,4-polyisoprene obtained in Table 1, run 1 (37 °C), although the melting

Table 2 Synthesis of stereodiblock polyisoprene using the Nd–Mg/Al system[a]

Run	Al/Cl source	Time (h)	Yield (%)	M_n[b] (10³)	PDI[b]	Cis/ trans[c]
1	None	1	15	11	1.1	5 : 93
2[d]	MMAO/^{t}BuCl	1 + 10	88	79	1.3	48 : 50
3[e]	dMMAO/Me$_2$SiCl$_2$	1 + 1	59	34	1.3	35 : 61
4[e]	dMMAO/Me$_2$SiCl$_2$	1 + 5	78	50	1.4	48 : 48

[a] Reaction conditions for the first block: [isoprene]/[Nd] = 625, [Bu$_2$Mg]/[Nd] = 1, temp. = 40 °C, time = 1 h, and solvent = toluene. [b] Determined by GPC calibrated with the polystyrene standard. [c] Determined by ^{1}H and ^{13}C NMR. [d] Nd = 37 mol, [Al]/[Nd] = 100, [Cl]/[Nd] = 1, temp. = 40 °C. [e] Nd = 50 mol, [Al]/[Nd] = 100, [Cl]/[Nd] = 0.25, temp. = r.t.
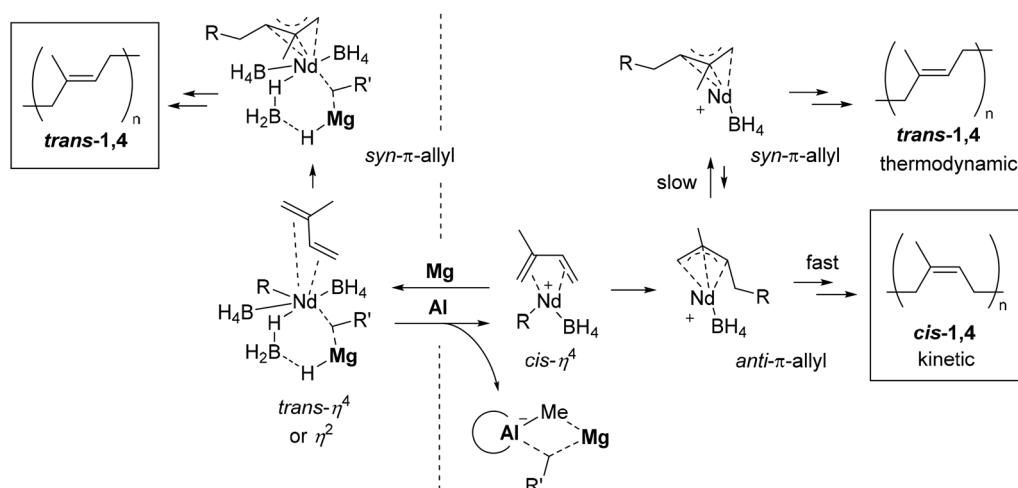

Fig. 2 Estimated active species and the mechanism of the change of stereospecificity in the polymerization of isoprene using the Nd–Mg/Al system.

Fig. 3 GPC traces of *trans*-1,4-polyisoprene (right, Table 1, run 1) and *trans*-1,4-*b*-*cis*-1,4-polyisoprene (left, Table 2, run 2) measured at 150 °C in 1,2,4-trichlorobenzene.

Fig. 4 A part of the ^{13}C NMR spectrum of *trans*-1,4-*b*-*cis*-1,4-polyisoprene obtained in Table 2, run 2 (125 MHz, in CDCl$_3$).

enthalpy (ΔH) was much smaller compared with *trans*-1,4-polyisoprene (7 *vs.* 62 J g^{-1}). The decrease of the melting enthalpy was probably because of the high miscibility of *cis*-1,4 and *trans*-1,4 blocks.[27] The tensile modulus of the stereodiblock polymer was 1.7 MPa, which was the typical value of an elastomeric material. Therefore, the synthesized stereodiblock polymer had both the crystallinity and elastomeric properties.

Conclusions

In conclusion, we succeeded in controlling the *cis*/*trans*-1,4 selectivity of isoprene polymerization initiated by Nd(BH$_4$)$_3$(thf)$_3$ by the addition of Bu$_2$Mg and MMAO. The *cis*-1,4 specificity reached 90% when the Al/Mg ratio was 100. The stereodiblock polymer which consists of *cis*-1,4 and *trans*-1,4 blocks was successfully synthesized by sequential addition of alkylmagnesium and MMAO in the presence of a monomer.

Experimental section

General

All manipulations were performed under nitrogen gas using standard Schlenk techniques. Modified methylaluminoxane

(MMAO, 6.5 wt% Al, 2.17 M in toluene) was donated by Tosoh-Finechem Co. Dried MMAO was prepared according to the literature.[28] Isoprene was distilled over CaH$_2$ and stored with 4A molecular sieves. Bu$_2$Mg (1 : 1 mixture of *s*-butyl and *n*-butyl, 1.0 M in heptane) was purchased and used as received. Nd(BH$_4$)$_3$(thf)$_3$ was synthesized according to the literature.[29] Dry toluene was purchased from Kanto Chemical Co., Inc., and further dried over sodium metal. ^{1}H and ^{13}C NMR spectra of the polymer were measured by using a Varian 500 MHz spectrometer using CDCl$_3$ as a solvent. The obtained spectra were calibrated by the peaks originating from the solvent (^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm). The number-average molecular weight (M_n) of the polymer was determined by using a Viscotec 350HT-GPC chromatograph at 150 °C using 1,2,4-trichlorobenzene as an eluent calibrated with a RI/Viscometer/MALS triple detector, or Tosoh HLC-8320 at 40 °C using THF as an eluent calibrated with the PS standard. The polymer concentration of the injecting solution was 1 mg mL^{-1} and the injection volume was 0.2 mL. DSC analyses of the polymer were performed by using a SII EXSTAR6000 system. The tensile modulus of the polymer was measured by using an Olientec RTC-1210A instrument following ISO 527-3/1B at 25 °C with a drawing rate of 50 mm min^{-1}.

Isoprene polymerization was carried out using the Nd(BH$_4$)$_3$(thf)$_3$–Bu$_2$Mg/MMAO system (Table 1, run 5)

To a 20 mL Schlenk flask, Nd(BH$_4$)$_3$(thf)$_3$ (18 mg, 44 μmol) and Bu$_2$Mg in toluene (44 μmol, 40 mM, 1.1 mL), and MMAO (2.0 mL, 4.4 mmol) were charged and stirred at room temperature for 3 minutes. To the yellow solution, isoprene (2.8 mL, 28 mmol) was added. The reaction mixture was stirred at room temperature for 1 hour. The resulting solution was poured into acidic methanol containing 1 wt% of BHT and the precipitated solid was recovered. The polymer was dried under vacuum overnight until constant weight. 909 mg (49%) of a colorless viscous polymer was obtained.

Synthesis of stereodiblock polyisoprene using the Nd(BH$_4$)$_3$(thf)$_3$–Bu$_2$Mg/MMAO/^{t}BuCl system (Table 2, run 2)

To a 20 mL Schlenk flask, Nd(BH$_4$)$_3$(thf)$_3$ (15 mg, 37 μmol) and Bu$_2$Mg in toluene (37 μmol, 40 mM, 0.93 mL) were charged and stirred at room temperature for 3 minutes. To the yellow solution, isoprene (2.34 mL, 23.4 mmol) was added. The reaction mixture was warmed to 40 °C and stirred for 1 hour. To the mixture was added the mixture of toluene solution of MMAO (2.3 mL, 4.9 mmol) and ^{t}BuCl (4.0 μL, 37 μmol) and further stirred for 10 hours. The resulting solution was poured into acidic methanol containing 1 wt% of BHT and the precipitated solid was recovered. The polymer was dried under vacuum overnight until constant weight. 1.40 g (88%) of a colorless polymer was obtained.
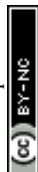
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