Polymer Chemistry

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Polymer Chemistry

COMMUNICATION

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

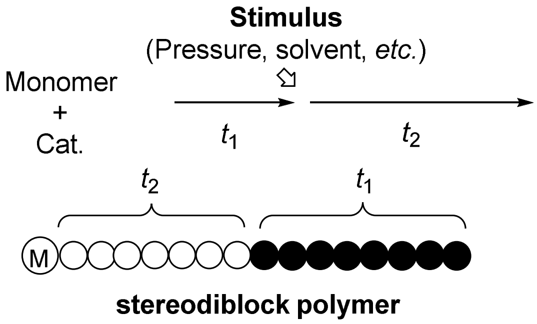
www.rsc.org/

Ryo Tanaka, Kaede Yuuya, Hiroki Sato, Peter Eberhardt, Yuushou Nakayama, Takeshi Shiono

The first example of the synthesis of stereodiblock polyisoprene which consist of *cis*-1,4 and *trans*-1,4 sequences was achieved by using neodymium catalyst. The stereospecificity was controlled by the ratio of Bu_2Mg and modified methylaluminoxane (MMAO), and by the sequential addition of Bu_2Mg and MMAO, geometrically well-defined stereodiblock polymer was obtained.

Stereoblock polymer, which contains multiple different stereosequences in one polymer chain, changes their physical properties from the original stereoregular polymers. One strategy to synthesize such a polymer is exchanging a propagating chain between two different metal species by the equilibrium. Sita applied activated cationic zirconium for the isospecific propylene polymerization and unactivated neutral zirconium species for the racemization of stereocenter which are in equilibrium, giving an isotactic-atactic stereomultiblock polypropylene.[1] This stereomultiblock polypropylene shows elastomeric property, whereas isotactic polypropylene shows crystallinity. More simply, mixing two different polymerization catalysts with chain transfer reagent can also afford the isotactic-capped syndiotactic polystyrene[2] and isotactic-syndiotactic stereomultiblock polypropylene.[3] Sometimes isostructural catalyst performs as an equilibrium of two kinds of catalyst with different symmetry by the 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 polymer is using a living polymerization system and changing the selectivity by external stimuli during the polymerization (Scheme 1). In this synthetic strategy, the lengths of each block can be controlled precisely by the polymerization time. We previously reported the synthesis of di- or triblock polypropylene which consists of syndiotactic and atactic sequences by changing reaction temperature,[6] solvent[7] or monomer concentration.[8] However, none of them can control over two different high stereoregularity. Namely, they just control over stereospecific polymerization and non-stereospecific polymerization.



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

Additives are one of 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, *cis*/*trans*- or 1,4/1,2- specificity of butadiene polymerization can be controlled by the ratio of phosphine and metal precursor 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. *Cis*/*trans*-1,4 specificity of the isoprene polymerization catalyzed by $Nd(BH_4)_3(thf)_3$[12-14] or $Y(allyl)_2Cl(MgCl_2)_2(thf)_4$[15] are varied with activators such as Bu_2Mg, $Ph_3CB(C_6F_5)_4$, $^iBu_3Al$ and MAO. Switching 3,4- and *cis*-1,4 specificities by the addition of Me_3Al to yttrium amidinate catalyst is also reported.[16] The application of these additive effects to living polymerization systems would open up the way

---

Graduate School of Engineering, Hiroshima University
1-4-1 Kagamiyama, Higashi-hiroshima, Hiroshima, 739-8527 Japan

Electronic Supplementary Information (ESI) available: [NMR spectra and DSC traces of the obtained polymer]. See DOI: 10.1039/x0xx00000x

Polymer Chemistry Accepted Manuscript

to the synthesis of stereodiblock polymer. As an first example, we were motivated to investigate the synthesis of geometrically well-defined stereodiblock[17] polyisoprene using neodymium catalyst activated by Bu_2Mg controlling *cis*-1,4 and *trans*-1,4 specificity keeping the living manner.

$Nd(BH_4)_3(thf)_3$ activated by Bu_2Mg can promote *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 keeping a living manner. Therefore, we first investigated the effect of several aluminum additives on the stereospecificity of isoprene polymerization. 1,4/3,4 specificity was determined by ^1H NMR and *cis*/*trans* specificity was determined by ^{13}C NMR.[18]

Excess amount of modified methylaluminoxane (MMAO), which was prepared by the partial hydrolysis of $^iBu_3Al$ and Me_3Al greatly increased *cis*-1,4 specificity and activity so that the reaction proceeded at room temperature. *Cis*-1,4 ratio increased according to the Al/Mg ratio, whereas the 3,4-selectivity was kept unchanged (run 1-5). Molecular weight distribution got narrower and *cis*-1,4 specificity was improved by the addition of ^tBuCl, although the polymerization rate was decreased (run 6). The addition of Me_2SiCl_2 to dried MMAO (dMMAO) also gave narrow molecular weight polymer (run 8). Use of $^iBu_3Al$ gave small molecular weight poly(*cis*-1,4-isoprene), which is because of frequent chain transfer between neodymium and aluminium (run 8). Such a tendency was also observed when $Cp^*La(BH_4)_2(thf)_2$ was used as catalyst precursor, although the change of selectivity from *trans* to *cis* did not take place.[19] Using MAO, which contains 30 mol% of Me_3Al (run 9), instead of MMAO decreased the activity probably because small Me_3Al 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 by MMAO (run 10).

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

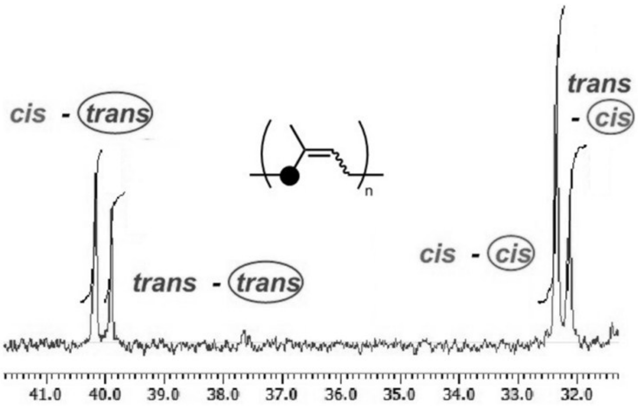
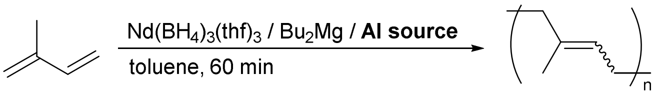


Fig. 1 A part of ^{13}C NMR spectrum of polyisoprene synthesized by Nd–Mg/Al catalyst system (125 MHz, in $CDCl_3$, Table 1, run 4).

Table 1 Effect of aluminum compounds on the polymerization of isoprene using $Nd(BH_4)_3(thf)_3$–Bu_2Mg system[a].



Run	Nd (μmol)	Al source	Al/Mg	Toluene (mL)	Temp. (°C)	Yield (%)	M_n[b] (10^3)	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	$^iBu_3Al$	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, $[Bu_2Mg]/[Nd] = 1$, Time = 60 min, Solvent = toluene. [b] Determined by GPC calibrated with polystyrene standard. [c] Determined by ^1H and ^{13}C NMR. [d] Not determined. [e] The amount of Bu_2Mg was 2 equiv. of Nd. [f] 1 equiv. of ^tBuCl was added and time was 10 h. [g] 0.25 equiv. of Me_2SiCl_2 was added. [h] Bu_2Mg was not added.

Polymer Chemistry Accepted Manuscript

Please do not adjust margins

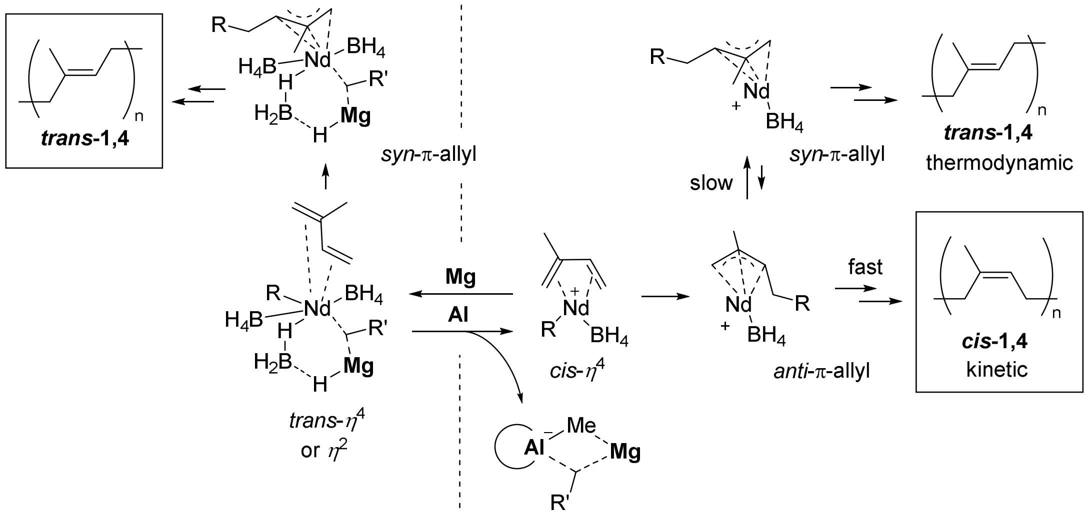


Fig. 2 Estimated active species and mechanism of the change of stereospecificity in the polymerization of isoprene using Nd-Mg/Al system.

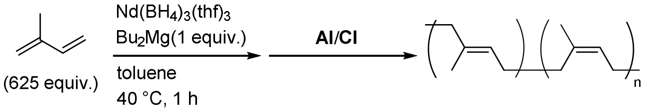
In general, the *cis*/*trans* stereospecificity in the coordination polymerization of isoprene is determined as followings: when isoprene coordinates to the metal center in a *cis*-η^4-manner, the following insertion gives *anti*-π-allyl species. Normally, *syn*-π-allyl configuration which gives *trans*-1,4 sequence is more stable than *anti*-π-allyl configuration which gives *cis*-1,4 sequence because of the steric hindrance of polymer chain. Therefore, *trans*-1,4 sequence is obtained when the *anti*-*syn* configurational equilibrium is fast enough compared with the propagation. *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, *syn*-π-allyl intermediate, which gives *trans*-1,4 sequence, would be obtained regardless of the rate of *anti*-*syn* equilibrium.[20]

Alkylmagnesium is considered as alkylating reagent and NMR investigation implies that Nd-Mg bimetallic species is formed in the previously reported Nd–Bu_2Mg system.[12,21] Taube reported *trans*-1,4 specific polymerization of butadiene using $(C_3H_5)_3Nd$ and the stereospecificity is because of the steric hindrance of the propagating chain forced butadiene monomer to bind in *trans*-η^4 or η^2 manner.[22] The *trans*-specificity of $Nd(BH_4)_3(thf)_3$–Bu_2Mg can also be derived following this mechanism: the isoprene coordinate to the neutral neodymium species in *trans*-η^4 or η^2 manner because of the steric hindrance of alkylmagnesium, and the following *syn*-π-allyl intermediate would give *trans*-1,4 sequence.

On the other hand, cationic neodymium catalyst from $Nd(BH_4)_3(thf)_3$[23] or neutral dialkyl neodymium $(C_3H_5)_2NdCl$[24] can promote *cis*-1,4 specific polymerization of conjugated dienes. Excess alkylaluminum can form dimer with magnesium and naked neodymium is generated, which can derive the enhancement of the propagation rate and allow isoprene to coordinate in *cis*-η^4 manner. As a result, 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). 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 polymer by the sequential addition of Bu_2Mg and MMAO/^{t}BuCl or dMMAO/Me_2SiCl_2 was performed (Table 2). In both system, polymer with 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 with Nd–Bu_2Mg system keeping narrow molecular weight distribution (Fig. 3). This result strongly suggested the polymer was obtained in a living manner. The integral ratios of *cis*-*cis* and *trans*-*trans* dyads from ^{13}C NMR were much larger than the others, indicating the formation of stereodiblock polymer which is consist of *cis*- and *trans*- polyisoprene sequences (Fig. 4).

Table 2 Synthesis of stereodiblock polyisoprene using Nd-Mg/Al system. [a].



Run	Al /Cl source	Time (h)	Yield (%)	M_n[b] (10^3)	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_2SiCl_2	1+1	59	34	1.3	35 : 61
4[e]	dMMAO/Me_2SiCl_2	1+5	78	50	1.4	48 : 48

[a] Reaction conditions for first block: [Isoprene]/[Nd] = 625, [Bu_2Mg]/[Nd] = 1, Temp. = 40 °C, Time = 1 h, Solvent = toluene. [b] Determined by GPC calibrated with polystyrene standard. [c] Determined by ^1H and ^{13}C NMR. [d] Nd = 37 μmol, [Al]/[Nd] = 100, [Cl]/[Nd] = 1, Temp. = 40 °C. [e] Nd = 50 μmol, [Al]/[Nd] = 100, [Cl]/[Nd] = 0.25, Temp. = r.t..

Polymer Chemistry Accepted Manuscript

Please do not adjust margins

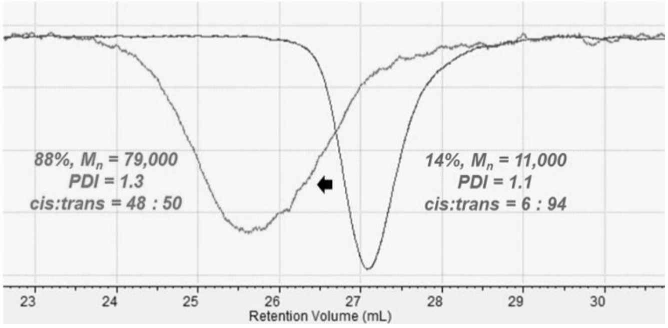


Fig. 3 GPC traces of *trans*-1,4-polyisoprene (right, Table 1, Run 1) and *trans*-1,4-*b*-*cis*-1,4-polyisoprene (left, Table 2, run 2) measured at 150 °C in 1,2,4-trichlorobenzene.

The synthesized *cis*-*trans* stereodiblock polyisoprene in Table 2, run 2 showed 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 enthalpy (ΔH) was much smaller compared with *trans*-1,4-polyisoprene (7 vs. 62 J/g). The decrease of 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 elastomeric material. Therefore, the synthesized stereodiblock polymer had both of the crystallinity and elastomeric property.

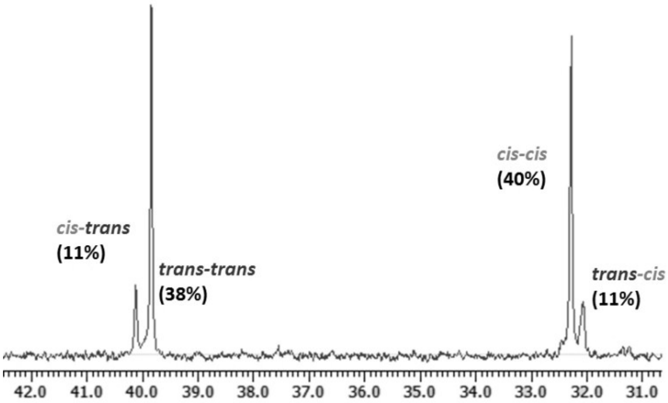


Fig. 4 A part of ^{13}C NMR spectrum of *trans*-1,4-*b*-*cis*-1,4-polyisoprene obtained in Table 2, run 2 (125MHz, in $CDCl_3$).

Conclusions

In conclusion, we succeeded in controlling *cis*/*trans*-1,4 selectivity of isoprene polymerization initiated by $Nd(BH_4)_3(thf)_3$ by the addition of Bu_2Mg and MMAO. *Cis*-1,4 specificity reached to 90% when Al/Mg ratio was 100. The stereodiblock polymer which consists of *cis*-1,4 and *trans*-1,4 block was successfully synthesized by the sequential addition of alkylmagnesium and MMAO under the presence of monomer.

Experimental Section

General.

All manipulations were performed under nitrogen gas using standard Schlenk techniques. Modified methylaluminoxane (MMAO, 6.5 wt%Al, 2.17M 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_2Mg (1:1 mixture of *s*-butyl and *n*-butyl, 1.0 M in heptane) was purchased 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 a Varian 500MHz spectrometer using $CDCl_3$ as a solvent. The obtained spectra were calibrated by the peaks originated from the solvent (^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm). Number-average molecular weight (M_n) of the polymer was determined by a Viscotec 350HT-GPC chromatograph at 150 °C using 1,2,4-trichlorobenzene as an eluent calibrated with RI/Viscometer/MALS triple detector, or Tosoh HLC-8320 at 40 °C using THF as an eluent calibrated with PS standard. The polymer concentration of the injecting solution was 1 mg/mL and the injection volume was 0.2 mL. DSC analyses of the polymer were performed by a SII EXSTAR6000 system. Tensile modulus of the polymer was measured by Olientec RTC-1210A instrument following ISO 527-3/1B at 25 °C with a drawing rate of 50 mm/min.

Isoprene polymerization using $Nd(BH_4)_3(thf)_3$–Bu_2Mg/MMAO system (Table 1, Run 5).

To a 20mL Schlenk flask, $Nd(BH_4)_3(thf)_3$ (18 mg, 44 μmol) and Bu_2Mg in toluene (44 μmol, 40 mM, 1.1 mL), and MMAO (2.0 mL, 4.4 mmol) were charged in this direction 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 colorless viscous polymer was obtained.

Synthesis of stereodiblock polyisoprene using $Nd(BH_4)_3(thf)_3$–Bu_2Mg/MMAO/^{t}BuCl system (Table 2, run 2).

To a 20mL Schlenk flask, $Nd(BH_4)_3(thf)_3$ (15 mg, 37 μmol) and Bu_2Mg 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 colorless polymer was obtained.

Notes and references

† We are grateful to Tosoh Finechem Co. for generous donation of chemicals. We also gratefully acknowledge the Natural Science Center for Basic Research and Development

Polymer Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

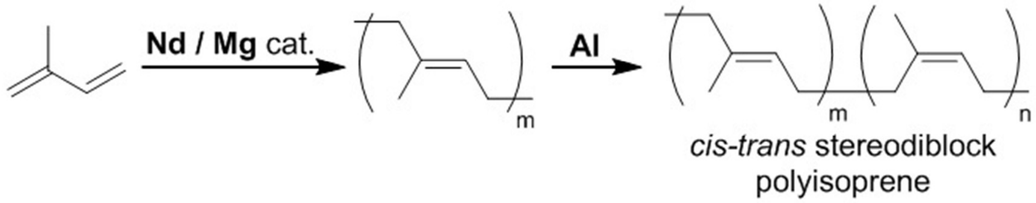
(N-BARD), Hiroshima University, for the high temperature NMR measurement.

1 M. B. Harney, Y. Zhang, L. R. Sita, *Angew. Chem. Int. Ed.,* 2006, **45**, 2400-2404.
2 R. Po, S. Spera, *Polym. J.,* 2010, **42**, 416-418.
3 C. Descour, T. Macko, D. Cavallo, M. Parkinson, G. Hubner, A. Spoelstra, M. Villani, R. Duchateau, *J. Polym. Sci. Part A: Polym. Chem.,* 2014, **52**, 1422-1434.
4 D. T. Mallin, M. D. Rausch, Y. –G. Lin, S. Dong, J. C. W. Chien, *J. Am. Chem. Soc.*, 1990, **112**, 2030-2031.
5 G. W. Coates, R. M. Waymouth, *Science*, 1995, **267**, 217-219.
6 Z. Cai, Y. Nakayma, T. Shiono, *Macromolcules,* 2008, **41**, 6596-6598.
7 Z. Cai, Y. Nakayma, T. Shiono, *Kinet. Catal.,* 2006, **47**, 274-277.
8 Z. Cai, Y. Nakayma, T. Shiono, *Macromol. Res.,* 2010, **18**, 737-741.
9 P. Hadjiandrreou, M. Julemont, P. Teyssie, *Macromolecules,* 1984, **17**, 2455-2456.
10 D. C. D. Nath, T. Shiono, T. Ikeda, *Macromol. Chem. Phys.,* 2003, **204**, 2017-2022.
11 Z. Cai, M. Shinzawa, Y. Nakayama, T. Shiono, *Macromolecules,* 2009, **42**, 7642-7643.
12 F. Bonnet, M. Visseaux, A. Pereira, D. Barbier-Baudry, *Macromolecules*, 2005, **38**, 3162-3169.
13 M. Terrier, M. Visseaux, T. Chenal, A. Mortreux, *J. Polym. Sci. Part A: Polym. Chem.,* 2007, **45**, 2400-2409.
14 F. Bonnet, C. E. Jones, S. Semlali, M. Bria, P. Roussel, M. Visseaux, P. L. Arnold, *Dalton Trans.,* 2013, **42**, 790-801.
15 N. Ajellal, L. Furlan, C. M. Thomas, O. L. Casagrande, J. –F. Carpentier, *Macromol. Rapid Commun.*, 2006, **27**, 338-343.
16 L. Zhang, M. Nishiura, M. Yuki, Y. Luo, Z. Hou, *Angew. Chem. Int. Ed.,* 2008, **47**, 2642-2645.
17 Currently the use of term ‘geometrical isomer’ was strongly discouraged and cis-trans isomer was categorized as a stereoisomer. Thus, these kinds of block polymer should be called as ‘stereoblock polymer’, although there is no stereogenic center in the polymer. See: (a) G. P. Moss, *Pure Appl. Chem.*, 1996, **68**, 2193-2222. (b) A. D. Jenkins, *Pure Appl. Chem.*, 1981, **53**, 733-752.
18 M. W. Duch, D. M. Grant, *Macromolecules,* 1970, **3**, 165-174.
19 A. Valente, P. Zinck, M. J. Vitorino, A. Mortreux, M. Visseaux, *J. Polym. Sci. Part A: Polym. Chem.*, 2010, **48**, 4640-4647.
20 R. Taube, H. Windisch, S. Maiwald, *Macromol. Symp.,* 1995, **89**, 393–409.
21 F. Bonnet, H. E. Dye, Y. El Kinani, C. Dietz, P. Roussel, M. Bria, M. Visseaux, P. Zinck, P. Mountford, *Dalton Trans*, 2015, **44**, 12312-12325.
22 S. Maiwald, H. Weissenborn, C. Sommer, R. Taube, *J. Organomet. Chem.* 2001, **640**, 1-9.
23 M. Visseaux, M. Mainil, M. Terrier, A. Mortreux, P. Roussel, T. Mathivet, M. Destarac, *Dalton Trans.*, 2008, **37**, 4558-4561.
24 S. Maiwald, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* 2002, 203, 1029-1039.
25 G. Kwag, H. Lee, S. Kim, *Macromolecules*, 2001, **34**, 5367-5369.
26 H. Guo, J. Bi, J. Wang, X. Zhang, S. Jiang, Z. Wu, *Dalton Trans.*, 2015, **44**, 9130-9139.
27 The properties of blended natural rubber and *trans*-1,4-polyisoprene is well investigated. See: J. –S. Song, B. –C. Huang, D. –S. Yu, *J. Appl. Polym. Sci.*, 2001, **82**, 81-89.
28 H. Hagimoto, T. Shiono, T. Ikeda, *Macomol. Rapid Commun.*, 2002, **23**, 73-78.
29 S. M. Cendrowski-Guillaume, G. Le Gland, M. Nierlich, M. Ephritikhine, *Organometallics*, 2000, **19**, 5654-5660.

Polymer Chemistry Accepted Manuscript

Please do not adjust margins

The synthesis of stereodiblock polyisoprene which consist of cis-1,4 and trans-1,4 sequences was achieved by using neodymium catalyst.



Polymer Chemistry Accepted Manuscript