

Asymmetric Hydroboration of Diene Polymers

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ABSTRACT: Asymmetric hydroboration of *cis*- and *trans*-1,4-polyisoprene was carried out using optically active triisopinocampheylborane and optically active polymers were obtained. In the case of the hydroboration of *cis*-1,4-polyisoprene, the use of dextrorotatory α -pinene ($[\alpha]_D +14.9^\circ$), yielded the laevorotatory polymer ($[\alpha]_D -2.3^\circ$) having a 98 per cent hydroxyl group content. On the contrary, the use of laevorotatory α -pinene ($[\alpha]_D -26.6^\circ$ and -28.6°) yielded the dextrorotatory polymers ($[\alpha]_D +2.4\sim 3.6^\circ$) having a 85—100 per cent hydroxyl group content. The absolute values of $[\alpha]_D$ for the polymers were increased with the increase in hydroxyl group content and the absolute value of $[\alpha]_D$ of α -pinene used. The optically rotatory dispersion curves were found to fit the simple Drude equation and the λ_c value of the polymers was about 164 $m\mu$. The λ_c value suggested that the chromophore which caused optical activity was —OH group.

The hydroboration of *trans*-1,4-polyisoprene was also carried out and optically active polymers ($[\alpha]_D +0.6\sim 1.2^\circ$) having a 90—100 per cent hydroxyl group content were obtained using α -pinene ($[\alpha]_D -28.6^\circ$). Furthermore, the asymmetric hydroboration of *cis*-polybutadiene, butadiene—styrene and random butadiene—acrylonitrile copolymers was carried out, but these hydroxylated polymers had no optical activity. The hydroxylated butadiene—acrylonitrile alternating copolymer showed optical activity.

KEY WORDS Optical Rotatory Dispersion / Optically Active Polymer / Asymmetric Hydroboration / Hydroboration / Polymer Reaction / Diene Polymer / Polyisoprene / Butadiene Acrylonitrile Copolymer / Butadiene—Styrene Copolymer / Triisopinocampheylborane /

Brown, *et al.*,¹ reported in 1961, for the first time, the asymmetric hydroboration of some olefines using diisopinocampheylborane (DIB). *cis*-2-Butene reacted with the reagents from α -pinene, $[\alpha]_D +47.6^\circ$, to produce an organoborane, which was oxidized with alkaline hydrogen peroxide to yield 2-butanol $[\alpha]_D -11.8^\circ$ (87 per cent optical purity).² Similarly, *cis*-3-hexene was converted to 3-hexanol $[\alpha]_D -6.5^\circ$ (91 per cent optical purity).

The results established that the boron atom at the asymmetric center, $R_1R_2C^*HB-$, was capable of maintaining asymmetry without significant racemization over a period of several hours. The unusually high optical purities realized in this asymmetric hydroboration and the fact that the organoboranes may be converted into other derivatives with retention of configuration promised to be a useful approach to optically active

derivatives.

The study on the hydroboration of the diene polymers such as polybutadiene and polyisoprene to produce the polymers having an hydroxyl group was carried out by one of the authors.³

In this paper, to synthesize optically active polymers from optically inactive polymer by polymer reaction, the asymmetric hydroboration of *cis*- and *trans*-polyisoprene was carried out using triisopinocampheylborane (TIDB). The hydroxylated polymers obtained were optically active. The specific rotation of the hydroxylated *cis*-1,4-polyisoprene was higher than that of the hydroxylated *trans* one.

The rotatory dispersion curves of the hydroxylated *cis*-polymers were found to fit the simple Drude equation and an average λ_c value of 164 $m\mu$ was obtained. The λ_c value suggested that the chromophore which caused optical activity

and -28.6° (lit.,⁴ $[\alpha]_D +48.3^\circ$ and -47.2°).

Polyisoprene, polybutadiene, butadiene—styrene copolymer and butadiene—acrylonitrile copolymer (random and alternating⁵) were purified by precipitation from a benzene solution with methanol.

The value of $[\eta]$, micro structure, probability of sequence, and composition of these polymers are shown in Table I.

Tetrahydrofuran(THF) and other solvents were purified by the usual method.

Preparation of a THF Solution of Diborane

A THF solution of diborane was prepared by Brown's method.⁶ In a three-necked flask equipped with a thermometer, condenser, and a pressure equalizing funnel, was placed 50 g (0.13 mol) of NaBH_4 and 50 ml of a di(ethylene glycol) dimethyl ether. The flask was immersed in an ice bath. BF_3OEt_2 (33 ml, 0.26 mol) was added dropwise to the solution and was well-stirred by a magnetic stirrer. The diborane gas produced was led with nitrogen gas and absorbed into 100 ml of THF cooled at 0°C . The concentration of the THF solution of diborane obtained was determined⁶ with measurement of the volume of hydrogen gas using a gas buret.

Preparation of Triisopinocampheylidiborane(TIDB)⁷

In a three-necked flask, equipped with a thermometer, condenser, and a pressure equalizing funnel was placed a THF solution of diborane 20 ml (0.02 mol). The flask was immersed in an ice bath. α -Pinene 9.5 ml (0.06 mol) was added dropwise to a well-stirred solution. Triisopinocampheylidiborane(TIDB) precipitated partially during α -pinene addition. The reagent was maintained for an additional 3 hr at 0°C prior to use.

Asymmetric Hydroboration

In a three-necked flask, equipped with a thermometer, condenser, and a pressure equalizing funnel was placed a THF solution (150 ml) of 1.0 g of polymer. A THF solution of TIDB was added to the well-stirred polymer solution under magnetic stirring. The reaction was carried out in an atmosphere of nitrogen at 0°C over a period of 5 min—5 hr. The reaction mixture was oxidized with alkaline-hydrogen peroxide (10 ml of 3-N aqueous sodium hydroxide and 10 ml of 30 per cent hydrogen peroxide). The reaction mixture

was precipitated into water and evaporated to remove THF. The obtained polymer was purified by precipitation from the THF solution with diethyl ether. The precipitation was carried out until the specific rotation of the polymer showed a constant value.

Measurements

The D-line optical rotation and optical rotatory dispersion were measured with a Shimadzu model QV-50 polarimeter equipped with xenon source.

The intrinsic viscosity of polymer was measured in THF at $30 \pm 0.1^\circ\text{C}$ with an Ubelohde's viscometer.

The infrared spectra of polymers were measured with the use of film on a NaCl plate.

RESULTS AND DISCUSSION

Asymmetric Hydroboration of *cis*- and *trans*-Polyisoprene

The asymmetric hydroboration of *cis*- and *trans*-polyisoprene was carried out in THF at 0°C (Tables II and III). During the reaction, the reaction mixture remained homogeneous. It was different from the previous result;³ in the case of hydroboration of diene polymers with diborane, the gelation of the reaction mixture occurred as soon as a THF solution of diborane was added to the polymer solution but it became homogeneous after oxidizing with alkaline hydrogen peroxide. In this paper the hydroboration of polyisoprene was carried out by TIDB instead of diborane. It is evident that the gel formation of the reaction mixture does not occur because a molecule of TIDB reacts with only one C=C double bond of the polymer and does not make the polymer—polymer linkage.

After several precipitations, a portion of the obtained polymer turned out insoluble, but THF soluble polymer was obtained. The gelation of the obtained polymer seemed to be caused by the residual impurity (trace organoboron compounds) in the obtained polymer. In the present paper, the precipitation was carried out in air. Thus the organoboron compounds remaining in the hydroxylated polymers were reacted with oxygen to give radicals during the precipitation. Welch⁸ and other authors^{9,10} reported the autoxidation of alkylboron compounds. Generally alkylboron compounds react with oxygen and readily produce

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Table II. Asymmetric hydroboration^a of *cis*-1,4-polyisoprene with triisopinocampheylidborane

Run no.	Molar ratio TIDE/ <i>cis</i> -1,4-polyisoprene	[α] _D ^b of used α -pinene, (°)	Hydroxylated polymer			
			[α] _D ^c , (°)	[η] ^d	-OH content, ^e %	Amount of gel
1	1.4	+14.9	-2.3	0.256	98	small
2	1.4	-26.6	+3.6	0.374	100	small
3	1.4	-28.6	+2.4	0.359	92	small
4	1.0	-28.6	+2.9	0.374	85	medium
5	0.6	-28.6	—	—	—	large ^f
6	0.4	-28.6	—	—	—	large ^f

^a The hydroboration was carried out for 3 hr at 0°C in THF.

^b Measured at 25°C (neat, $l=0.1$).

^c Measured in THF at 25°C ($C=1.0$, $l=1.0$).

^d Measured in THF at 30°C.

^e Calculated from C% by elementary analysis.

^f THF soluble polymer was not obtained.

Table III. Asymmetric hydroboration^a of *trans*-1,4-polyisoprene with triisopinocampheylidborane

Run no.	Molar ratio, TIDB/ <i>trans</i> -1,4-polyisoprene	[α] _D ^b of used α -pinene, (°)	Hydroxylated polymer			
			[α] _D ^c , (°)	[η] ^d	-OH content, ^e %	Amount of gel
10 ^f	1.4	-28.6	+1.2	0.280	90	small
11	0.9	-28.6	+0.6	0.435	85	medium
12	0.7	-28.6	—	—	—	large ^g

^a The hydroboration was carried out for 3 hr at 0°C in THF.

^b Measured at 25°C (neat, $l=0.1$).

^c Measured in THF at 25°C ($C=1.0$, $l=1.0$).

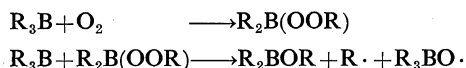
^d Measured in THF at 30°C.

^e Calculated from C% by elementary analysis.

^f The hydroboration was carried out for 1 hr at 0°C in THF.

^g THF soluble polymer was not obtained.

peroxide to yield free radicals.



As shown in Tables II and III, THF soluble polymers were obtained only on the condition of the hydroboration in which the molar ratio of TIDB/polyisoprene was more than unity. The carbon—carbon double bond was converted to the allyl radical by the elimination of hydroxyl radical, and thus the gelation occurred.

The THF soluble polymers had the hydroxyl group content of 80—100 percent and were not already rubber-like materials. As shown in Figure

1, the infrared spectrum for the THF soluble polymer gave the absorption band at 3400 cm⁻¹ due to the associated hydroxyl group and did not give the absorption band at 1670 cm⁻¹ due to the carbon—carbon double bond. The newly induced absorption band at 1700 cm⁻¹ was due to the carbonyl group which was produced by the oxidation of polyisoprene.

Optical Behavior of Hydroxylated Polyisoprene

The obtained polymers by oxidation after the asymmetric hydroboration of *cis*-polyisoprene had positive optical rotation (Table II). The hydroxylated polymers were purified by precipitation until the specific rotation showed a constant

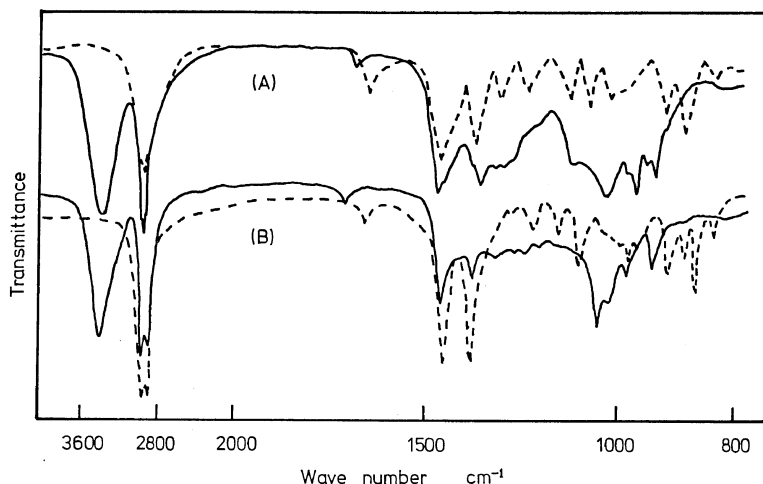


Figure 1. Infrared spectra of (A) *cis*-1,4-polyisoprene (----); hydroxylated *cis*-polyisoprene (—) and (B) *trans*-1,4-polyisoprene (----); hydroxylated *trans*-1,4-polyisoprene (—).

value. It is thought that the optical rotation was not caused by the impurity. It is also evident from the result that the optical rotations of hydroxylated polybutadiene, butadiene—styrene and butadiene—acrylonitrile copolymers were not detectable ($[\alpha]_D 0$) as described later. The optical rotatory dispersion curves for these polymers are shown in Figure 2. The curves were found to fit the simple Drude equation. The average value of λ_c for the polymers was about $164 \text{ m}\mu$. On the other hand, the λ_c for pinocampheol was $174 \text{ m}\mu$ and that for α -pinene was $124 \text{ m}\mu$. It would seem that the chromophore which cause optical activity for the polymer is the hydroxyl group.

In the case of the hydroboration of *cis*-polyisoprene, the use of dextrorotatory α -pinene ($[\alpha]_D +14.9^\circ$), yielded the laevorotatory polymer ($[\alpha]_D -2.3^\circ$) having a 98-% hydroxyl group content. On the contrary, the use of laevorotatory α -pinene ($[\alpha]_D -26.6$ and -28.6°) yielded the dextrorotatory polymers ($[\alpha]_D +2.4-3.6^\circ$) having a 85–100 per cent hydroxyl group content. The specific rotations of hydroxylated *cis*-polyisoprene increased with increase in the -OH content (hydroxylated carbon—carbon double bond), which was determined from the value of the carbon percent obtained from the elements analysis. A similar result was reported by Brown, *et al.*,² on

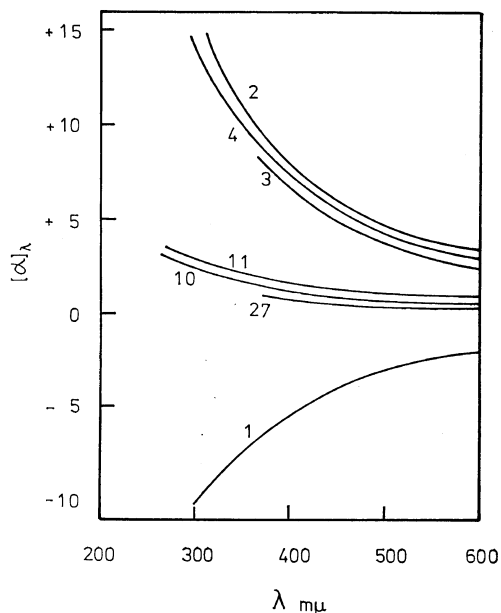


Figure 2. Optical rotatory dispersions of hydroxylated *cis*- and *trans*-1,4-polyisoprene: run no. 1, 2, 3, and 4 (Table II); run no. 10 and 11 (Table III); run no. 27 (Table IV).

the asymmetric hydroboration of low-molecular-weight olefines. For example, *cis*-2-butene was converted to dextrorotatory 2-butanol ($[\alpha]_D +11.7^\circ$) using laevorotatory α -pinene ($[\alpha]_D$

corresponding reactions of the reagents with *trans* or hinder olefins are slow, proceeding only with the displacement of α -pinene from the reagent, and the oxidized products exhibit much lower optical activities. For example, the hydroboration of *cis*-butene produced (+)-2-butanol of 86–87 per cent optical purity.² In contrast, the reaction of *trans*-2-butene produced (–)-2-butanol of 13 per cent optical purity.¹¹ Similarly, 3-methylcyclopentanol, *cis*-derivatives of 45 per cent optical purity¹¹ and *trans* one of 3 per cent of optical purity.¹¹

Although polyisoprene is tri-substituted olefin, there is no steric difference between the transition state of the hydroboration of *cis*-polyisoprene and that of *trans*-polyisoprene. Thus it is thought the fact that the specific rotation of the hydroxylated *cis*-polymer is higher than that of the *trans* one is not caused by the difference between the asymmetric inducing efficiency of the hydroboration of *cis*-polyisoprene and that of *trans* one, but is caused by the difference of the configuration of hydroxylated *cis*- and *trans*-polyisoprene. Two asymmetric carbon atoms (*i.e.*,

$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}^* - \\ | \\ \text{H} \end{array}$ and $\begin{array}{c} \text{H} \\ | \\ -\text{C}^* - \\ | \\ \text{OH} \end{array}$) are newly induced by the hydro-

boration of 1,4-polyisoprene with TIDB. In the case of the hydroboration of *cis*-polyisoprene, the configuration of the former type asymmetric

carbon atom ($\begin{array}{c} \text{H} \\ | \\ -\text{C}^* - \\ | \\ \text{OH} \end{array}$) is the same as one of the

latter type asymmetric carbon atom $\begin{array}{c} \text{H} \\ | \\ -\text{C}^* - \\ | \\ \text{OH} \end{array}$ of the

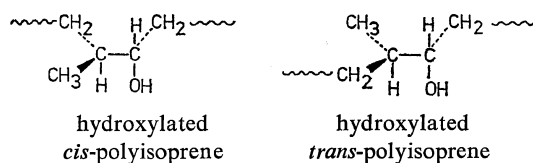
hydroxylated *trans*-polyisoprene. On the other

hand, the configuration of the $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}^* - \\ | \\ \text{H} \end{array}$ type asymmetric

carbon atom has the opposite configuration compared with that of the ($\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}^* - \\ | \\ \text{H} \end{array}$) type for hydro-

xylated *trans*-polyisoprene.

It is thought that in the case of hydroxylated *cis*-polymer, two asymmetric carbon atoms enhanced its optical rotation but the asymmetric carbon atoms of the hydroxylated *trans*-polymer

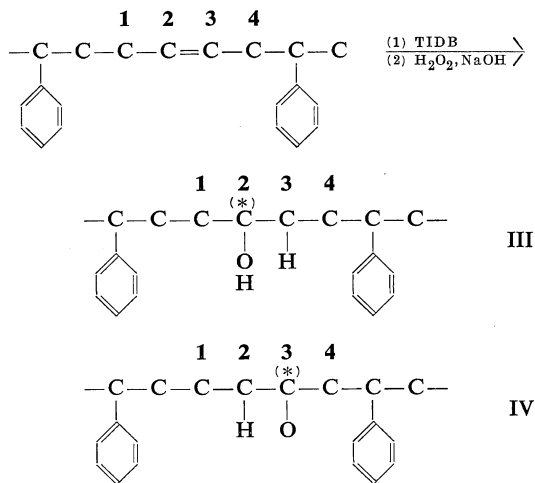


cancelled it. Thus the former has higher optical rotatory power than the latter.

Asymmetric Hydroboration of Polybutadiene and Butadiene—Styrene Copolymers

The asymmetric hydroborations of *cis*-polybutadiene and butadiene—styrene random copolymers were attempted in THF at 0°C using TIDB. The reaction conditions and results are summarized in Table IV. The hydroxylated polymers obtained by oxidation after the hydroboration of polybutadiene were not optically active. The results agree with the authors' expectation that the asymmetric carbon atoms induced in the polymer obtained by the hydroboration of polybutadiene are pseudo asymmetric.

In the case of hydroboration of butadiene—styrene copolymer, the reaction is shown as follows



The hydroxylated polymer such as type III is optically inactive. On the contrary, the hydroxylated polymer such as type IV is optically active. It is thought that the statistical probability of formation of type III is equal to that of type IV in the asymmetric hydroboration. Thus the authors hoped that the obtained hydroxylated butadiene—styrene copolymer would be optically active.

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Table IV. Asymmetric hydroboration^a of polybutadiene, butadiene—styrene copolymer, and butadiene—acrylonitrile copolymer with triisopinocampheylborane^b

Run no.	Diene polymers			Hydroxylated polymers		
	Name	Butadiene unit content, mol %	$[\eta]^c$	$[\eta]^c$	-OH ^d content, %	$[\alpha]_D^e$
20	Polybutadiene	100	2.70	0.64	82.3	0
21		85	1.03	0.89	66.4	0
22	Butadiene—styrene copolymer	85	1.03	0.70	86.0	0
23		68	1.54	0.63	40.9	0
24		68	1.54	0.72	36.8	0
25		25	0.54	0.36	62.4	0
26		25	0.54	0.42	87.6	0
27 ^f	Alternating butadiene—acrylonitrile	51	1.04	0.182	65.0	+0.5
28 ^g		51	1.04	0.588	71.1	+0.8
29 ^f	Butadiene—acrylonitrile ^h	76	1.65	0.501	80.5	0

^a Asymmetric hydroboration was carried out at 0°C in THF. The molar ratio of triisopinocampheylborane(TIDB)/butadiene unit=1.0.

^b α -pinene $[\alpha]+26.6^\circ$.

^c Measured in THF at 30°C.

^d Calculated from analytical value (C%). These values were calculated as $\frac{\text{hydroxylated C=C}}{\text{original C=C}} \times 100$.

^e Measured in THF at 25°C ($C=1.0$, $l=1.0$).

^f The hydroboration was carried out for 5 min.

^g The hydroboration was carried out for 5 min. The molar ratio of triisopinocampheylborane(TIDB)/butadiene unit=0.5.

^h Obtained by free radical copolymerization.

The hydroxylated polymers obtained by oxidation after the asymmetric hydroboration of butadiene—styrene copolymers were also optically inactive although the authors expected that the hydroxylated polymers would be optically active as the symmetric structure was destroyed due to the styrene unit of the copolymers.¹²

The copolymer having alternative structure (styrene—butadiene—styrene) is the most effectively hydroborated one for showing optical activity. However, the values of $F_{\text{St-Bu-St}}$ (probability of styrene—butadiene—styrene unit arrangement in main chain) of the used butadiene—styrene copolymers were 0.04—0.09. Thus it is thought that the rotation of polarized light of hydroxylated copolymers cannot be observed as the contents of “true” asymmetric carbon atoms are very small.

Asymmetric Hydroboration of Butadiene—Acrylonitrile Copolymers

The asymmetric hydroboration of butadiene—

acrylonitrile alternating and random copolymers was carried out in THF at 0°C using TIDB. The reaction conditions and results are summarized in Table IV.

The infrared spectrum of the hydroxylated copolymer is shown in Figure 4. The absorption band at 2237 cm^{-1} due to the $\text{C}\equiv\text{N}$ group and that due to the carbon—carbon double bond was decreased. The absorption band at 3300 cm^{-1} due to the hydroxyl group was observed and those at 1720 cm^{-1} and 1650 cm^{-1} were also newly induced. The result of infrared spectrum suggested that the hydroxylation of carbon—carbon double bonds occurred and a part of $\text{C}\equiv\text{N}$ group converted to $\text{C}=\text{N}-\text{OH}$.

The hydroxylated butadiene—acrylonitrile alternating copolymer had positive optical rotation as shown in Table IV and the optical rotatory dispersion curve is shown in Figure 2. On the other hand, the hydroxylated butadiene—acrylonitrile random copolymer was not optically

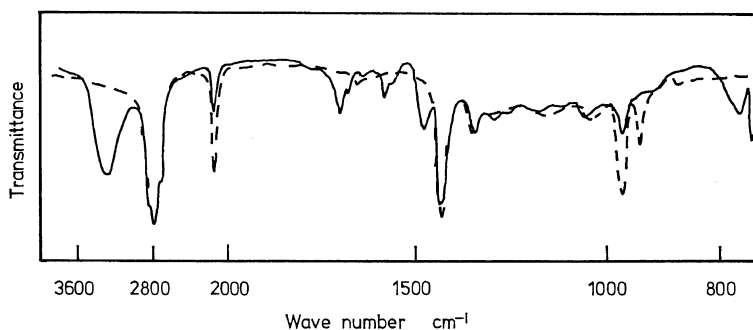


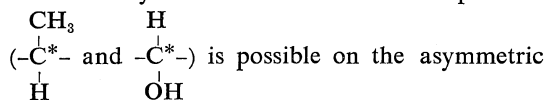
Figure 4. Infrared spectra of alternating butadiene—acrylonitrile copolymer (----) and its hydroxylated polymer (—).

active.

As described in the hydroboration of butadiene—styrene random copolymer, the fact that the hydroxylated butadiene—acrylonitrile alternating copolymer having the $F_{AN-Bu-AN}$ high value (0.46) was optically active was also caused by the high concentration of “true” asymmetric carbon atoms. On the contrary, the hydroxylated butadiene—acrylonitrile random copolymer does not have a high concentration of “true” asymmetric carbon atoms and does not show the optical rotation because the $F_{AN-Bu-AN}$ value of the butadiene—acrylonitrile copolymer is small (0.16).

Thus it is evident that the high value of probability of the comonomer—butadiene—comonomer unit arrangement in diene copolymer is essential for the formation of optically active polymer by the hydroboration.

It is confirmed from the results in this work that the asymmetric induction of two position



hydroboration of diene polymers with TIDB.

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