Isoprene Polymerization by Catalyst Systems of Rhodium Complex and Allyl Alcohol

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ABSTRACT

To prepare polyisoprene of controlled microstructure and molecular weight in emulsion systems, a series of polymerizations was carried out with catalyst systems of rhodium complexes and allyl alcohol, with variation of the type of rhodium salts, emulsifiers, and other conditions. A dramatic change in the structure of polyisoprene and also an increase of the polymer yield were brought about by the addition of sodium dodecyl sulfate and allyl alcohol. p-Toluenesulfonic acid and other strong acids exhibited an effect similar to that of the

sulfate type emulsifiers on the isoprene polymerization. The degree of polymerization of polyisoprene was increased from 150 to 2000 when the amount of allyl alcohol in the system was decreased from 100 mole % to less than 10 mole % with respect to isoprene monomer. Most samples of polyisoprene prepared with above catalyst systems were found to have almost equibinary 1,4-cis- and trans- enchainments. The effects of several phosphines and phosphites as additives on the microstructure of polyisoprene prepared with the rhodium complex systems were also examined.

INTRODUCTION

It was reported previously [1] that butadiene undergoes a stereospecific all-trans polymerization with rhodium salt in micellar systems, but that isoprene is not polymerized under similar reaction conditions. Rhodium trichloride was reported to react with isoprene in the presence of ethanol to give rise to oligomers [2]. On the other hand, it was claimed in a patent [3] that rhodium nitrate polymerizes isoprene in the presence of allyl alcohol. Entezami et al. [4] studied in detail the rates of consumption of isoprene and allyl alcohol in polymerization systems of isoprene catalyzed by rhodium nitrate and allyl alcohol.

Isoprene polymers prepared with these catalyst systems were viscous liquids of low molecular weight, and they had microstructures rich in 1,4-cis enchainment. Another characteristic feature of the polymers was that they contained some carbonyl and hydroxyl groups.

This study was undertaken to obtain isoprene polymers possessing controlled microstructures by using coordination catalysts in micellar systems. Isoprene polymerizations were investigated with variation of the type of rhodium salts, emulsifiers, and other reaction conditions.

EXPERIMENTAL

Materials

Solvents and reagents were purified by the usual methods [5], and all purification procedures were carried out under nitrogen.
Isoprene was dried over Drierite, refluxed over calcium hydride,

and then fractionally distilled under nitrogen. Allyl alcohol and ethyl alcohol were dried over Drierite, and distilled fractionally. Methylene chloride was dried over Drierite, refluxed over calcium hydride, and then distilled fractionally. Chloroform was washed with sulfuric acid, water, aqueous sodium hydroxide, and water, respectively. It was then dried with calcium chloride, refluxed over calcium hydride, and then distilled fractionally. Water was distilled under reduced pressure and stored under nitrogen.

Rhodium Salt and Complex

Rhodium trichloride was used as the form of trihydrate. μ-Dichlorobis (π-cyclooctadiene-1,5)-dirhodium, [Rh(COD)Cl]$_2$, was prepared according to Chatt [6]. First, 1,5-cyclooctadiene (20 ml) was added to a red solution of rhodium trichloride trihydrate (10 g) in ethanol (300 ml). Then the solution was refluxed with vigorous stirring for 3 hr. The reaction mixture was allowed to stand at room temperature to precipitate yellow crystals of rhodium cyclooctadiene, which were purified by a reprecipitation from methylene chloride by cyclohexane. All procedures were carried out under nitrogen.

Analysis. Calcd for [Rh(C$_8$H$_{12}$)Cl]$_2$: C, 38.98%; H, 4.91%. Found: C, 39.08%; H, 5.08%.

Polymerization of Isoprene

Isoprene and other reagents were added to an allyl alcohol solution of rhodium trichloride in ampoules under nitrogen atmosphere. These ampoules were sealed under vacuum after freezing of the contents in liquid nitrogen, then allowed to stand at certain temperatures. The rhodium cyclooctadiene complex was used as a solution in methylene chloride or chloroform.

Separation and Purification of Polyisoprene

An aqueous saturated solution of sodium chloride was added to an emulsion of polyisoprene to separate an organic layer. The organic layer containing polyisoprene was poured into an excess of methanol to precipitate polyisoprene. The polymer was washed with methanol several times, then dried in a vacuum oven at 90°C for 10 hr to constant weight.

Determination of $\overline{DP}$ of Polyisoprene

$\overline{DP}$ was determined by the viscosity method in toluene [7] (or benzene [8]) at 30°C (or at 25°C) by using the Mark-Houwink-Sakurada equation, Eq. (1):

$$[\eta] = KM^a \tag{1}$$

where $K = 15 \times 10^{-3}$ (13.3×10^{-3}) ml/g and $a = 0.74$ (0.78).

Determination of Microstructures of Polyisoprene

Microstructures were determined by ^{1}H-NMR method [9] (100 MHz, JEOL-PS-100) from Eqs. (2), (3), and (4), and four peak areas, A, B, C, and D (solvent, carbon tetrachloride; standard, tetramethylsilane).

$$1,4\text{-cis }\% = [C/(D + C)]\ 100 \tag{2}$$

$$1,4\text{-trans }\% = 100 - 1,4\text{ cis }\% - 3,4\% \tag{3}$$

$$3,4\% = [B/(2A + B)]\ 100 \tag{4}$$

where A, B, C, and D are the areas of ^{1}H-NMR signals: A, δ 5.08 ppm; B, δ 4.68 ppm; C, δ 1.66 ppm; D, δ 1.56 ppm.

Measurement of Dynamic Properties of Polyisoprene

The green strength of an equibinary polyisoprene (EQB-IR) sample in the form of sheet (2 mm thick) pressed at room temperature prepared according to Table 5 was measured by a Universal tensile testing instrument. The molecular weight of Nipol-IR (high cis-polyisoprene) was lowered by roll-milling.

The Wallace plasticity of sheet samples (3 mm thick) of polymer was measured by Wallace Rapid Plastimeter MK II at 100°C.

RESULTS AND DISCUSSION

Influence of Emulsifiers on Isoprene Polymerization

While Entezami et al. examined isoprene polymerization with rhodium nitrate in the absence of emulsifiers in both aqueous and non-aqueous systems, we started our study with isoprene polymerization in micellar systems with the variation of the type of rhodium salts and emulsifiers. We used primarily μ-dichlorobis(π-cyclooctadiene-1,5)-dirhodium, [Rh(COD)Cl]$_2$ (referred hereafter as rhodium cyclo-octadiene) rather than inorganic rhodium salts as the rhodium species, because the structure of rhodium cyclooctadiene had been elucidated and it was fairly soluble in methylene chloride and orther organic solvents.

The isoprene polymer produced with a catalyst system consisting of rhodium trichloride and allyl alcohol in the absence of emulsifier at 65°C was found to have similar structure to that obtained by radical copolymerization of isoprene, acrolein, and allyl alcohol, significant
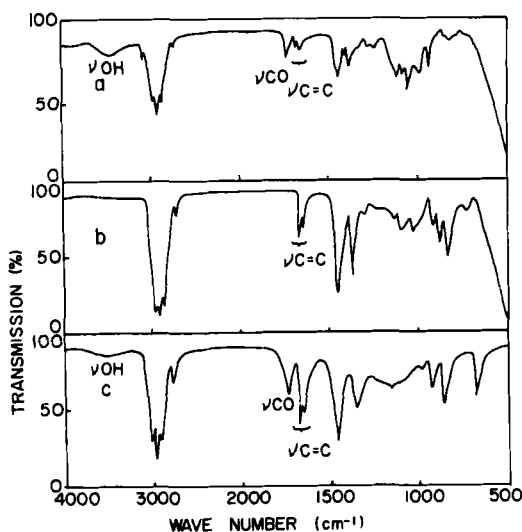
FIG. 1. IR spectra of polyisoprenes prepared with some rhodium catalyst systems: (a) system of Table 1, run 4; (b) system of Table 1, run 5; (c) system of Table 1, run 6.

TABLE 1. Isoprene Polymerization with Rhodium Complexes[a]

Run	Rh complex	Alcohol	Emulsifier	Solvent	Temp (°C)	Time (hr)	Yield (%)[b]	Structure of polyisoprene[c]
1	$RhCl_3 \cdot 3H_2O$[d]	None	SDBS	H_2O	50	(2.4 g/hr)		Trans 99%, vinyl 0.3% and cis < 1%
2	$RhCl_3 \cdot 3H_2O$	None	SDS	H_2O	65	72	0	—
3	$RhCl_3 \cdot 3H_2O$[e]	EtOH	None	None	60	3	63	$EtO(Ip)_n$ H (n = 1 - 4)
4	$RhCl_3 \cdot 3H_2O$	AllOH	None	None	65	72	2	Liquid copolymer of isoprene, allyl alcohol, and acrolein
5	$RhCl_3 \cdot 3H_2O$	AllOH	SDS	H_2O	65	72	94	Viscous, liquid polymer cis 47%, trans 46%, and 3,4 7%
6	$Rh(NO_3)_3 \cdot 2H_2O$[f]	AllOH	None	Benzene	65	20	62	cis 50%, trans 42%, and 3,4 5%
7	$[Rh(COD)Cl]_2$	None	None	CH_2Cl_2	65	72	0	—
8	"	AllOH	None	CH_2Cl_2	65	72	0	—
9	"	None	SDS	CH_2Cl_2 and H_2O	65	72	0	—
10	"	AllOH	SDS	CH_2Cl_2	65	72	72	cis 59%, trans 34%, and 3,4 7%
11	"	"	SDS	CH_2Cl_2 and H_2O	65	72	99	cis 55%, trans 38%, and 3,4 7%, $\overline{DP}$ 150

| 12 | " | SDS | CH$_2$Cl$_2$ and H$_2$O | 65 | 72 | 96 | cis 55%, trans 40%, and 3,4 5% |

aReaction conditions: (run 1) butadiene, 100 g; RhCl$_3\cdot$3H$_2$O, 1 g; sodium dodecylbenzenesulfonate (SDBS), 5 g; H$_2$O, 200 ml; (run 3) isoprene, 27 g; RhCl$_3\cdot$3H$_2$O, 1.5 g; EtOH, 300 ml; (runs 2, 4, 5, and 7-12) isoprene, 2.5 ml; RhCl$_3\cdot$3H$_2$O, 80 mg; or [Rh(COD)Cl]$_2$, 75 mg; allyl alcohol (AllOH), 1.7 ml; sodium dodecyl sulfate (SDS), 350 mg; CH$_2$Cl$_2$, 5 ml; H$_2$O, 15 ml; (run 6) isoprene, 2.5 ml; Rh(NO$_3$)$_3\cdot$2H$_2$O, 25 mg; AllOH, 5 ml; benzene, 5 ml.

bMethanol-insoluble portion except run 3, where value reported is total oligomer yield.

cSee Experimental Section.

dData of Rinehart et al. [1].

eData of Dewhirst [2].

fData of Entezami et al. [4].

amounts of carbonyl and hydroxyl groups being detectable in the infrared spectrum of the polymer obtained (Fig. 1a). The yield of methanol-insoluble portion of the polymer was only about 2% based on the isoprene monomer feed (Table 1, run 4).

The polymer yield in the isoprene polymerization was dramatically increased when sodium dodecyl sulfate was added to a catalyst system consisting of rhodium trichloride and allyl alcohol (Table 1, run 5). The isoprene polymer thus obtained was found to have no carbonyl or hydroxyl groups (Fig. 1b), in contrast with that prepared by Entezami et al. [4], which is estimated to contain carbonyl and hydroxyl groups in the ratio of about 1:10 with respect to isoprene units (Fig. 1c). Another series of examination with various types of emulsifier revealed that only anionic emulsifiers of sulfate or sulfonate type (such as sodium alkyl sulfate or sodium alkylbenzenesulfonate) were effective as the additive, neither cationic nor non-ionic emulsifiers being effective. Anionic emulsifier of carboxylate type did not work either (Table 2). It is concluded from the results obtained that the presence of alkyl sulfate or alkylbenzenesulfonate in the catalyst system should be responsible for the drastic change in the nature of the active species. Several years ago, Morton et al. reported, in a paper on emulsion polymerization of butadiene with rhodium catalyst [10], that only sulfate and sulfonate type emulsifiers possessing appropriate lengths of alkyl chain were effective for the polymerization of butadiene, but they did not elucidate this further.

The degree of polymerization $(\overline{DP})$ of viscous liquid polyisoprene prepared by emulsion polymerization with sodium dodecyl sulfate was about 150 when more than 1 mole of allyl alcohol was used per mole of isoprene monomer. If the amount of allyl alcohol was decreased to less than 10 mole % of isoprene, rubberlike polyisoprene $(\overline{DP}$ about 2000) was produced after a longer reaction time such as 134 hr (Table 5). With the increase of $\overline{DP}$, the content of 1,4-cis enchainment decreased from 60% to 51%, approaching an equibinary 1,4-polyisoprene. Some of physical properties of these isoprene polymers are described in detail in a later section.

Role of Alkyl Sulfate or Alkylbenzenesulfonate in Catalyst Systems

To elucidate the role of alkyl sulfate or alkylbenzenesulfonate in the rhodium-catalyzed polymerization of isoprene (Ip), reactions (5)-(9), were examined by using rhodium cyclooctadiene complex dissolved in methylene chloride (Table 1, runs 7-12). The products listed for each reaction are those obtained after 72 hr at 65°C.

TABLE 2. Effects of Emulsifiers on Isoprene Polymerization with Rhodium Complex[a]
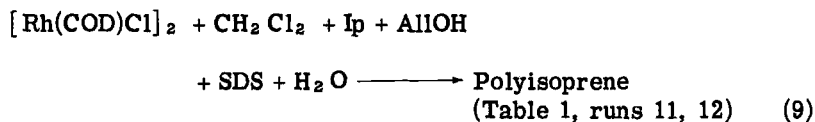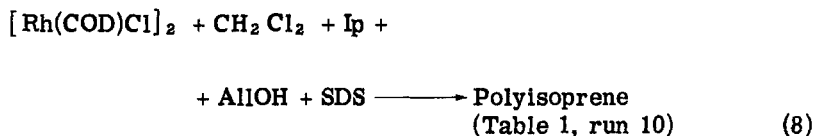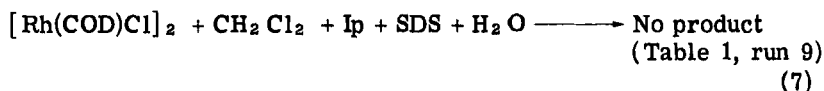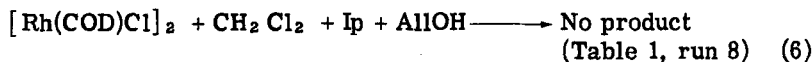
Run	Emulsifier	Type	Yield (%)	Microstructure of polyisoprene (%)		
				Cis	Trans	3,4
1	SDS $n\text{-}C_{12}H_{25}\,OSO_3^-Na^+$	Anion	99	55	38	7
2	SDBS $n\text{-}C_{12}H_{25}\text{-}C_6H_4\text{-}SO_3^-Na^+$	Anion	64	43	51	6
3	DBTMAC $n\text{-}C_{12}H_{25}\text{-}C_6H_4\text{-}CH_2(CH_3)_3N^+Cl^-$	Cation	0	—	—	—
4	K233LL $C_{17}H_{33}COO^-K^+$	Anion	0.4	—	—	—
5	E 930 $C_9H_{19}\text{-}C_6H_4\text{-}O(CH_2CH_2O)_nH$	Nonion	1.2	cis < trans		
6	Tween 80 $O(CH_2CH_2O)_xH$, $O(CH_2CH_2O)_zH$, $C_{17}H_{33}COOCH_2\,CHCHCHCHCH_2$, $H(OCH_2CH_2)_yO$	Nonion	3.5	cis < trans		

[a]Reaction conditions: (runs 1–3) isoprene, 2.5 ml; allyl alcohol, 1.7 ml; $[Rh(COD)Cl]_2$, 75 mg; CH_2Cl_2, 5 ml; H_2O 10 ml; and emulsifier, 400 mg; 65°C, 72 hr; (runs 4–6) isoprene, 5 ml; allyl alcohol, 1 ml; $RhCl_3\cdot3H_2O$ 40 mg (run 4) or 50 mg (runs 5 and 6); H_2O, 10 ml; emulsifier, 170 mg (run 4), or 100 mg (runs 5 and 6); 50°C, 50 hr.
[b]Methanol-insoluble portion.

$[Rh(COD)Cl]_2 + CH_2Cl_2 + Ip \longrightarrow$ No product

(Table 1, run 7)   (5)

$[Rh(COD)Cl]_2 + CH_2Cl_2 + Ip + AllOH \longrightarrow$ No product

(Table 1, run 8)   (6)

$[Rh(COD)Cl]_2 + CH_2Cl_2 + Ip + SDS + H_2O \longrightarrow$ No product

(Table 1, run 9)

(7)

$[Rh(COD)Cl]_2 + CH_2Cl_2 + Ip +$

$+ AllOH + SDS \longrightarrow$ Polyisoprene

(Table 1, run 10)   (8)

$[Rh(COD)Cl]_2 + CH_2Cl_2 + Ip + AllOH$

$+ SDS + H_2O \longrightarrow$ Polyisoprene

(Table 1, runs 11, 12)   (9)

where Ip denotes isoprene, AllOH is allyl alcohol, and SDS is sodium dodecyl sulfate.

Among these reactions only reactions (8) and (9) were able to polymerize isoprene. The isoprene polymer obtained from the emulsion system (9) was a viscous liquid with $\overline{DP}$ of about 150, the microstructure of which was 1,4-cis, 55%, 1,4-trans, 38%, and 3,4, 7%. The isoprene polymer prepared in the nonaqueous system (8) actually had the same physical properties and microstructure as polyisoprene prepared in the aqueous system. This suggests that these isoprene polymers were formed through the same reaction mechanism. It is to be noted that the polymer yield decreased to 72% in the nonaqueous system from 99% in the micellar system.

It was considered from the above results that the strong acids should be responsible for the formation of active species in the isoprene polymerization with rhodium complex in the presence of allyl alcohol. A series of studies on isoprene polymerization revealed that toluenesulfonic acid, for example, was able to give high yield of polyisoprene in the presence of rhodium cyclooctadiene and allyl alcohol, even in a nonaqueous system (Table 3, run 1). Polyisoprene prepared in this reaction system also had much the same microstructure as that of polyisoprene prepared in system (9). Therefore, the reaction mechanism of the rhodium catalyzed polymerization with sulfonic acid should presumably be the same as that of system (9).

TABLE 3. Effects of Strong Acids on Isoprene Polymerization with Rhodium Complex[a]

Run	Strong acid	Time (hr)	Yield (%)	Microstructure of polyisoprene (%)		
				1,4-cis	1,4-trans	3,4
1	$CH_3-C_6H_4-SO_3H\cdot H_2O$	96	98	59	32	9
2	CF_3COOH	96	9	43	53	4
3	$H_2SO_4 + H_2O$ (3 ml)	72	20	50	44	6
4	$CF_3SO_3H + H_2O$ (3 ml)	72	93	54	40	6

[a]Reaction conditions: isoprene, 15 mmole; $[Rh(COD)Cl]_2$, 0.09 mmole; allyl alcohol, 15 mmole, strong acid, 0.72 mmole; CH_2Cl_2, 3 ml; polymerization temperature, 20°C (run 1), 65°C (runs 2-4).

On the basis of the results described above, we propose here a possible formation of allyl toluenesulfonate from allyl alcohol and toluenesulfonic acid. Allyl toluenesulfonate will have a chance to form active species of polymerization, presumably a π-allyl complex, on reaction with the rhodium complex present in the system. Details of our study on polymerization mechanism will be reported elsewhere.

Isoprene polymerizations were also carried out with other strong acids: trifluoroacetic acid in a nonaqueous system and sulfonic and trifluoromethanesulfonic acid in aqueous systems (Table 3, run 2-4). The microstructure and other properties of polymers formed were found almost the same as those of polymers formed by system (9), though the polymer yields were very much different from one another.

Effects of Phosphine and Phosphite on the Stereo-specificity of Catalyst Systems

In order to have information on the effect of additives upon stereo-specificity of the rhodium catalyst, a series of experiments on isoprene polymerization was carried out at 65°C for 72 hr in the presence of phosphine, phosphite, and amine. The results for polyisoprene prepared in reaction system (10) are shown in Table 4.

TABLE 4. Effects of Phosphines, Phosphites, and Amine on the Microstructure of Polyisoprene Formed[a]

Run	Additive	Yield (%)[b]	Microstructure of polyisoprene (%)[c]		
			1,4-cis	1,4-trans	3,4
1	None	99	55	38	7
2	$P(C_6H_5)_3$	22	32	65	3
3	$P(C_6H_4CH_3)_3$	46	25	70	5
4	$P(C_6H_4Cl)_3$	13	27	69	4
5	$P(C_6H_4-OCH_3)_3$	45	30	65	5
6	$P(cyclo-C_6H_{11})_3$	32	32	64	4
7	$P(n-C_4H_9)_3$	20	33	64	3
8	$P(OCH_3)_3$	32	60	32	7
9	$P(OC_6H_5)_3$	2	40	33	27
10	$N(C_2H_5)_3$	44	41	54	5

[a]Reaction conditions: isoprene, 2.5 ml; allyl alcohol, 1.7 ml; [Rh(COD)Cl]$_2$, 75 mg (0.15 mmole); CH_2Cl_2, 5 ml; H_2O, 10 ml; additive, 1.2 mmole; polymerization temperature, 65°C; polymerization time, 72 hr.

[b]Methanol insoluble portion.

[c]By NMR method, see Experimental.

$$[Rh(COD)Cl]_2 + CH_2Cl_2 + AllOH + Ip + SDS$$

$$+ H_2O + (Additive) \longrightarrow Polyisoprene \qquad (10)$$
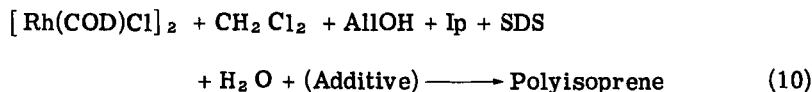
Triphenylphosphine increased the content of 1,4-trans structure by 27% (Table 4, run 2). The influence of para-substituted triphenyl-phosphine on the microstructure of isoprene polymer was not significant, as shown in Table 4, runs 3-5. Tricyclohexyl- and tri-n-butylphosphine also enhanced 1,4-trans structure (Table 4, run 6 and 7).

In contrast with phosphine, trimethyl phosphite increased 1,4-cis content of isoprene polymer (Table 4, run 8). Triphenyl phosphite, on the other hand, increased 3,4 content though the polymer yield was

TABLE 5. Synthesis of Rubberlike Polyisoprene with Catalyst System
of Rhodium Complex and Allyl Alcohol at 50°C[a]

Time (hr)	Microstructure of polyisoprene (%)			Conversion (%)	$[\eta]$ (ml/g)[b]	$\overline{DP}$[c]
	1,4-cis	1,4-trans	3,4			
44	60	←——— 40 ———→		34	22	280
88	58	41	1	46	38	580
110	52	←——— 48 ———→		64	68	1300
118	51	48	1	67	77	1500
134	51	44	5	74	94	2000

[a]Reaction conditions: isoprene, 3.83×10^3 mole/liter; allyl alcohol,
2.83×10^2 mole/liter; $[\text{Rh(COD)Cl}]_2$, 3.18 mole/liter; sodium dode-
cylbenzenesulfonate, 57.5 mole/liter; CHCl₃, 482 mole/liter; and
H_2O, 32×10^3 mole/liter.
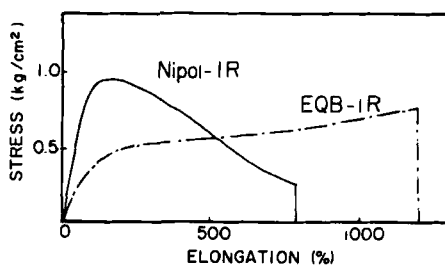[b]At 30°C in toluene.
[c]See Experimental.

FIG. 2. Green strength of pure gum stock. EQB-IR (equibinary
polyisoprene) was prepared according to Table 5, and molecular
weight of Nipol-IR (high cis-polyisoprene) was lowered by roll-
milling, see Experimental Section.

TABLE 6. Green Strength of Pure Gum Stock[a]

Poly-isoprene	Wallace plasticity	Yield stress (kg/cm^2)	Stress at break (kg/cm^2)	Elongation at break (%)	Breaking energy $(kg\text{-}cm/cm^3)$
Nipol-IR	11.5	1.0	0.3	800	5.19
EQB-IR	6.5	0.5	0.8	1200	6.86

[a]See Fig. 2.

very poor (Table 4, run 9). Triethylamine exhibited a smaller effect on 1,4-trans enchainment than did phosphine (Table 4, run 10).

A few years ago, Dolgoplosk et al. [11] proposed a theory on the correlation between the microstructure of polybutadiene and the nature of ligands for catalyst species: electron-attracting ligands increased 1,4-cis contents and electron-donating ligands increased 1,4-trans contents [6]. The trend of effects of phosphine and phosphite stated in the present study is understandable in the light of Dolgoplosk's theory, because phosphine, an electron-donating ligand, increased 1,4-trans content, while trimethyl phosphite, an electron-attracting ligand, increased 1,4-cis content.

Some Physical Properties of the Polyisoprene Sample

As described above, a rubberlike sample of polyisoprene ($\overline{DP}$ 2000) could be prepared in the presence of a smaller quantity of allyl alcohol. The polymer was found to be approximately equibinary polyisoprene (EQB-IR) (Table 5). Some physical properties of the EQB-IR were compared with those of, Nipol IR, a high-cis-polyisoprene (cis > 98%). The Wallace plasticity of the latter polymer was intentionally lowered from 30 to 11.5 so as to have nearly the same $\overline{DP}$ as that of the EQB-IR. Results are shown in Fig. 2 and Table 6. EQB-IR was found to have fairly large green strength (6.86 kg-cm/cm^3), which showed the energy required for breaking, in comparison with that of Nipol-IR (5.19 kg-cm/cm^3). This is resulted from the larger breaking stress of EQB-IR (0.8 kg/cm^2) in comparison with that of Nipol-IR (0.3 kg/cm^2).

ACKNOWLEDGMENT

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