

Hydroboration of Diene Polymers

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Synopsis

Diene polymers (i.e., polyisoprene, polybutadiene, and butadiene-styrene copolymers) were hydroxylated in tetrahydrofuran by hydroboration with diborane and subsequent alkaline oxidative hydrolysis. The strong, broad infrared absorption of the product at 3340 cm^{-1} shows the introduction of hydroxyl group. The properties of hydroxylated diene polymers depend upon the extent of hydroxylation. The less hydroxylated polymers are rubbery. As the extent of hydroxylation increases, the product becomes a white thermoplastic which is soluble in alcohol. The hydroboration of diene polymers with diborane is very rapid. However, if the reaction is continued further, the extent of hydroxylation decreases because of side reactions. The results of acetylation and formylation of the hydroxylated products and the grafting of vinyl monomers onto hydroborated diene polymers are also presented.

INTRODUCTION

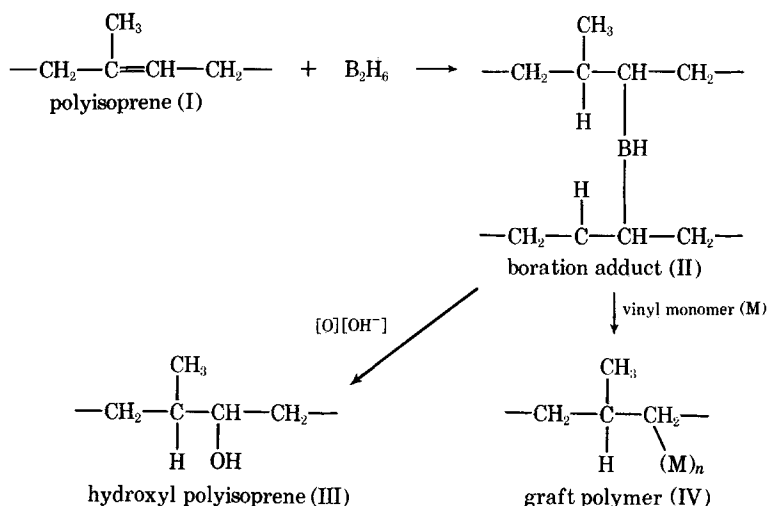
The hydroboration of low-molecular olefinic compounds, i.e., reactions of mono-olefins and diolefins with diborane, has been studied by Brown et al.¹ The present authors attempted the syntheses of derivatives of diene polymers and graft copolymers by the hydroborations of diene polymers obtained from diene monomers such as isoprene, butadiene, etc.

When diborane adds to polyisoprene (I), a boration adduct (II) is formed. By the oxidation and hydrolysis of II in alkaline medium, an hydroxyl derivative (III) is formed. When a vinyl monomer (M) is added to II, the formation of graft copolymer (IV) is expected as in equation on next page.

The hydroxylated diene polymers obtained by hydroboration with diborane and subsequent alkaline oxidative hydrolysis showed an infrared absorption band at 3340 cm^{-1} due to hydroxyl groups. The product gradually became a white thermoplastic as the extent of hydroxylation increased. Acetylation and formylation of the hydroxylated products have also been carried out.

It was found that the hydroborated diene polymer initiated free-radical polymerization of vinyl monomers, and in this manner graft copolymers of vinyl monomers on diene polymers were obtained.

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EXPERIMENTAL

Materials

The diene polymers used were Cariflex IR 305 (*cis*-1,4-polyisoprene), Balata (*trans*-1,4-polyisoprene), Cis-4 (*cis*-1,4-polybutadiene), and three kinds of butadiene-styrene copolymers (St/Bu wt-%: 76.5/23.5, 42/28, and 15/85), as shown in Table I. All polymers were purified by precipitation using benzene-methanol. Squalene distilled at 203°C/0.5 mm Hg was used as model compound of polyisoprene.

The sodium borohydride (NaBH₄) used was made by Metal Hydride Inc. Commercial boron trifluoride etherate (BF₃OEt₂) was distilled in nitrogen atmosphere at bp 126.5°C.

Diethylene glycol dimethyl ester was prepared from methyl bromide and alcoholate made from sodium and dimethylene glycol monomethyl ester.

TABLE I
Diene Polymers

Polymers	[η] in toluene at 30°C	<i>cis</i> -1,4, %	<i>trans</i> -1,4, %	1,2-, %	3,4-, %
<i>cis</i> -1,4-Polyisoprene (Cariflex IR 305)	5.4	92	3	0	5
<i>trans</i> -1,4-Polyisoprene (Balata)	1.6	—	95	—	—
<i>cis</i> -1,4-Polybutadiene (<i>cis</i> 4)	2.8	92	3	5	—
<i>trans</i> -1,4-Polybutadiene	1.6	—	95	5	—
<i>cis</i> -1,4-Polyisoprene (liq.)	0.15	92	3	0	5
<i>cis</i> -1,4-Polybutadiene (liq.)	0.3	89	7	4	—

After the unreacted monomethyl ester was reacted with sodium, it was distilled under reduced pressure. Moreover, it was distilled over lithium aluminum hydride at reduced pressure before use (bp 84–85°C/27 mm Hg). Tetrahydrofuran (THF), benzene, and other solvents used were purified as usual.

Preparation of THF Solution of Diborane

THF solution of diborane was prepared by Brown's method.² In a three-necked flask equipped with a thermometer, condenser, and pressure-equalizing funnel was placed 50 g NaBH₄. The flask was immersed in an ice bath, and 33 ml BF₃OEt₂ was added dropwise to the well-stirred mixture. The diborane gas produced was led with nitrogen gas and absorbed into 100 ml THF cooled to 0°C. The concentration of the THF solution of diborane obtained was determined by measuring the volume of hydrogen gas using a gas buret.

Hydroboration of Diene Polymer

The preparations of the hydroxyl derivatives were carried out as follows: a tetrahydrofuran (or mixture of toluene with tetrahydrofuran) solution of a diene polymer was mixed with a tetrahydrofuran solution of diborane² and reacted at 0–20°C for a required length of time. After reaction, 3*N* sodium hydroxide solution and 30% hydrogen peroxide were added, and the mixture was stirred at 40°C for 15–60 min. A large amount of water was added to the mixture, and the solvent was distilled off. The hydroxylated polymer thus obtained was acetylated with a mixture of pyridine with acetic anhydride³ and was formylated with formaldehyde using H₂SO₄ as catalyst in alcohol.⁴

Graft Copolymerization

In the case of graft copolymerization, diborane was added to the polymer solution, and then the excess diborane was deactivated with a small amount of ethanol. A 50–100 molar amount of a vinyl monomer with respect to the diborane was added to the mixture and polymerized at required temperatures.

Measurements

The hydroxyl group of the hydroxylated polymer was determined by infrared spectroscopy⁵ and by elemental analysis. The per cent of reacted double bonds was taken as the degree of hydroxylation.

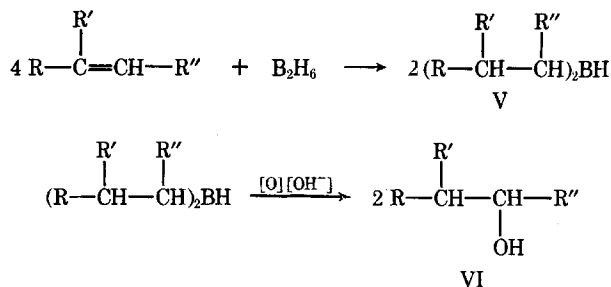
The intrinsic viscosity $[\eta]$ of the hydroxylated polymer was determined by an Ubbelohde viscometer at 30°C in THF.

The infrared spectra were obtained with a Perkin-Elmer Model 337 photometer and KBr pellets.

RESULTS AND DISCUSSION

Hydroxylation of Polyisoprene

The reaction of low-molecular-weight α -, α' -, and β -substituted olefin compounds with diborane was thought to yield borane (V) by the equation shown below. The B-H bond in the boration adduct did not react with a third olefin owing to steric hindrance.⁶ Hydrolysis of adduct V gave the hydroxylated compound VI:



where R, R', and R'' are alkyl groups.

On this basis, 1 mole of diborane is equivalent to 4 moles of isoprene repeat units.

When a THF solution of diborane was added to a THF solution of polyisoprene, gelation usually occurred immediately, but this gel of the boration adduct could be dissolved by hydrolysis.

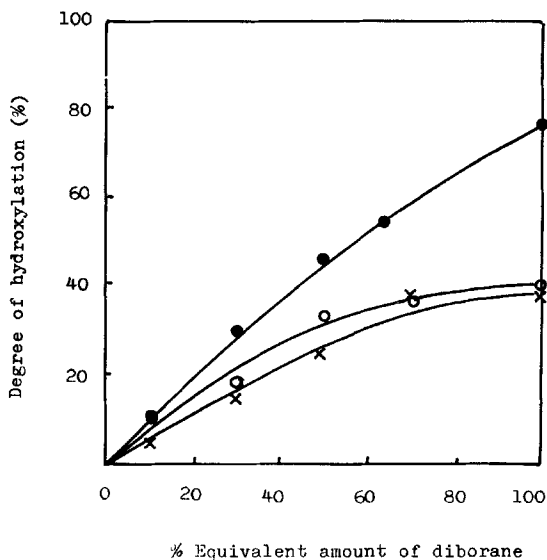


Fig. 1. Effect of equivalent amount of diborane on hydroxylation of diene polymers: (○) *cis*-1,4-polyisoprene (0°C × 15 min and then 25°C × 60 min.); (×) *trans*-1,4-polyisoprene (0°C × 15 min and then 25°C × 60 min.); (●) *trans*-1,4-polybutadiene (5°C × 10 min).

TABLE II
Hydroxylation of *cis*-1,4- and *trans*-1,4-Polyisoprene^a

	Polymer, g	B ₂ H ₆ equiv. amount, %	Yield, g	Part soluble in THF, %	OH content of mono-mer unit, %	[η] in THF (30°C)	Appearance	Apparent mp, °C
<i>cis</i> -1,4-	0.536	20	0.601	96.2	14	0.94	Viscous material, rubber-like	65
	0.742	50	0.868	75.6	34	0.82	Solid	110
	0.509	100	0.637	97.5	52	0.64	White solid	155
	0.469	200	0.628	84.4	45	0.42	White solid	
	1.231 ^b	10	1.223	60.7	9	0.28	Viscous material, rubber-like	
<i>trans</i> -1,4-	1.280 ^b	25	1.302	37.3	17	0.68	Rubber-like	
	1.245 ^b	50	1.456	79.2	34	0.56	Solid	
	1.203 ^b	75	1.401	56.8	37	0.37	Solid	
	1.170 ^b	100	1.600	26.3	39	0.25	Solid	
	1.006 ^b	10	1.057	97.4	6	0.70	Solid	
	1.002 ^b	25	1.063	98.0	14	0.47	Rubber-like	
	0.984 ^b	50	1.124	67.8	25	0.44	Solid	
	1.020 ^b	75	1.237	65.5	38	0.38	Solid	
	1.072 ^b	84	1.180	80.9	38	—	Solid	

^a Hydroboration conditions: 0°C for 15 min.

^b 0°C for 15 min and then 25°C for 60 min.

TABLE III
Effect of Reaction Temperature and Time on Hydroboration of Polyisoprene

Reaction temp., °C	Reaction time, min	Polymer, g	B ₂ H ₆ equiv. amount, %	Yield, g	Part soluble in THF, %	OH content of monomer unit, %	[η] in THF (30°C)
0	15	0.509	100	0.637	97.5	52	0.64
0	30	0.585	100	0.730	94.0	51	0.66
0	60	0.571	100	0.761	89.2	39	0.20
0	180	0.578	100	0.759	49.8	42	0.32
0	15	1.174	100	1.600	26.3	39	0.25
25	plus 60						
0	15	0.586	100	0.688	56.3	44	0.31
25	plus 180						
0	15	0.500	100	0.666	94.9	42	0.31
25	plus 60						
40	plus 60						
0	15	0.543	100	0.682	67.3	39	0.30
25	plus 60						
40	plus 180						

Table II shows the results of hydroboration of *cis*-1,4- and *trans*-1,4-polyisoprene. When an equivalent of diborane was reacted with rubbery *cis*-1,4-polyisoprene at 5°C for 15 min, a polymer with a 52% degree of hydroxylation was obtained. No appreciable difference in the reactivity was observed when Balata, i.e., *trans*-1,4-polyisoprene, $[\eta] = 1.6$, was used.

The relation between the degree of hydroxylation and diborane added is shown in Figure 1. The hydroxyl content in polyisoprene increased with increasing amounts of diborane, and saturation was reached at 35–40% hydroxylation, probably because crosslinking between polymers occurred.

The effects of reaction time and temperature on the hydroxylation of *cis*-1,4-polyisoprene are shown in Table III. In the hydroxylation at 0°C, the hydroxyl content in the polymer was 51–52% after 15–30 min and was about 40% after 60 min. With increasing reaction time, the gel increased and the $[\eta]$ of the hydroxylated polymer decreased. Similarly, with increasing temperature, the amount of gel increased and the hydroxyl content decreased.

Hydroxylation of Polybutadiene

With polybutadiene, 1 mole diborane is equivalent to 6 moles butadiene units,⁶

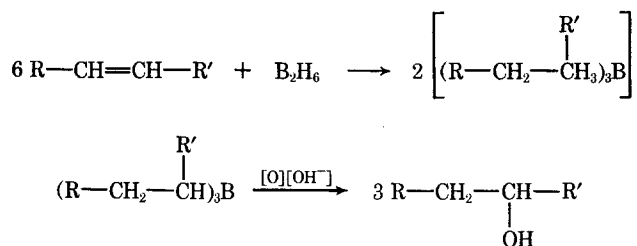


Table IV shows the results of hydroxylation of *cis*-1,4- and *trans*-1,4-polybutadiene by hydroboration.

The hydroxylated *cis*-1,4-polybutadiene ($[\eta] = 2.79$) was insoluble in benzene, THF, methanol water, etc., which indicated gelation (Table IV). However, the infrared spectrum showed the hydroxyl absorption band.

In the hydroxylation of *trans*-1,4-polybutadiene ($[\eta] = 1.56$), the degree of hydroxylation increased with increasing amounts of diborane added, as shown in Figure 1. With small amounts of diborane, the reaction proceeded almost quantitatively and the yield decreased with increasing amounts of diborane added. With an equivalent amount of diborane, the degree of hydroxylation was 78%.

The degrees of hydroxylation of three different butadiene–styrene copolymers (BU/St = 76.5/23.5, 42/58, and 15/85 mole-%) carried out at 5°C for 2 min were found to be 38, 31, and 18%, respectively, as shown in Table V. The greater the styrene content, the lower the degree of hydroxylation. The lower degrees of hydroxylation of the copolymers than those of poly-

TABLE IV
 Hydroxylation of *cis*-1,4- and *trans*-1,4-Polybutadiene

Polymer, g	B ₂ H ₆ equiv. amount, %	Temp., °C	Time, min	Yield, g	Gel, %	[η]	Degree of hydroxylation, %		Appearance
							IR	OH	
<i>cis</i> -1,4-	1.40 ^a	5	10	1.73	0.6	—	—	84	White solid
	0.529 ^b	5	15	0.636	100	—	—	—	Gel
	0.803 ^b	5	15	—	100	—	—	—	Gel
	0.400 ^b	5	2	—	80	—	—	—	Gel
<i>trans</i> -1,4-	0.496 ^c	5	10	0.386	Trace	1.66	7	13	White solid
	0.496 ^c	5	10	0.532	7.3	1.61	19	28	Semitransparent elastic solid
	0.576 ^c	5	10	0.625	1.2	1.65	33	46	White rubber- like solid
	0.636 ^c	5	10	0.562	0.5	1.45	40	56	White solid
0.644 ^c	100	5	10	0.556	1.9	—	—	78	White solid

^a Liquid *cis*-1,4-polybutadiene, [η] = 0.23, *cis*-1,4- = 89%, *trans*-1,4- = 7%, 1,2- = 4%.

^b Rubbery polybutadiene, [η] = 2.79, *cis*-1,4- = 92%, *trans*-1,4- = 3%, 1,2- = 5%.

^c *trans*-1,4-Polybutadiene, [η] = 1.56, *trans*-1,4- = 95%, 1,2- = 5%.

TABLE V
Hydroxylation of Butadiene-Styrene Copolymer

BD/ST, mole-%	Polymer, g	B ₂ H ₆ equiv. amount, %	Temp., °C	Time, min	Yield, g	Gel, %	[η]	OH (IR), %	Appearance
76.5/23.5	0.487	100	5	10	0.660	0.9	1.5	39	White solid
76.5/23.5	0.487	100	5	2	0.502	3.3	1.2	38	White solid
42.0/58.0	0.482	100	5	2	0.512	1.6	2.25	31	White solid
15.0/85.0	0.496	100	5	10	0.492	0.8	1.2	32	White solid
15.0/85.0	0.496	100	5	5	0.506	0	1.35	19	White solid
15.0/85.0	0.496	100	5	2	0.507	—	—	18	White solid

butadiene are probably due to the steric effect of the bulky phenyl groups in the styrene units.

Hydroxylation of Liquid Diene Polymers

To avoid gelation which took place during the hydroxylation of the rubbery polymers, the hydroxylation of liquid *cis*-1,4-polyisoprene ($[\eta] = 0.15$) was attempted. As can be seen in Figure 1, the degree of hydroxylation in the polymers increased with increase in the amount of diborane. With 150% equivalent diborane at 20°C for 30 min, 99% hydroxylation was obtained (Table VI). This polymer can be regarded as a head-to-head alternating copolymer of propylene with vinyl alcohol. A polymer with 84%

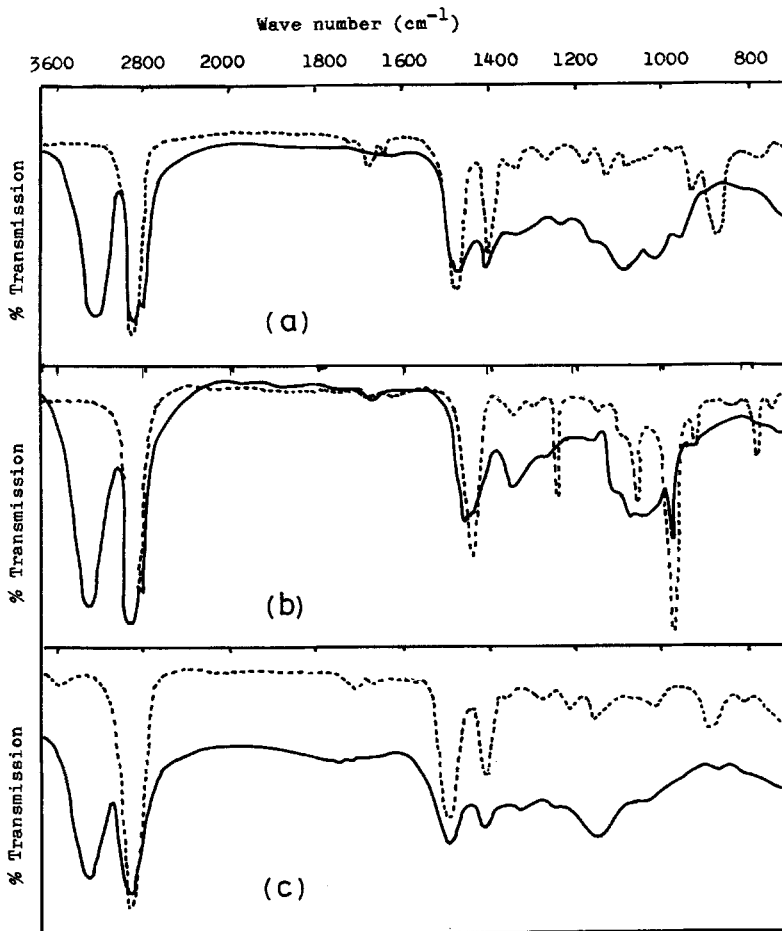


Fig. 2. Infrared spectrum of hydroxylated product of *cis*-1,4-polyisoprene, *trans*-1,4-polybutadiene, and squalene: (—) hydroxylated product; (---) original diene polymer; (a) hydroxylated *cis*-1,4-polyisoprene (degree of hydroxylation 52%); (b) hydroxylated *trans*-1,4-polybutadiene (78%); (c) hydroxylated squalene (46%).

TABLE VI
Hydroxylation of Liquid *cis*-1,4-Polyisoprene^a

Polymer, g	B ₂ H ₆ equiv. amount, %	Temp., °C	Time, min	Yield, g	Gel, %	[η]	Degree of hydroxylation, %		Appearance
							IR	OH	
0.76	10	5	10	0	Trace	0.14	8	—	Liquid adhesive, semisolid
0.84	50	5	10	0.722	Trace	0.15	30	44	Transparent semisolid
1.54	100	20	10	1.18	Trace	0.16	65	88	Crystalline powder
1.81	100	5	10	1.59	Trace	0.15	73	92	Crystalline powder
0.83	150	20	30	0.46	Trace	0.13	52	99	Crystalline powder

^a Polyisoprene, [η] = 0.15 (MW = 7100) (liquid), *cis*-1,4- = 92%, *trans*-1,4- = 3%, 3,4- = 5%.

hydroxylation was obtained by the hydroxylation of liquid *cis*-1,4-polybutadiene ($[\eta] = 0.3-0.2$) using 1 equivalent diborane. This polymer, shown in Table VI, corresponds to a terpolymer consisting of 84% ethylene-vinyl alcohol alternating units and 16% butadiene units.

The appearance of the hydroxylated liquid polyisoprene differed depending on the degree of hydroxylation. They were, for example, liquids (8%), transparent soft solids (44%), crystalline powders (86%), etc. The hydroxylates with greater than 86% hydroxylation were soluble in methanol and insoluble in benzene, carbon tetrachloride, etc.

Infrared Spectra

The spectra of hydroxylated *cis*-1,4- and *trans*-1,4-polyisoprene and squalene in Figures 2a, 2b, and 2c show broad, intense hydroxyl bands at $3300 \sim 3400 \text{ cm}^{-1}$.

The infrared spectrum of hydroxylated *cis*-1,4-polyisoprene showed an absorption band at 3340 cm^{-1} for the hydroxyl group, one at 1055 cm^{-1} for the alcoholic C—O, and one at 1712 cm^{-1} due to C=O. The intensities of the band at 1665 cm^{-1} due to internal C=C and that at 385 cm^{-1} due to *cis*-C=C were decreased.

Figure 3 shows a variation of absorption bands at 1665 cm^{-1} due to internal C=C and at 1645 cm^{-1} due to isopropenyl C=C by the hydroxylation of polyisoprene.⁷ The intensity of the absorption band due to internal

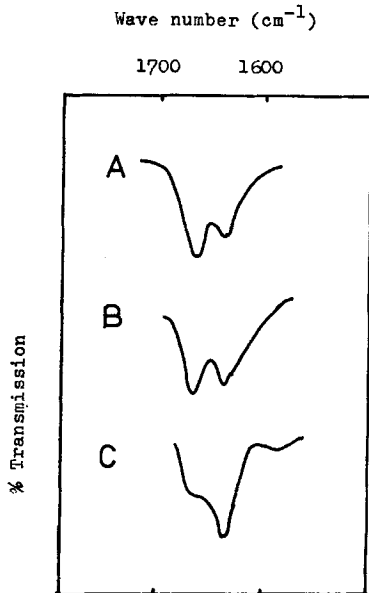


Fig. 3. Absorption of internal C=C (1665 cm^{-1}) and isopropenyl C=C (1645 cm^{-1}): (A) *cis*-1,4-polyisoprene; (B) hydroxylated *cis*-1,4-polyisoprene (degree of hydroxylation 17%); (C) hydroxylated *cis*-1,4-polyisoprene (degree of hydroxylation 37%).

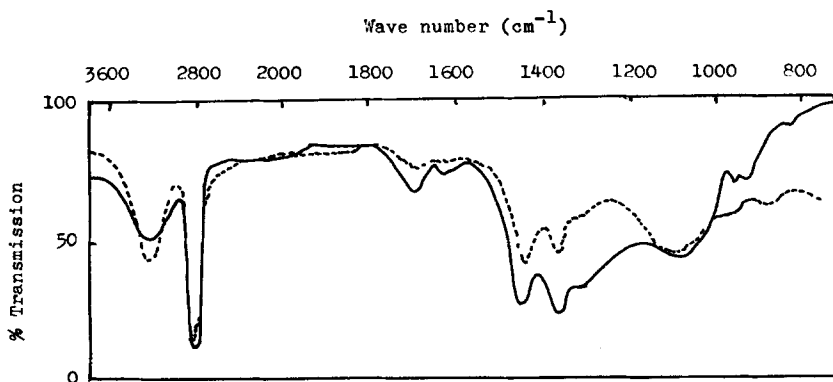


Fig. 4. Infrared spectrum of boration adduct and hydroxylated product of *cis*-1,4 polyisoprene: (—) boration adduct; (---) hydroxylated product.

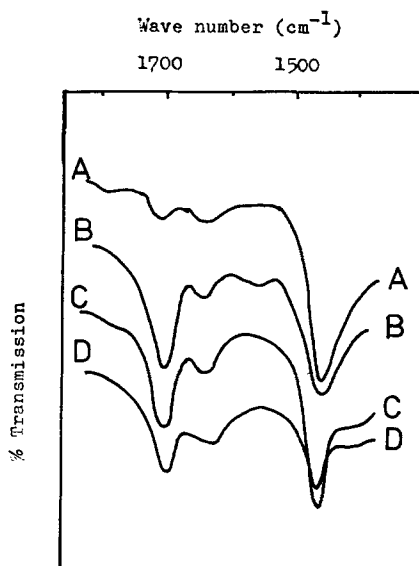


Fig. 5. Absorption of carbonyl group of hydroxylated polyisoprene. Reaction condition: (A) $0^{\circ}\text{C} \times 15$ min; (B) $0^{\circ}\text{C} \times 60$ min; (C) $0^{\circ}\text{C} \times 15$ min and then $25^{\circ}\text{C} \times 60$ min; (D) $0^{\circ}\text{C} \times 15$ min, then $25^{\circ}\text{C} \times 60$ min, and then $40^{\circ}\text{C} \times 180$ min.

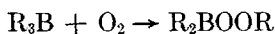
$\text{C}=\text{C}$ decreased with increase in the hydroxylation, but the intensity of the absorption band due to the isopropenyl $\text{C}=\text{C}$ did not change.

The infrared spectrum of the boration adduct of polyisoprene which was coagulated with water-methanol was determined by KBr pellet technique. As shown in Figure 4, an absorption band due to ROB was observed at 1340 cm^{-1} .⁸ Therefore it was thought that the boration adduct was oxidized by oxygen in the air, as is well known for alkyl borane.

As already described, with increasing reaction time the degree of hydroxylation $[\eta]$ and the THF-soluble part decrease. Figure 5 shows the absorp-

tion band due to C=O of hydroxylated polyisoprene obtained under different reaction conditions. The intensity of this band increased with an increase in reaction time and temperature.

These results indicate that the cleavage of the polymer chain, crosslinking, and other side reactions have taken place during hydroboration. Hansen⁹ and Welch¹⁰ have reported that the reaction of alkyl borane with oxygen easily produced peroxide and then radicals, as follows:



Although in these experiments the reaction was carried out under nitrogen, traces of oxygen in the nitrogen gas could have started the side reactions.

Properties of Hydroxylated Polymer

The nature of hydroxylated *cis*-1,4-polyisoprene changed with the degree of hydroxylation from a rubbery solid (14%) to a thermoplastic white solid (52%). The melting points of the hydroxylates increased with an increase in the degree¹¹ of hydroxylation, as shown in Figure 6. The solubility of the hydroxylates also varied with the degree of hydroxylation, as shown in Table VII. Thus the solubility in alcohols increased and solubilities in benzene and in chloroform decreased with increase in the degree of hydroxylation.

The nature of the hydroxylated *trans*-1,4-polybutadiene also differed depending on the degree of hydroxylation. It changed from a thermoplastic

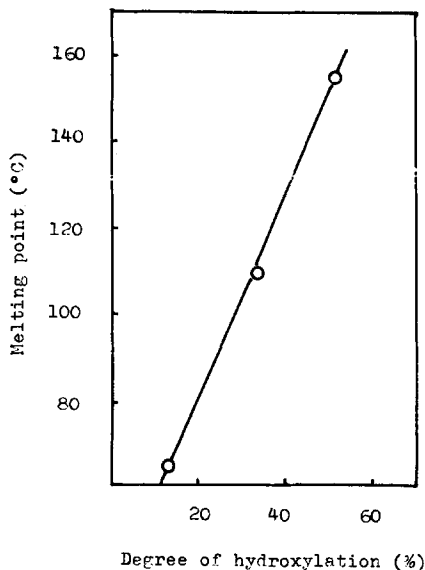


Fig. 6. Melting points of hydroxylated *cis*-1,4-polyisoprene.

TABLE VII
Solubility of Hydroxylated *cis*-1,4-Polyisoprene

Solvent	Solubility ^a		
	14%	Hydroxylation 34%	52%
Water	X	X	X
MeOH	X	□H	○
EtOH	X	□H	○
<i>n</i> -BuOH	H	○	○
Ethylene glycol	X	X	△
THF	○	○	○
Et ₂ O	X	X	X
MEK	X	△	X
Pyridine	○	○	○
DMF	○	○	○
DESO	X	○	○
CHCl ₃	○	□	△
CCl ₄	□	△	X
CS ₂	□	X	X
Benzene	○	△	△

^a (○) Soluble; (△) swell; (H) soluble at elevated temp.; (X) insoluble; (□) partially soluble.

white solid (13%), semitransparent elastic hard solid (28%), plastic white solid (46%), to a thermoplastic white solid (78%). The polymers with low degrees of hydroxylation were soluble in THF and those with high degrees of hydroxylation, e.g., 78%, were insoluble in THF but were soluble in methanol.

Acetylation of Hydroxylated Polymers

The hydroxylated polyisoprene (51%) was readily acetylated with a mixture of pyridine-acetic anhydride, as shown in Figure 7.

The acetylation of hydroxylated *trans*-1,4-polybutadiene (78%) also proceeded. The ester obtained from hydroxylated *cis*-1,4-polyisoprene

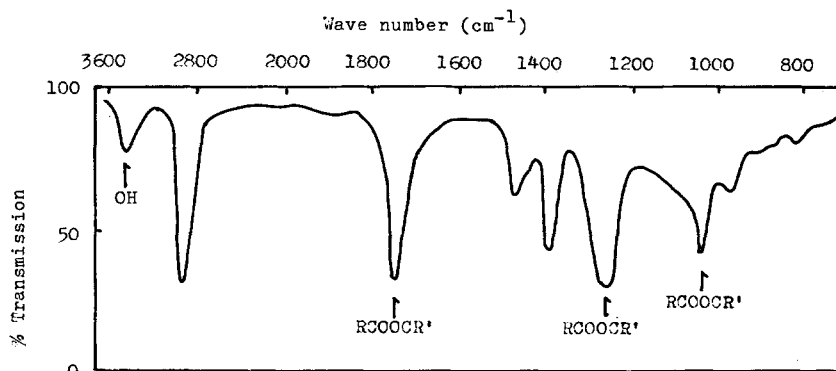


Fig. 7. Infrared spectrum of acetylated product from hydroxylated polyisoprene (51%).

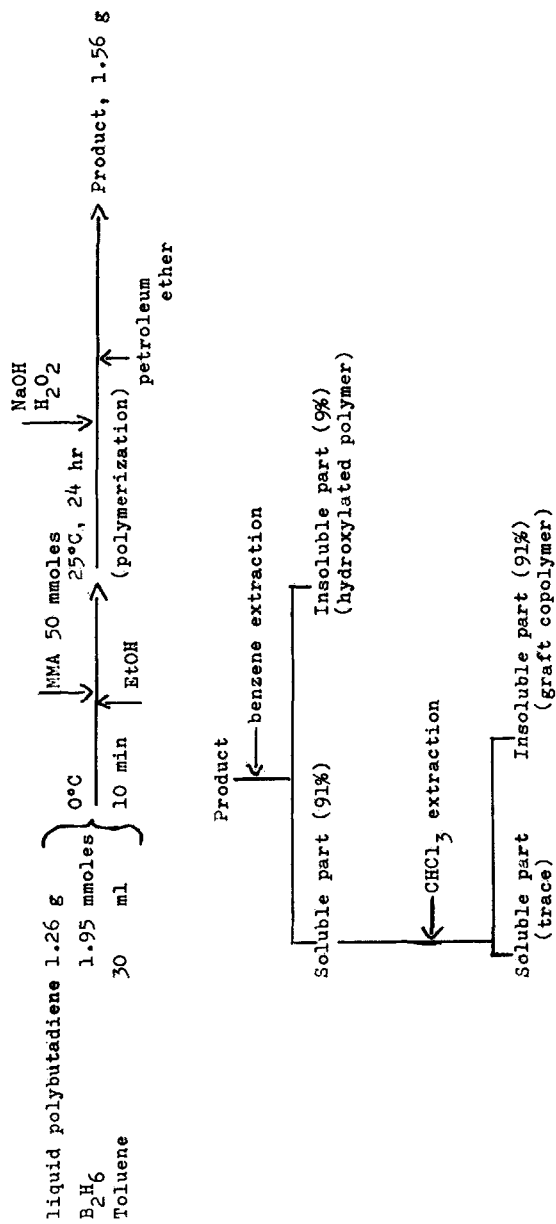
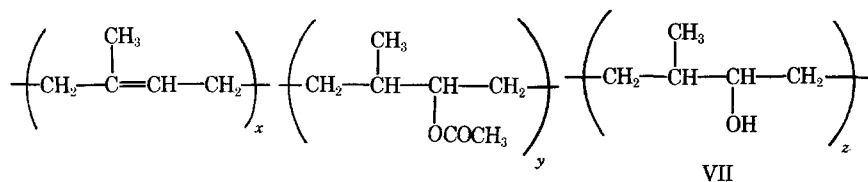


Fig. 8. Preparation and separation of methyl methacrylate (MMA) graft copolymer.

(52%) was a soft polymer soluble in benzene and THF, and its infrared spectrum showed absorption peaks at 1730, 1245, and 1022 cm^{-1} due to the ester group.

The structure of the ester derived from hydroxylated polybutadiene is thought to be compound VII, corresponding to an ethylene-vinyl acetate-butadiene terpolymer:



The hydroxylated polyisoprene (51%) was treated with formaldehyde in alcohol in the presence of H_2SO_4 , and a white solid was obtained that was insoluble in common organic solvents (e.g., alcohol, ethylene glycol, THF, ether, methyl ethyl ketone, acetone, chloroform, CCl_4 , CS_2 , benzene, pyridine, DMF, DMSO, etc.). Evidently crosslinking between hydroxylated polymers has taken place.

Graft Copolymerization

Various vinyl monomers have been added to the diborane-hydroborated liquid *cis*-1,4-polyisoprene. The subsequent polymerizations were carried out at room temperature.

The outline of the preparation of the graft copolymers is shown in Figure 8. Diborane was added to the polymer solution, and the unreacted diborane was deactivated with a small amount of ethanol. A 50–100 molar excess of vinyl monomer with respect to diborane was added to the mixture. Polymerization was carried out for the required time at room temperature under nitrogen atmosphere.

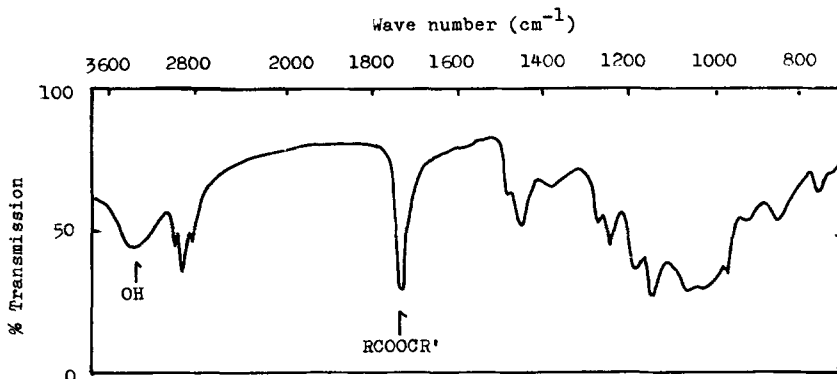


Fig. 9. Infrared spectrum of MMA-liquid *cis*-1,4-polyisoprene graft copolymer.

With methyl methacrylate, the product was a soft solid. It contained a small amount of benzene-insoluble and a trace of chloroform-insoluble portion. As can be seen in Figure 9, the infrared spectrum of the benzene-soluble portion shows an intense absorption band due to the ester group.

With vinyl acetate, the product was a transparent, soft solid, soluble in methanol and THF, and its infrared spectrum showed an intense absorption band due to the ester group.

With acrylonitrile, the system became pale yellow, and its viscosity increased, indicating that acrylonitrile polymerized. The mixture was hydrolyzed by alkali and poured into a large amount of methanol to precipitate the polymer. The product was pale yellow, and its infrared spectrum had an absorption band due to the nitrile group at about 2200 cm^{-1} .

From the above results, it was concluded that vinyl monomers can be grafted onto hydroborated diene polymers, after deactivating the excess diborane in the system by ethanol.

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