

Modification of Butadiene Rubber with 1,3-Dipolar Cycloaddition Reaction. I. Preparation and Properties of the Modified Polybutadiene

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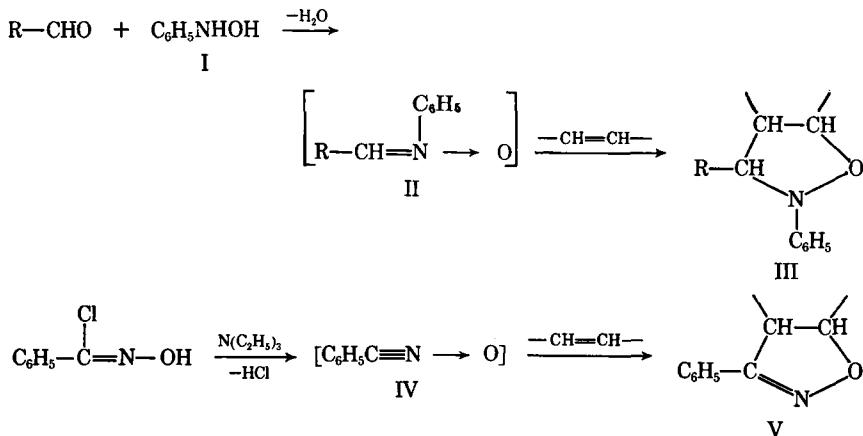
Synopsis

Polybutadiene of low *cis*-content was modified with the precursors of nitrones and nitrile oxide. The carbon-black-filled vulcanizates of the modified rubbers containing isoxazolidine and isoxazoline groups showed good tensile properties. The effect of modification was ascribed to the interaction between active sites of carbon black particles and the heterorings.

INTRODUCTION

The 1,3-dipolar cycloaddition reaction has already been employed for the synthesis of polymers, especially of the heat-stable polymers. Recently, this reaction was applied to some unsaturated polymers, for example, unsaturated polyester¹ and polybutadiene.^{2,3} As a crosslinking agent, the bifunctional 1,3-dipolar compound or its precursor was also applied to unsaturated rubber.⁴⁻⁶

In this paper, polybutadiene rubber was treated with an aldehyde-phenylhydroxylamine (I) system or a benzhydroxamic acid chloride-triethylamine system. These systems generate nitron (II)^{7,8} and nitrile oxide (IV),^{9,10} respectively. The resulting polymers were proved to contain isoxazolidine (III) or isoxazoline (V) groups:



In compound Ia and IIIa (mentioned later), R = C₆H₅—; in Ib, IIIb, R = C₂H₆—; in Ic, IIIc, R = *p*-C₆H₄N.

The tensile properties of their vulcanizates filled and unfilled with carbon black were examined. The filled vulcanizate showed improved tensile modulus by the introduction of these heterorings, while the unfilled one showed small change. Tensile strength at break of the filled vulcanizate was also much improved. These effects were attributed to the interaction between carbon black particles and the electrodonating heterorings introduced in the polymer.

Such heterocyclic compounds as isoxazolidine and isoxazoline are very effective for reinforcing rubber with carbon black.

EXPERIMENTAL

Materials

Commercially available butadiene rubber, Diene NF55R (Asahi Chemical Industry), produced by alkyl lithium catalyst was used.

Phenylhydroxylamine¹¹ and benzhydroxamic acid chloride^{12,13} were prepared by known methods.

Other chemicals of reagent grade were used without further purification.

Preparation of Modified Polybutadiene

Aldehyde-Phenylhydroxylamine System. A typical procedure was as follows: In a 500-ml four-necked round-bottomed flask equipped with a mechanical stirrer, a condenser, a thermometer, and a nitrogen gas inlet tube, 16.2 g (0.3 mole of butadiene unit) of rubber was dissolved in toluene at room temperature to a 10 wt-% solution, 2 phr of Noerac SP, an antioxidant (styrenated phenol), being added. Into this solution, 0.0015 mole (5 mole-% to butadiene unit) of benzaldehyde and the same amount of phenylhydroxylamine were added. Then, the reaction mixture was heated and refluxed under a slow stream of nitrogen gas. After 12 hr, the mixture was cooled, diluted with toluene to about twice the volume, and poured into a large excess of methanol containing several parts of Noerac SP. After repeating this reprecipitation once more, the polymer was dried in vacuo at 40°C for 20 hr. Its inherent viscosity was 1.86 in toluene at 30°C (that of the original Diene NF55R was 2.00). From the intensity of the IR absorption band of the phenyl group and the nitrogen content by the elemental analysis, 3.1 mole-% of butadiene unit was estimated to be modified to isoxazolidine unit (IIIa).

Benzhydroxamic Acid Chloride-Triethylamine System. The procedure was similar to that mentioned above, except that benzhydroxamic acid chloride was dissolved with butadiene rubber and that 50 vol-% toluene solution of triethylamine was added dropwise to the mixture at room temperature. The reaction was carried out for 6 hr.

Compound Formulations, Mixing, and Vulcanization. The compound formulations are given in Table I. The compounds were mixed on a hot

TABLE I
Compound Formulations

Ingredients	Formulations (parts by weight)	
	unfilled	filled
Polymer	100	100
Zinc oxide	5.0	5.0
Stearic acid	1.0	1.0
Nocceler DM ^a	1.0	1.0
Nocceler D ^b	0.25	0.25
Nocrac SP ^c	2.0	2.0
Sulfur	1.2	1.2
Carbon black ISAF	—	40.0

^a Dibenzothiazyl disulfide.

^b Diphenylguanidine.

^c Styrenated phenol.

3-in. roll mill with 14 g of rubber. The vulcanization was carried out in a 40 mm × 60 mm × 0.6 mm mold at 150°C for 10, 20, and 40 min.

Measurement of Tensile Properties

Three straight specimens 5 mm wide and 60 mm long were cut from a vulcanized sheet. The test was carried out by using a Shimadzu Autograph IM-100. Test conditions: grip distance, 20 mm; tensile rate, 500 mm/min; temperature, 23°C.

The values at curing time showing maximum tensile strength at break were taken as the characteristics of the rubber tested.

Preparation of Donor Compounds for IR Measurement

Styrene was reacted with the precursors of 1,3-dipolar compounds, aldehyde-phenylhydroxylamine and benzhydroxamic acid chloride-triethylamine, under condition similar to that of the modification of rubber. The products obtained were as follows:

2,3,5-Triphenylisoxazolidine, mp 99–101°C (lit.¹⁴ 99–100°C):

ANAL. Calcd for C₂₅H₁₉NO: C, 83.7%; H, 6.32%; N, 4.65%. Found: C, 84.0%; H, 6.30%; N, 4.74%.

3-Ethyl-2,5-diphenylisoxazolidine:

ANAL. Calcd for C₁₇H₁₉NO: C, 80.6%; H, 7.52%; N, 5.54%. Found: C, 80.9%; H, 7.27%; N, 5.69%.

3-*p*-Pyridyl-2,5-diphenylisoxazolidine:

ANAL. Calcd for C₂₀H₁₈N₂O: C, 79.5%; H, 5.96%; N, 9.27%. Found: C, 79.5%; H, 6.19%; N, 9.21%.

3,5-Diphenylisoxazoline, mp 74–75°C (lit.¹⁵ 74–75°C):

ANAL. Calcd for C₁₉H₁₃NO: C, 80.7%; H, 5.84%; N, 6.28%. Found: C, 80.8%; H, 6.13%; N, 6.06%.

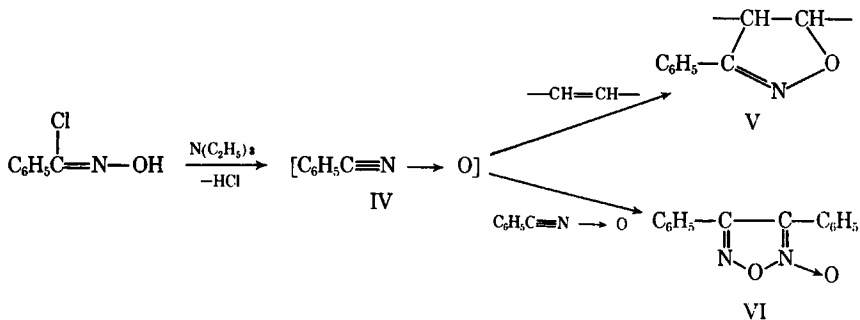
IR Shift Measurement of Methanol-*d*

A Hitachi IR spectrophotometer EPI-G₃ was used for the measurement of the shift of the O-D stretching band of methanol-*d* caused by the interaction of the donor. The method was in accordance with the literature.¹⁶ The concentrations of methanol-*d* and the donor were 0.4 and 1.0 mole/l., respectively.

RESULTS AND DISCUSSION

Modification of Butadiene Rubber

Table II gives the results of the modification of Diene NF55R. As shown in the table, the addition reaction of 1,3-dipolar compounds to unsaturated bonds in rubber is nearly stoichiometric in toluene, but not completely so in tetrahydrofuran (Samples 28 and 30). Nitrile oxide is very reactive and tends to dimerize to furoxan (VI) spontaneously. In the modification reaction, two types of addition reaction seem to compete. One is the addition to carbon-carbon double bond in rubber and the other is that to nitrile oxide itself. The modification reaction of rubber appears to exceed the furoxan formation reaction in toluene, but the latter becomes comparable to the former in the more polar solvent, tetrahydrofuran:



Most of the modified rubber showed lower solution viscosities than the original Diene. It may partly be attributed to the change of polar nature of the polymer chain by the introduction of heterorings, but mainly to the damage of the chain because no simple relation is found between the inherent viscosity and the content of heteroring.

Figure 1 shows the IR spectra of the modified rubbers and those of the original rubber. The characteristic absorption bands of the mono-substituted benzene ring are found near 1600, 1490, 760, and 700 cm^{-1} in both spectra of the modified rubbers. Besides, several new bands appear at 1260, 1175, and 1030 cm^{-1} in the spectrum of the benzaldehyde-phenylhydroxylamine-modified rubber, and at 1570 cm^{-1} in that of the benzhydroxamic acid chloride-triethylamine-modified rubber. All of these are weak, and their identification is not clear. The spectra of propion- and

TABLE II
Some Properties of Modified Butadiene Rubbers

Modifiers Sample No.	Diene NF55R	C ₂ H ₅ CHO/C ₆ H ₅ NHOH			C ₆ H ₅ CHO/ C ₆ H ₅ NHOH		p-C ₆ H ₄ NCHO/ C ₆ H ₅ NHOH		C ₆ H ₅ C(Cl) = N-OH/ N(C ₂ H ₅) ₃	
		23	25	26	33	36	24	27	28 ^a	30 ^a
Charged amount of modifiers, mole-%	—	5	10	22	5	12	5	12.4	5	10
Reaction temperature, °C	—	110	110	110	110	110	110	110	50	68
Reaction time, hr	—	11	19	19	12	20	11	13	6	6
Gel produced, (wt-%)	0	3.7	0	1.9	0	0	0	0	0	1.1
Heteroring content, mole-%	—	5.0	9.3	21.7	3.1	11.4	5.0	11.0	2.7	5.0
η _{inh} at 30°C in toluene, c = 0.6 g/dl	2.00	1.87	2.08	1.54	1.86	1.80	1.62	1.65	1.62	1.76

^a Tetrahydrofuran was used as solvent.

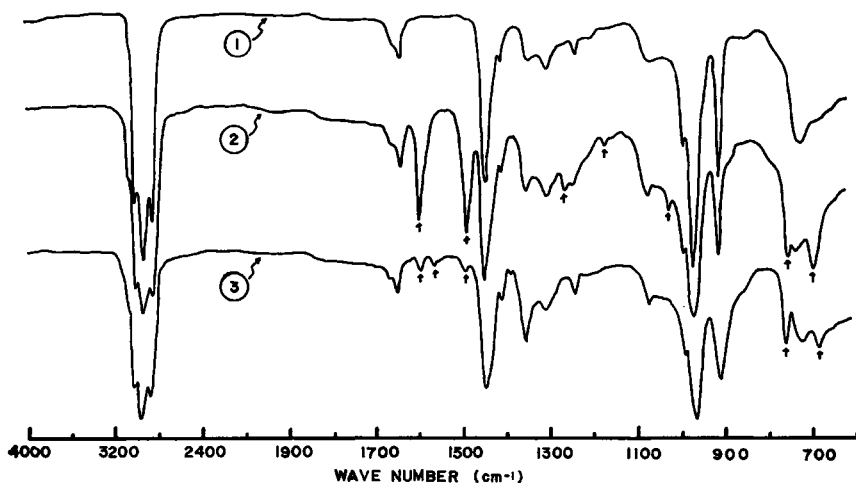


Fig. 1. IR Spectra of original and modified rubbers: (1) original butadiene rubber (Diene NF55R); (2) rubber modified with benzaldehyde-phenylhydroxylamine; (3) rubber modified with benzhydroxamic acid chloride-triethylamine.

p-pyridinealdehyde-phenylhydroxylamine-modified rubbers resemble closely that of the benzaldehyde-phenylhydroxylamine-modified one.

Tensile Properties of Modified Rubbers

Table III gives the tensile properties of modified rubbers, and Figure 2 is a plot of the 100% modulus (M_{100}) and tensile strength at break (T_B) versus the content of heterorings.

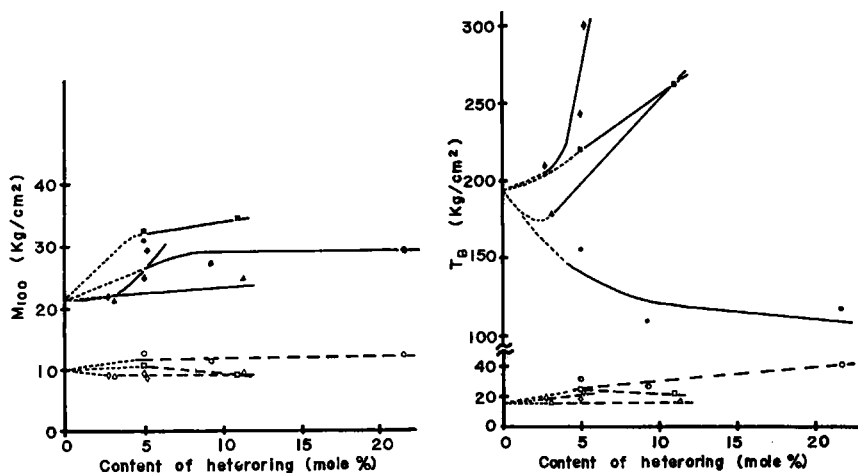
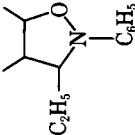
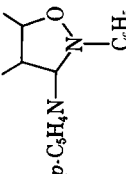
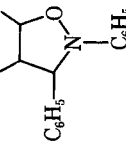
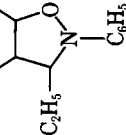
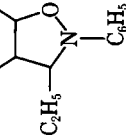


Fig. 2. Tensile modulus and strength at break of modified rubbers. Modified with propionaldehyde-(phenylhydroxylamine: (○) unfilled; (●) filled. Modified with benzaldehyde-phenylhydroxylamine: (Δ) unfilled; (▲) filled. Modified with *p*-pyridinealdehyde-phenylhydroxylamine: (□) unfilled; (■) filled. Modified with benzhydroxamic acid chloride-triethylamine: (◇) unfilled; (◆) filled.

TABLE III
Tensile Properties of Modified Rubbers (Unfilled/Filled)

Structure of Heteroring	Diene		23		25		26		33		36		24		27		28		21		30	
	Sample No.	NF55R	5.0	10/20	20/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	
 C_2H_5 C_6H_5	23	—	5.0	10/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	20/20	
	Heteroring content, mole-%	—	5.0	10/20	20/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	20/20
 $p-C_6H_4N$ C_6H_5	24	—	5.0	10/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	20/20	
	Curing time at 150°C, min	—	5.0	10/20	20/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	20/20
 C_6H_5 C_6H_5	25	—	9.3	20/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	20/20	
	M_{100}^a , kg/cm ²	10.3/21.4	11.2/27.0	11.2/27.0	12.0/28.9	8.7/21.0	9.2/24.4	10.4/32.3	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2	8.9/34.2
 C_2H_5 C_6H_5	26	—	21.7	20/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	20/20	
	T_B^b , kg/cm ²	15.1/194	26.3/109	39.6/116	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178	15.7/178
 C_2H_5 C_6H_5	27	—	3.1	20/20	20/20	20/20	20/20	20/20	20/20	20/20	40/40	40/40	10/40	40/10	40/10	20/20	20/20	20/20	20/20	20/20	20/20	
	E_B^c , %	255/875	429/640	370/488	412/451	437/899	341/865	448/637	516/626	457/947	426/1033	592/946	426/1033	592/946	426/1033	592/946	426/1033	592/946	426/1033	592/946	426/1033	592/946

^a 100% Modulus.

^b Tensile strength at break.

^c Elongation at break.

The M_{100} values of the unfilled vulcanizates are similar to that of the original vulcanizate, and do not seem to depend on heteroring content. On the contrary, those of the filled vulcanizates are higher than the original and increase with heteroring content, except in the case of the propionaldehyde modification.

As to T_B , the filled vulcanizates of the modified rubbers, except for the propionaldehyde-modified rubber, show much higher values than the original vulcanizate, and they are increasingly dependent on the content of heteroring structure, while the unfilled vulcanizates show a similar tendency but not to such a marked degree. In the case of the propionaldehyde modification, the unfilled vulcanizates have higher T_B values than the original, but the filled ones are markedly lower. This behavior is quite different from that in the other cases, although its reason is obscure.

Effects of the Heteroring

As mentioned above, the tensile modulus and strength of the filled vulcanizate of the modified rubber are higher than those of the original polymer. It was confirmed that the tensile strength of Diene NF55R decreased or increased much more slowly than those of the modified rubbers with increased loading of sulfur and accelerators or carbon black, respectively (Tables IV and V).

TABLE IV
Tensile Modulus and Strength of Filled Diene NF55R

Curing agents, ^a phr			M_{100} , ^b kg/cm ²	M_{300} , ^c kg/cm ²	T_B , ^d kg/cm ²	E_B , ^e %
Sulfur	Noc-celer DM	Noc-celer D				
1.20	1.00	0.250	21.4	49.7	194	875
1.35	1.12	0.282	20.6	52.2	210	915
1.50	1.25	0.312	21.4	54.1	189	760
1.80	1.50	0.375	25.5	75.6	153	547

^a The other ingredients and their amounts are as shown in Table I.

^b 100% Modulus.

^c 300% Modulus.

^d Tensile strength at break.

^e Elongation at break.

Figure 3 gives the relation between M_{100} and T_B . Almost all the points of the modified rubbers are in the upper region divided by the curve of the original Diene. These facts suggest that the improved tensile strength of the modified rubber cannot be attributed to the high-level modulus owing to chemical crosslinks. The effect rather resembles that of carbon black, and it may reasonably be assumed that the heteroring makes the carbon black reinforcement much more efficient.

TABLE V
Tensile Modulus and Strength of Filled Diene NF55R

Carbon black, ^a phr	M_{100} , ^b kg/cm ²	M_{300} , ^c kg/cm ²	T_B , ^d kg/cm ²	E_B , ^e %
40	19.1	49.2	186	680
50	23.4	59.7	203	650
60	32.3	88.8	214	545
70	37.6	102.0	201	565

^a The other ingredients and their amounts are as shown in Table I.

^b 100% Modulus.

^c 300% Modulus.

^d Tensile strength at break.

^e Elongation at break.

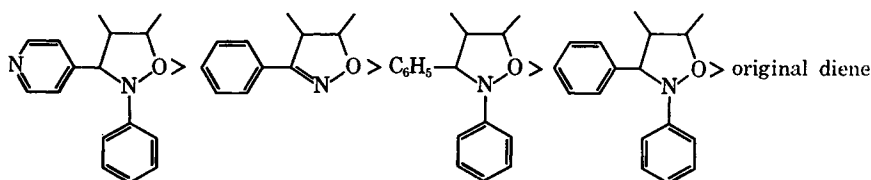
TABLE VI
Effect of Modification of Rubber (5 mole-% Modified)

	M_{100} , kg/cm ²			T_B , kg/cm ²			
	Unfilled	Filled	Δ^a	Un-filled	Filled	Δ^a	
Original Diene NF55R	10.3	21.4	11.1	15	194	179	
Structure of heteroring							
	R =	9.4	22.4	13.0	16	197	181
	R = C ₂ H ₅	11.6	26.5	14.9	24	140	116
	R =	10.4	31.9	21.5	24	219	195
	R =	8.7	26.5	17.8	20	273	253

^a Δ = Difference between values of unfilled and filled rubbers.

In order to compare the influence of various heterorings on the tensile properties, the results of modulus and strength of 5 mole-% modified rubber are given in Table VI, which were taken from Figure 2. The difference Δ between the characteristic values of the filled and unfilled rubbers indicates the degree of carbon black reinforcement of rubber.

The Δ values of M_{100} decrease in the following order:



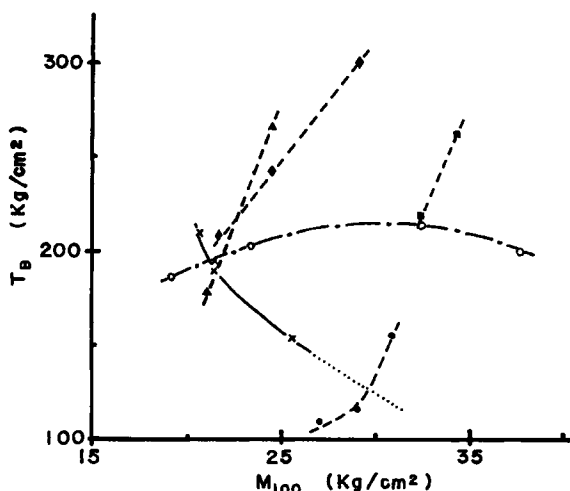


Fig. 3. Relation between M_{100} and T_B of filled vulcanizates: original Diene NF55R modified with (×) various loading of sulfur and accelerators, and (O) with various loading of carbon black; (●) rubbers modified with propionaldehyde-phenylhydroxylamine; (▲) rubbers modified with benzaldehyde-phenylhydroxylamine; (■) rubbers modified with *p*-pyridinealdehyde-phenylhydroxylamine; (◆) rubbers modified with benzhydroxamic acid chloride-triethylamine.

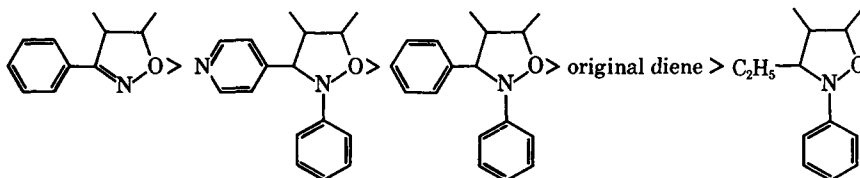
This order appears to agree closely with that of the donating nature of the ring. The donabilities of heteroring were estimated from methanol-*d* interaction by means of IR spectroscopy.

The IR shifts of the O-D stretching bands of methanol-*d* ($\Delta\nu$) caused by the interaction with model heteroring compounds whose structures correspond to each heteroring introduced in rubber were measured (Table VII). Unexpectedly, $\Delta\nu$ of 3,5-diphenylisoxazoline hardly differs from that of 2,3,5-triphenylisoxazolidine. The relation between $\Delta(M_{100})$ of the modified rubber and of the corresponding model compound is illustrated in Figure 4. In case of the isoxazolidine-containing rubber, a parallelism between $\Delta(M_{100})$ and $\Delta\nu$ was observed. This does not contradict the concept that the isoxazolidine groups in rubber interact with acid sites on the surface of carbon black particles and that the degree of crosslinking increases, resulting in an increasing modulus. Although in case of the isoxazoline-containing rubber $\Delta(M_{100})$ is much larger than that expected from the $\Delta\nu$ value.

TABLE VII
IR Shift of Methanol-*d*

Compounds	ν_{O-D} , cm^{-1}	$\Delta\nu$, cm^{-1}
Benzene	2666	—
3,5-Diphenylisoxazoline	2572	94
2,3,5-Triphenylisoxazolidine	2571	95
3-Ethyl-2,5-diphenylisoxazolidine	2538	128
3- <i>p</i> -Pyridyl-2,5-diphenylisoxazolidine	2480	186

As to T_B , the following order is obtained:



Tensile strength is difficult to evaluate because it depends very much upon the damage to the polymer chain during the course of the modification reaction. The order of T_B is similar to that of M_{100} , but the effect of the

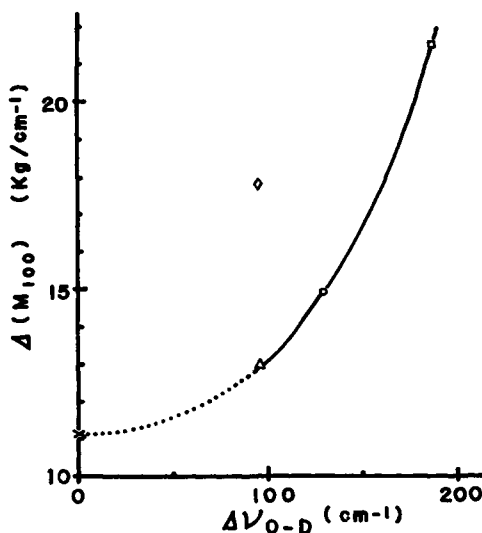


Fig. 4. Relation between Δ value of M_{100} and Δv_{0-D} of modified rubbers: (x) original Diene NF55R; (o) rubber modified with propionaldehyde-phenylhydroxylamine; (Δ) rubber modified with benzaldehyde-phenylhydroxylamine; (\square) rubber modified with *p*-pyridinealdehyde-phenylhydroxylamine; (\diamond) rubber modified with benzhydroxamic acid chloride-triethylamine.

heteroring on T_B cannot be explained only by increasing crosslinking density, which was mentioned previously. The properties of the interaction between heteroring and carbon black and of the polymer chain containing the five-membered heterocyclic ring have to be considered together.

CONCLUSION

A polybutadiene rubber of low *cis*-content was modified with 1,3-dipolar systems, aldehyde-phenylhydroxylamine and hydroxamic acid chloride-triethylamine. The modified rubbers had higher tensile modulus values and were much improved in tensile strength at break. The latter is not caused only by the higher modulus value, but is also owing somewhat to

the heterocyclic ring introduced into the polymer chain by the modification. The differences between the moduli of the filled and unfilled vulcanizates parallel the IR shift of the O-D stretching band of methanol-*d* caused by the interaction with the donor substances, which correspond to the heterorings introduced into the rubber polymer. The modification in tensile properties may be owing mainly to the interaction between the carbon black particles and the isoxazolidine and isoxazoline groups, which have electrodonating properties.

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