

1-Chloro-1,3-Butadiene Copolymers. I. Synthesis of Copolymer with 1,3-Butadiene and Physical Properties of Its Vulcanizate

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Synopsis

Emulsion copolymerization of 1-chloro-1,3-butadiene and 1,3-butadiene was carried out using potassium persulfate at 50°C. The thus synthesized 1-chloro-1,3-butadiene copolymer was possible to be cured with 2-mercaptoimidazoline (MI) as well as with sulfur. The tensile strength of the MI vulcanizate of the copolymer compounded with 30 phr HAF black reached 100 kg/cm² and was higher than that of the sulfur vulcanizate. Moreover, these two vulcanizates showed higher tensile strengths than the sulfur vulcanizate of emulsion butadiene rubber. The addition of the copolymer to the blend of chloroprene rubber (Neoprene GRT) and butadiene rubber extremely improved the elongation and the tensile strength. Dynamic measurements of the vulcanizates showed that the glass transition temperature of the copolymer was situated at the region between that of butadiene rubber and that of chloroprene rubber.

INTRODUCTION

It has been known that the radical copolymerization of chloroprene with 1,3-butadiene (Bd) is practically impossible, on account of the large difference of monomer reactivity ratios for chloroprene ($r_1 = 3.41 \pm 0.07$) and Bd ($r_2 = 0.059 \pm 0.014$).¹ Accordingly, to our knowledge, there has been no study concerning the development of a synthetic rubber which has the intermediate properties of butadiene rubber (BR) and chloroprene rubber (CR). Carothers² estimated that the relative rates of homopolymerizations of chloroprene, 1-chloro-1,3-butadiene (CB), isoprene, and Bd were to be 700, 7, 1, and 0.8, respectively. Klebanskyi et al.³ reported that the polymerization of CB took place predominantly in the 3,4-configuration due to the steric hindrance of the chlorine atom. On the other hand, there has been no study of copolymerization with CB, though Bauchwitz et al.⁴ mentioned the possibility of copolymerization; and

recently it was reported that CB had worsening effects on chloroprene polymerization, presumably because CB was acting as a comonomer for chloroprene.⁵

Hence, CB possibly undergoes copolymerization with Bd and produces a copolymer having a chlorine atom, which probably shows properties intermediate between BR and CR. Thus, in the present study we have undertaken the synthesis of CB copolymer with Bd and investigated the properties of its vulcanizate. CB, employed here, is a by-product in the reactions leading to chloroprene from Bd, and was purified effectively to be used for polymerization.

EXPERIMENTAL

Materials

1-Chloro-1,3-Butadiene (CB). CB was purified several times by fractional distillation with 2,6-di-*t*-butyl-*p*-cresol as a polymerization inhibitor. CB rectified in this manner has a boiling point of 66.5°C (lit.³ 66.8–67.2°C) and a refractive index n_D^{20} of 1.4710 (lit.³ 1.4718). There are *cis* and *trans* isomers for CB, but no attempt was made to separate the isomers since both isomers show virtually the same physical properties. The purity of the monomer exceeded 98% by gas-chromatographic analysis, and the impurities were chloroprene and chlorobutenes, the quantities of which were below 2% and below 1%, respectively.

1,3-Butadiene (Bd). Bd gas was passed through KOH pellets and molecular sieve 5A, and distilled into a graduated flask in a Dry Ice-methanol bath and further distilled into an ampoule under vacuum.

Other Reagents. *n*-Dodecylmercaptan was purified by distillation (bp 125.3 °C/5 mm Hg, lit.⁶ 124°C/5 mm Hg) under reduced nitrogen pressure. Sodium oleate was recrystallized from 95% ethanol solution. The other reagents and additives which were commercially available were used without further purification.

Emulsion Copolymerization of CB and Bd

Reagents other than Bd were introduced in a glass ampoule according to recipe A or B shown in Table I. The ampoule was connected to a vacuum line into which Bd was distilled. It was then sealed off under vacuum and placed in a water bath at 50°C. The agitation of the polymerization solution was practiced by the rotation of the whole ampoule at a speed of 24 rpm. After a definite time of polymerization, the emulsified solution was poured into a methanol solution of 2,6-di-*t*-butyl-*p*-cresol (0.2 wt-%), phenothiazine (0.2 wt-%), di-*n*-butyltin dimaleate (1.0 wt-%), and di-*n*-butyltin dilaurate (0.1 wt-%). The last two reagents were used as stabilizers against dehydrochlorination of the copolymer. The resulting polymer was filtered and dried under vacuum, and then purified by reprecipitation (cyclohexane-methanol) several times. The chlorine con-

TABLE I
Recipes for Emulsion Polymerization (Parts by Weight)

	Recipe A (pH = 10)	Recipe B (pH = 12)
Monomer	100	100
<i>n</i> -Dodecyl mercaptan	1.4	1.4
Water	180	200
K ₂ S ₂ O ₈	0.23	2.0
Sodium oleate	4.3	—
K salt of rosin acid ^a	—	8
Na salt of condensation product ^b	—	0.8
NaOH	—	0.8

^a Potassium salt of disproportionated rosin acid soap.

^b Sodium salt of a formaldehyde-naphthalene sulfonic acid condensation product.

tents of the copolymer were determined by elemental analysis. Infrared spectra of the polymers were recorded on a Japanese Spectroscopic Co. Model 402 G spectrometer. As the CB content of the copolymer was relatively low, the number-average molecular weight was calculated according to the equation which had been obtained for polybutadiene by emulsion polymerization.⁷

Compounding and Vulcanization

The rubbers were masticated at room temperature on an open roll and the required amounts of compounding ingredients were added. The compounding recipes are shown in Tables II and III. Rubber blends were prepared from the rubbers shown in Table III, which were further roll milled at various blending ratios. It is noticeable that the copolymer was compounded with sulfur and MI as vulcanizers. The rubber compounds were cured at 150°C for a definite time on a hot press. The degree of swelling of the vulcanizate was measured by dipping the sample in benzene

TABLE II
Compounding Recipes for Copolymer (Parts by Weight)

	Sulfur vulcanization	MI vulcanization
Rubber	100	100
Stearic acid	1	1
Antioxidant D ^a	0.5	0.5
HAF black	0 or 30	0 or 30
Sulfur	2	—
Zinc oxide	5	—
Accelerator CZ ^b	1.5	—
Nocceler #22 ^c	—	1.5
Pb ₃ O ₄	—	5

^a Phenyl- β -naphthylamine.

^b N-Cyclohexyl-2-benzothiazyl sulfenamide.

^c 2-Mercaptoimidazoline (MI).

TABLE III
Compounding Recipes of Rubbers for Blending

Ingredients	BR ^a	CR ^b	Copolymer
Rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	1	1	1
Antioxidant D ^c	0.5	0.5	0.5
HAF black	30	30	30
Sulfur	2	—	1
Accelerator CZ ^c	1.5	—	0.75
Nocceler #22 ^c	—	0.5	0.25
Magnesium oxide	—	2	1

^a Low-*cis* polybutadiene rubber (Diene NF-35R, Asahi Chemical Industry Co. Ltd.).

^b Neoprene GRT.

^c See Table II.

at 25°C for 30 hr, and the crosslinking density (ν) of the vulcanizate was calculated by the Flory-Rehner equation.⁸

Mechanical Measurements

The stress-strain curves were obtained on an autographic tensile tester at room temperature. The rate of elongation was set at 50 mm/min. Measurements of the dynamic storage moduli and loss moduli of the vulcanizates were carried out on a Vibron DDV-2 (Toyo Baldwin Co., Ltd.) at 110 cps as a function of temperature.

RESULTS AND DISCUSSION

Effect of *n*-Dodecylmercaptan on Copolymerization

The copolymerizations were carried out with various amounts of *n*-dodecylmercaptan according to the polymerization recipe B in Table I. Figure 1 illustrates the relationship between the amount of *n*-dodecylmercaptan and the number-average molecular weight of the copolymer produced. The molecular weight of the copolymer decreases abruptly from 10⁶ to 10⁴ with an increase in *n*-dodecylmercaptan in the range of 1.2 to 1.6 parts. Based on the results in Figure 1, the molecular weight of the copolymer could be controlled.

Emulsion Copolymerizations and Confirmation of Copolymer Formation

Table IV shows the results of the copolymerizations of CB and Bd. The copolymerizations according to recipe A (runs no. 1, 5, 6, and 7) reveal that conversion becomes lower and the gel fraction increases as the feed ratio of CB to Bd increases. In the extreme case, i.e., in the case of homopolymerization of CB, conversion was lowest and the gel fraction was large. This may be attributed at least partly to hydrolysis⁹ of CB and poly-CB, and/or dehydrochlorination of the latter, which were effective in

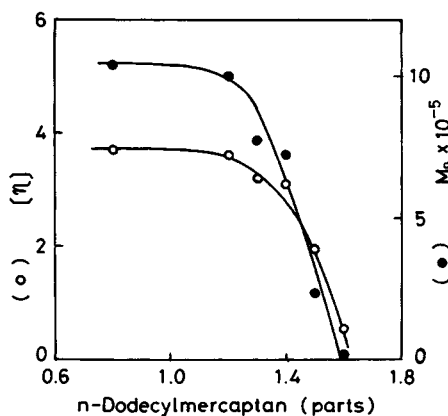


Fig. 1. Effect of *n*-dodecyl mercaptan on molecular weight of copolymer obtained by emulsion polymerization (recipe B in Table I, monomer feed ratio CB/Bd = 5/95): (○) limiting viscosity number; (●) number-average molecular weight.

destroying the emulsion by hydrochloric acid formation during polymerization. On the other hand, polymerization recipe B afforded more satisfactory results, namely, the gel fraction of the copolymer was minor and intrinsic viscosity was much larger.

The CB homopolymer was insoluble in cyclohexane and carbon tetrachloride, but soluble in benzene, chloroform, and chlorobenzene. The copolymer was purified by repeating several times the process of dissolving in cyclohexane and precipitating with methanol. Ultimately, the cyclohexane solution of the copolymer was filtered through a wire cloth of 200 mesh, the gel fraction and CB homopolymer being separated in this manner. The resulting copolymer was studied by IR, NMR, and elemental analyses.

TABLE IV
Copolymerization of CB and Bd at 50°C

Run no.	Polymerization recipe	Monomer feed ratio CB/Bd ^a	Polymerization time, hr	Conv., %	CB content, ^b mole-%	Gel fraction, ^c %	[η] ^d
1	A ^e	100/0	9	7.3	100	69.0	—
2	A	5/95	14	60.2	1.24	0	1.60
3	B	5/95	10	49.4	1.83	2.1	3.14
4	B	0/100	10	41.5	0	0.8	3.29
5	A ^e	5/95	9	29.9	1.26	43.1	—
6	A ^e	10/90	9	27.5	7.68	61.3	—
7	A ^e	15/85	9	20.3	12.9	87.3	—

^a Weight ratio.

^b Calculated from Cl% by elemental analysis.

^c Benzene-insoluble part.

^d In toluene at 25.9°C.

^e 0.5 Parts of *n*-dodecyl mercaptan was used.

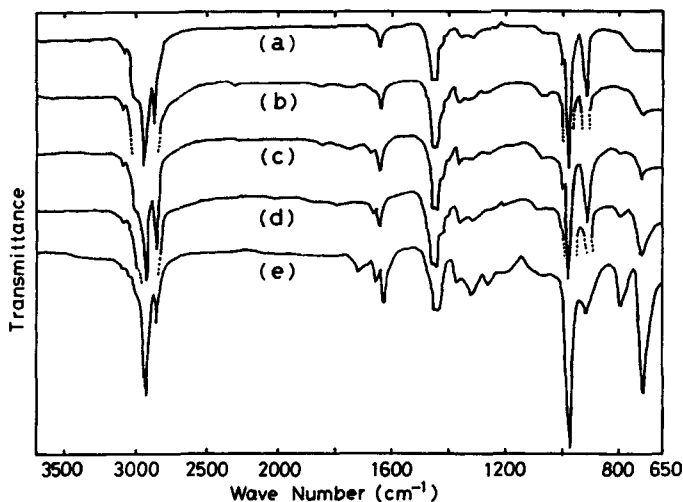


Fig. 2. Infrared spectra of CB-Bd copolymers: (a) polybutadiene; (b) copolymer (CB content, 1.24 mole-%); (c) copolymer (7.68 mole-%); (d) copolymer (12.9 mole-%); (e) poly(1-chloro-1,3-butadiene).

Figure 2 shows the IR spectra of the copolymers purified as described above. The band of C-Cl stretching vibration at 715 cm^{-1} is noted in the spectra of CB homopolymer and the copolymers, but disappears in the polybutadiene spectrum. The relative intensity of this band becomes larger with increase in CB content, which was determined by elemental analysis of chlorine. The microstructure of the butadiene units in the copolymer was determined from IR peaks according to the method of Morero et al.¹⁰ The results were 17% of *cis*-1,4-, 57% of *trans*-1,4-, and 26% of 1,2-enchainments of monomeric units, which were almost the same as those of the emulsion polybutadiene.⁷

The NMR spectrum of the copolymer is shown in Figure 3. On account of the low CB content (1.24 mole-%) of the copolymer, the influence of chlorine atom on the spectrum was impossible to be detected. From the intensity ratio of the proton signals at 1.23 ppm and 1.98 ppm,¹¹ the microstructure of the copolymer was calculated as 76% for 1,4-structures and 24% for 1,2-structures. These values are almost equal to those of the IR method mentioned above.

Physical Properties of Copolymer Vulcanizates

Vulcanizations were carried out according to either of the recipes shown in Table II. Consequently, it was found that the vulcanization of the copolymer was possible to be achieved either by sulfur or by 2-mercaptoimidazoline (MI) vulcanization. Table V shows the effect of cure time on tensile properties. As can be easily seen, the highest tensile strengths at the break of copolymer vulcanizates were superior to those of the polybutadiene vulcanizates either in HAF black stocks or in gum stocks.

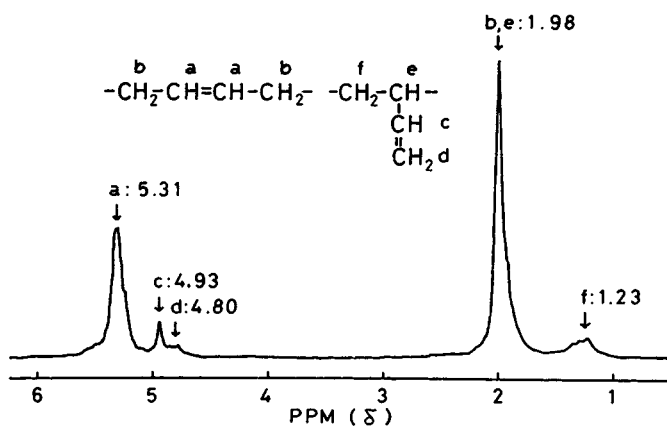


Fig. 3. NMR spectrum of CB-Bd copolymer. CB content in copolymer, 1.24 mole-%. In CCl_4 at room temperature; TMS as internal standard.

Between the filled copolymer vulcanizates, the highest T_B or MI vulcanizate was superior to that of the sulfur vulcanizate and reached 100 kg/cm^2 of T_B . It was found that 150% moduli (M_{150}) of the copolymer vulcanizates were much higher than those of emulsion BR vulcanizates.

The relationship between crosslinking density and cure time indicates that the optimum cure time of the sulfur vulcanization is about 40 min for BR and the copolymer. Concerning the vulcanization of chloroprene rubber with sulfur-substituted thiourea-zinc oxide system, Pariser¹² noted

TABLE V
The Effect of Cure Time on Tensile Properties

	Cure time min	Gum stock				HAF black stock			
		Copolymer ^a		BR		Copolymer ^a		BR	
		S ^b	MI ^c	Em. ^{b,d}	So. ^{b,e}	S ^b	MI ^c	Em. ^{b,d}	So. ^{b,e}
T_B , kg/cm^2	20	21	25	4.8	12	89	71	79	72
	40	27	26	15	—	75	100	80	—
	60	20	26	15	11	79	71	83	60
E_B , %	20	205	255	370	80	225	230	280	235
	40	175	230	205	—	205	215	300	—
	60	175	190	205	70	200	185	305	215
M_{150} , kg/cm^2	20	13	13	2.6	—	40	31	23	47
	40	23	15	11	—	40	44	22	—
	60	16	20	11	—	42	47	20	42
$\nu_s \times 10^4$, mole/g	20	1.31	0.96	0.06	1.86	—	—	—	—
	40	2.14	1.45	1.34	2.54	—	—	—	—
	60	1.97	1.63	1.24	2.66	—	—	—	—

^a CB content, 1.83 mole-%; $M_n = 724,000$.

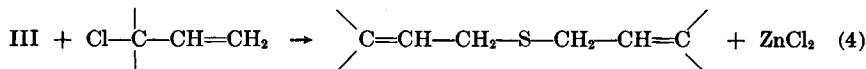
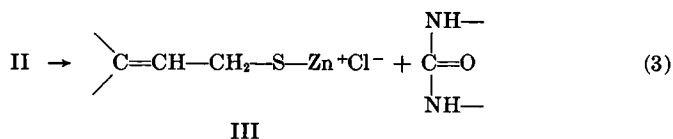
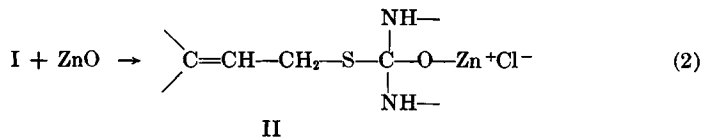
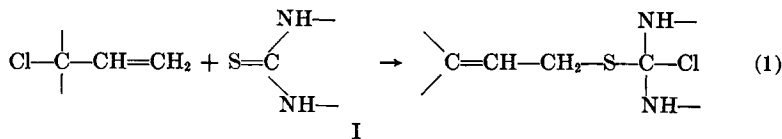
^b Sulfur vulcanizate, see Table II.

^c MI vulcanizate, see Table II.

^d Polybutadiene obtained by recipe B in Table I; $M_n = 802,000$.

^e Commercial solution-polymerization polybutadiene; $M_n = 296,000$.

the formation of the sulfur crosslinking of a monothioether type and proposed the following mechanism:



The configuration of the CB unit in the copolymer was impossible to be identified, so Pariser's mechanism cannot be applied to the present system. Nevertheless, assuming the same mechanism as stated above, the curing efficiency $(CE)_{\text{Cl}}$ of the copolymer cured with MI (employed 0.88 = fold amount of theoretical value) was possible to be calculated as follows:

Assuming that the concentration of CB in copolymer and the molecular weight of butadiene unit are x (mole-%) and M_u (g/mole), respectively, thus the average molecular weight among the crosslinked points at 100% curing efficiency for chlorine atoms, M_c^s (g/mole), is

$$M_c^s = \frac{100 \cdot M_u}{x}$$

Therefore, the crosslinking density at 100% curing efficiency, ν_s (mole/g), is

$$\nu_s = \frac{1}{M_c^s} = \frac{x}{100 \cdot M_u}$$

The curing efficiency, $(CE)_{\text{Cl}}$, is represented by the equation

$$(CE)_{\text{Cl}} = \frac{\nu}{\nu_s} = \frac{\nu}{(x/100 \cdot M_u)} \quad (5)$$

where ν is the crosslinking density (mole/g) of the vulcanizate at any curing time.

With regard to the vulcanizate cured for 60 min in Table V, crosslinking density $\nu = 1.63 \times 10^{-4}$ and CB content $x = 1.83$ were employed to obtain

a value 0.48 for $(CE)_{Cl}$. Namely, the 48% of chlorine atoms in the copolymer was used for vulcanization. In addition, the efficiency based on an MI $(CE)_{MI}$ was found to be 0.55.

Dynamic Behavior of Vulcanizates

Dynamic properties of the copolymer cured with MI are shown in Figures 4 and 5 as a function of temperature. The results of CR and BR which were obtained under the same conditions were also included in the figures. Chloroprene rubber has its transition region from freezing to the elastic state in the range of -50°C to -20°C , while that of the copolymer is -80°C to -50°C and that of BR -120°C to -50°C . In the rubbery region, E' of curve II falls as the temperature rises, which may be attributed to the low molecular weight of the copolymer used.

Figure 5 depicts the temperature dispersion of the loss tangent of BR, CR, and copolymer. The temperatures of the maximum in $\tan \delta$ are -25°C for CR, -67°C for copolymer, and -77°C for BR. These values are in conformity with the true copolymer formation as described above, as it is known that the random copolymer has one T_g at the intermediate region of the two homopolymers.¹³

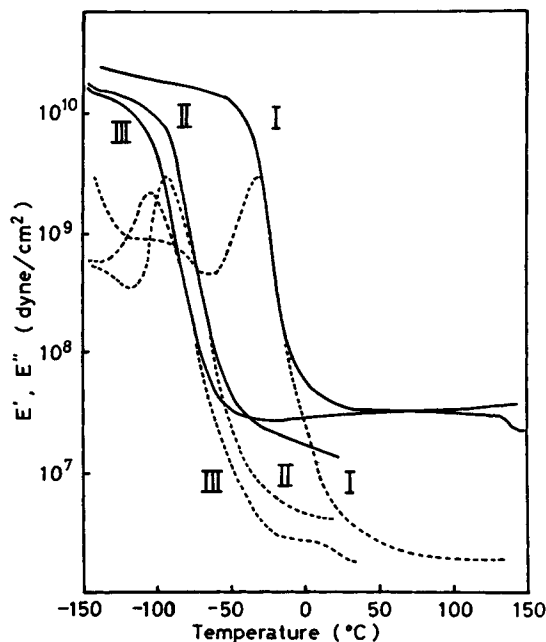


Fig. 4. Temperature dependence of storage modulus E' and loss modulus E'' for gum stocks: (—) storage modulus; (-----) loss modulus; (I) CR cured with MI; (II) copolymer cured with MI; (III) BR cured with sulfur. Copolymer CB content 1.24 mole-%, $M_n = 162,000$; cure temperature, 150°C ; cure time, 60 min. Measured at frequency of 110 cps.

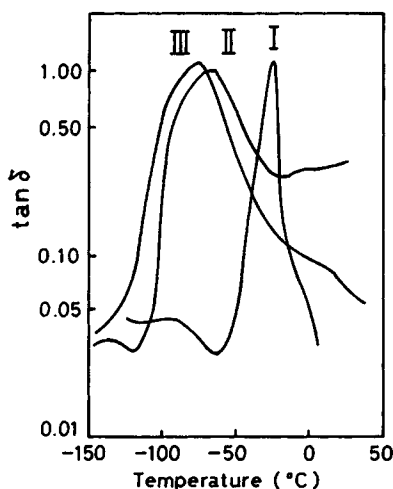


Fig. 5. Temperature dependence of loss tangent ($\tan \delta$) for gum stocks: (I) CR cured with MI; (II) copolymer cured with MI; (III) BR cured with sulfur. Other conditions are the same as in Fig. 4.

Tensile Properties of Rubber Blends

Two kinds of rubber blends were prepared, i.e., one a binary blend of BR and CR (Neoprene GRT), the other a ternary blend of BR, CR, and copolymer. All the blends were filled with 30 phr of HAF black. Tensile

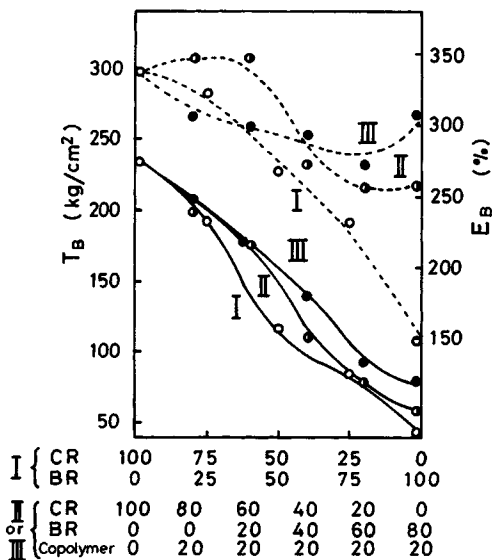


Fig. 6. Tensile strength T_B and elongation E_B of HAF black-filled vulcanizates of rubber blends: (—) T_B ; (---) E_B ; cure temperature, 150°C; cure time, 40 min; (I) CR + BR; (II) CR + BR + copolymer (CB content, 1.24 mole-%, $M_n = 162,000$); (III) CR + BR + copolymer (CB content, 1.83 mole-%, $M_n = 724,000$). Blend ratios are shown under the abscissa.

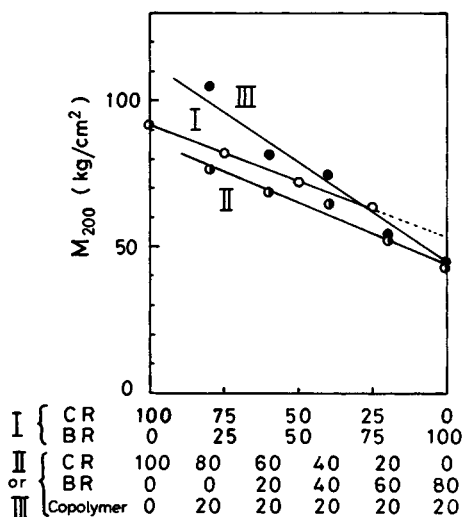


Fig. 7. Relationship between 200% modulus (M_{200}) and blend ratio for HAF black-filled vulcanizates. Samples are the same as in Fig. 6.

properties of the rubber blends are shown in Figures 6 and 7 as a function of blend ratios of the rubbers. The ternary blends (curves II and III) were superior to the binary one (curve I) in both T_B and E_B . Especially in the high blend ratio of BR, the rubbers were extremely improved in elongation by the copolymer blending. These improvements of BR ($M_n = 30 \times 10^4$) were achieved by either the low molecular weight copolymer ($M_n = 16.2 \times 10^4$) or the high molecular weight copolymer ($M_n = 72.4 \times 10^4$), but the tensile strength of the rubber blend was much more improved by using the high molecular weight copolymer.

The difference in molecular weight of the third component, copolymer, seems to be more clearly indicated in M_{200} . As is shown in Figure 7, the blend of the low molecular weight copolymer as a third component has a smaller modulus than that of the binary rubber blend, irrespective of the blend ratio, whereas the blend with the high molecular weight copolymer has a larger modulus. Summing up the results, we have found that CB-Bd copolymer is effective in improving the tensile properties of the CR-BR blend, especially when the CR content is low.

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