

Effects of Termonomers on Crosslinking Rate and Crosslinking Structure of Ethylene Propylene Terpolymers

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Synopsis

Study was made concerning both the rate of crosslinking and the structure of crosslinks of terpolymers that have dicyclopentadiene, 1,4-hexadiene, methylene norbornene, and ethylidene norbornene for termonomers so as to look into the role of termonomers during crosslinking of ethylene propylene terpolymers. In the study, activation energy and frequency factor, both apparent were determined by the rate constant of crosslinking and differences in crosslinks were analyzed following both chemical and physical methods. Infrared analysis into the volume of consumption of double bond was adopted to examine the manner of crosslinking. In respect to the magnitude of the rate constant, ethylidene norbornene came in first being followed by 1,4-hexadiene, methylene norbornene, and dicyclopentadiene. The structure of termonomers affected the apparent activation energy and the apparent frequency factor was subject to the influences of said structure and others including the variation in the degree of unsaturation. During the early stage of crosslinking, the formation of the crosslink of polysulfide-type was paramount to all others and the speed of conversion therefrom either to disulfide-type or to monosulfide varied with the kind of terpolymers and was in proportion to the rate constant of crosslinking.

INTRODUCTION

In recent years there have been developed such ethylene propylene terpolymers (EPDM) as being made sulfur curable by dint of nonconjugate termonomers like dicyclopentadiene, 1,4-hexadiene, methylene norbornene and ethylidene norbornene being induced into their main chains. Compared with other general purpose rubbers, however, such EPDM is slow of crosslinking. To improve this, therefore, great efforts have been made toward developing faster crosslinking systems like super accelerators or toward increasing the content of termonomers. That the rate constant of crosslinking in the case of such EPDM varies with the kind of termonomers is well known,¹ and in the meantime, there have been researches made as to the crosslinking rate from the point of view of kinetics.² On the other hand, there is no example of studies being known to have ever been made so closely on terpolymers as to establish relations of their such elemental matters as structure and content with their such properties as speed, structure and efficiency in crosslinking. This paper deals with results of kinetic studies

TABLE I
Samples

Termonomer	No.	Dicyclopentadiene		1,4-Hexadiene		III	IVA	IVB	IVC
		IA	IB	IC	IIA				
Commercial name		Royalene	Royalene	Royalene	Nordel	Nordel	Royalene	Ethylidene-norbornene	
		301	304	305	1070	1145	501	EP84	EP77
Iodine number		12.8	6.6	18.5	13.0	9.3	17.8	8	20.8
$[\eta]$ (in cyclohexane, 30°C)		1.9	2.9	1.9	3.3	2.7	2.2	2.6	1.9
μ (in toluene)		0.49 ± 0.01	0.48 ± 0.01	0.49 ± 0.01	0.49 ± 0.01	0.50 ± 0.01	0.47 ± 0.01		

having been made on crosslinks and, in addition to infrared analysis of the conversion of unsaturation, with the analysis of the conversion of unsaturation, with the analysis of the structure of various crosslinks of EPDM of various sorts which had dicyclopentadiene, 1,4-hexadiene, methylene norbornene and ethylidene norbornene for termonomers.

EXPERIMENTS

Samples

The terpolymers were of such kind and properties as summarized in Table I. For determination of the iodine value of a polymer, the Rosenmund-Kuhnenn's method was adopted. The polymer-solvent interaction parameter as obtained from the stress-strain diagram and the degree of the equilibrium swelling in toluene as to the crosslinked sample for tetraline swelling averaged 0.49, while the literature gives figures of 0.49³ and 0.47-0.48.⁴

Compounding

Compounding was done on the test roll according to the formula given in Table II. For the samples to compare the rate constant and to analyse the structure of various kinds of terpolymers, compounding by the formula of Sample *a* referred to therein was undertaken.

TABLE II
Compounding Formula

Samples	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
Polymer	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	0.5	1	1	1
Tetramethylthiuram disulfide	1.20	1.20	0.60	—	—	1.20
Zinc dimethyl dithiocarbamate	—	—	—	1.53	—	—
2-Mercaptobenzothiazole	0.50	0.50	0.25	—	—	0.50
Morpholine disulfide	—	—	—	—	—	2.36
Sulfur	1.29	1.29	0.65	1.29	—	—
Dicumyl peroxide	—	—	—	—	5.40	—
React. Temp. (°C)	160	180	160	160	160	160

Preparation of Crosslinking Samples

Samples to study the crosslinking density were prepared in the form of either a sheet of about 2 mm in thickness or a film as thin as some 0.1 mm, while, for samples to measure the infrared spectrum, thickness was reduced further to about 0.05 mm.

Determination of Crosslinking Density

To determine the swelling of the crosslinked sample in toluene, both gravimetric and optical methods⁵ were followed and the results obtained by

each method were found in a good state of mutual agreement. The calculation for the crosslinking density (Mc^{-1}) was conducted according to the Flory-Rehner's equation, assuming 0.49 for the polymer-solvent interaction parameter.

Method of Kinetic Data Analysis

The rate constants of both crosslinking and reversion were determined on the time-conversion curve of crosslinking density, i.e., the first order equation previously published was employed for crosslinking reaction:²

$$\alpha U_2 \xrightarrow{k_1} X, \quad \frac{d(X)}{dt} = k_1 (\alpha U_2)$$

where the symbols, respectively, representing

U_2 = unsaturate degree of the rubber

X = crosslinking density

α = efficiency constant of the use of unsaturation.

For the assessment of the reversion, the rate thereof was assumed to be in proportion to the density of crosslink, i.e.,

$$-\frac{d(X)}{dt} = k_2 (X)$$

As for the over-all reaction, the following equation can be induced,

$$X_t = -X_\infty \frac{k_1}{k_1 - k_2} (e^{-k_1 t} - e^{-k_2 t}) \quad (1)$$

and if the reversion is negligible, i.e., $k_2 = 0$, the following is applicable,

$$X_t = X_\infty (1 - e^{-k_1 t}) \quad (2)$$

where X_t is the crosslinking density at the time of t , and X_∞ is its maximum value when there occurred no reversions.

Actual analysis of the experimental data on the rate constant was by means of the graphic presentation method⁶ and followed by the process where part of the data was applied to the above-stated equation for proving.

Analysis of the Structure of Crosslinks

The concentration of polysulfide crosslink was determined by the Coran's formula.⁵ Specimens of about $5 \times 5 \times 0.1$ mm (thickness) in dimensions were taken from crosslinked sheets by following the microtomic method. The swelling of these samples was optically observed with the dipping time in toluene limited to 30 min, and for the complete scission of their polysulfide crosslink in a fresh dispersed toluene tetrahydrofuran (1:1) solution of LiAlH_4 , 40 min was allowed for the reversion time. Other processes were the same as in the case of Coran's formula.

The organically combined amount of sulfur and that of disulfuration by triphenylphosphine were determined according to the Moore's method.⁷

Infrared Examination of Crosslinked Samples

To measure the spectrum, sample films were crosslinked or a crosslinked sample of the shape of a board was sliced by the use of a microtome into films of the thickness of same 0.05 mm.

Kinetic experiment such as mentioned below was conducted to select the standard peak for use in the peak ratio method. The thin film that had been scraped off the sample compound was sandwiched in between the two plates of KBr held stationary by supports and the crosslinking was carried out by heating the said whole unit in an oven whose temperature was maintained at 160°C. The measurement of the spectrum was performed for each period of the reaction time by keeping the unit in as constant conditions as possible.

RESULTS AND DISCUSSION

Reaction Rate

The typical examples of the time-conversion curves of the crosslinking density are as shown in Figures 1-3.

The solid lines in Figures 1 and 2 are theoretical as calculated by the eq. (1) mentioned before into which the experimental data were put for the constants. The result showed that the theoretical treatment well agreed with the experimental facts except in the latter part of the reaction period, where disagreement occurred due to perhaps the complexity of real reversion mechanism of crosslinking k_1 and of the reversion k_2 as analyzed, thus

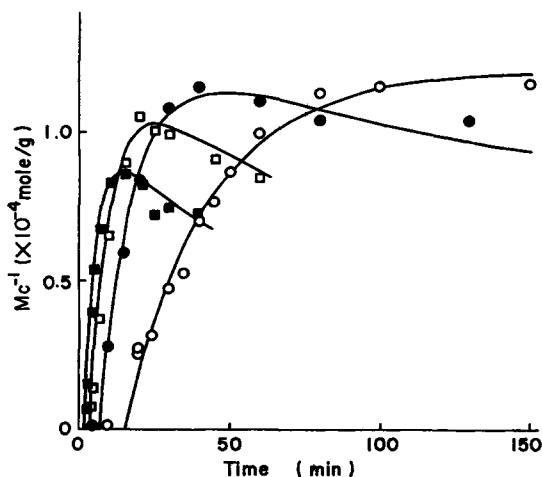


Fig. 1. Reaction time-conversion curves of crosslinking for IA: (○) 150°C; (●) 160°C; (□) 170°C; (■) 180°C; (—) theoretical curve.

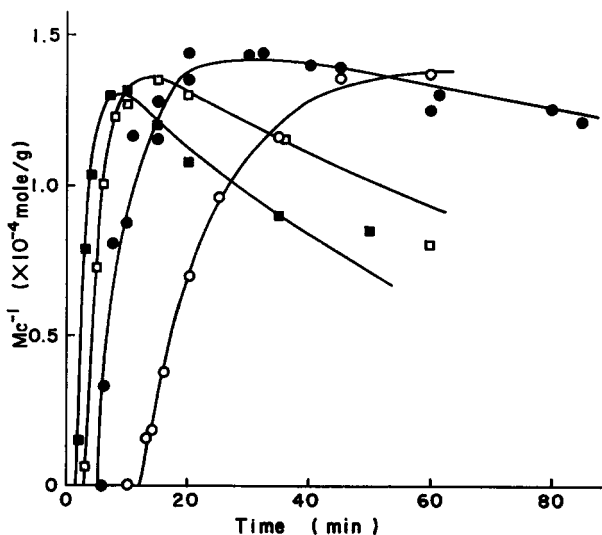


Fig. 2. Reaction time-conversion curves of crosslinking for IIA: (○) 150°C; (●) 160°C; (□) 170°C; (■) 180°C; (—) theoretical curve.

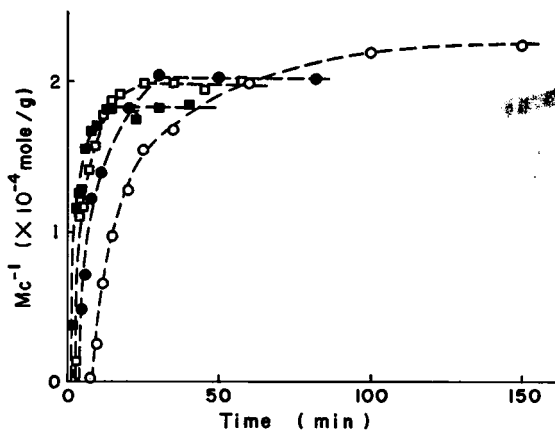


Fig. 3. Reaction time-conversion curves of crosslinking for III: (○) 150°C; (●) 160°C; (□) 170°C; (■) 180°C.

far the maximum values of crosslinking densities of each polymer are as indicated in Table III.

The order of the size of the rate constants of crosslinking for different terpolymers turned out as follows: IV > II > III > I.

In the crosslinking of dicyclopentadiene terpolymer, the rate constant, although not changed in other terpolymers, increased with the increase of unsaturation.

It was considered that the apparent rate constant for dicyclopentadiene terpolymers might change with the ratio of sulfur to unsaturation.

TABLE III
Rate Constant

Polymer	k_1 or k_2 ($\times 10^{-2}$ min $^{-1}$) ^a										M_c^{-1} max. at 150°C ($\times 10^{-4}$ mole/g)	E_2 (kcal/mole)	Log A
	130°C	135	140	150	155	160	165	170	175	180			
IA k_1	—	—	—	3.6	—	10.0	10.7	16.1	25.1	28.4	1.16	25.2	11.6
IA k_2	—	—	—	N	—	0.25	0.44	0.54	0.80	1.0	—	—	—
IB k_1	—	—	—	3.3	—	7.8	—	13.5	16.8	21.1	1.32	23.7	10.8
IB k_2	—	—	—	N	—	N	—	0.32	0.95	1.2	—	—	—
IC k_1	—	—	—	9.4	—	15.0	27.1	33.0	48.1	67.8	1.80	25.7	12.0
IC k_2	—	—	—	N	—	N	0.11	0.19	0.30	0.37	—	—	—
IIA k_1	—	—	—	8.9	—	17.1	24.5	39.1	41.9	54.9	1.36	23.8	11.2
IIA k_2	—	—	—	N	—	0.17	0.43	0.79	0.96	2.1	—	—	—
IIB k_1	—	—	—	7.2	—	18.4	24.0	31.1	44.0	57.1	2.42	26.8	12.8
IIB k_2	—	—	—	N	—	0.24	0.50	0.70	0.87	2.0	—	—	—
III k_1	—	—	—	6.9	—	13.9	—	22.2	26.6	35.5	2.22	20.7	9.6
III k_2	—	—	—	N	—	N	—	N	N	N	—	—	—
IVA k_1	3.7	4.5	8.5	16.0	24.0	23.0	—	—	—	—	1.68	24.3	11.1
IVA k_2	N	N	N	N	N	N	—	—	—	—	—	—	—
IVB k_1	4.8	4.1	8.5	21.0	19.0	22.0	—	—	—	—	1.60	21.0	10.0
IVB k_2	N	N	N	N	N	N	—	—	—	—	—	—	—
IVC k_1	3.6	5.0	5.0	12.0	—	40.0	—	—	—	—	2.00	26.5	12.9
IVC k_2	N	N	N	N	—	N	—	—	—	—	—	—	—

^a N: Negligible.

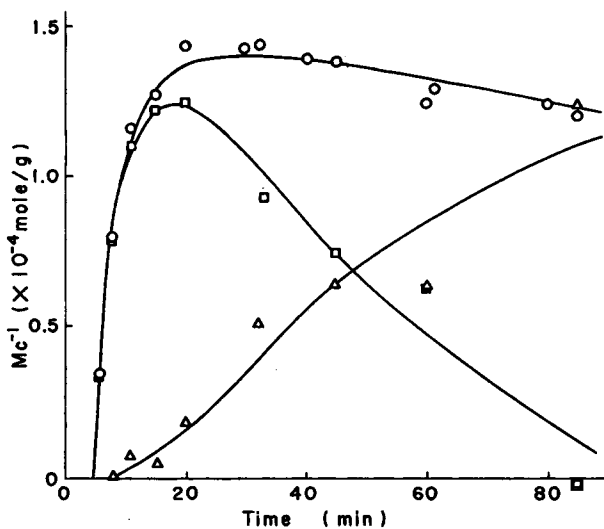


Fig. 5. Reaction time-conversion curves of various crosslinks for IIA at 160°C: (○) ν_T ; (□) ν_P ; (Δ) ν_M .

the initial period in dicyclopentadiene terpolymers, but in others the formation of nothing but polysulfide crosslink occurred.

The organically combined sulfur and the number of sulfur atoms combined per crosslink are presented in Table IV.

TABLE IV
Amount of Organically Combined Sulfur (Sc) and the
Number of Sulfur Atoms Combined per Crosslink (2 Sc/Mc⁻¹)

Polymer	React. Temp. (°C)	React. time (min)	Mc ⁻¹ (× 10 ⁻⁴ mole/g)	Sc (× 10 ⁻⁴ mole/g)	2 Sc/Mc ⁻¹
IA	160	15	0.59	3.25	11.0
		40	1.16	4.12	7.1
		80	1.04	4.10	7.9
IB	"	20	0.71	2.97	8.4
		50	1.24	4.21	6.8
		80	1.07	3.73	7.0
IIA	"	8	0.81	2.78	6.9
		20	1.43	3.60	5.3
IIB	"	80	1.21	2.34	3.9
		10	1.60	3.13	3.9
		30	2.32	3.69	3.2
III	"	80	2.07	2.75	2.7
		8	1.21	3.15	5.2
		30	2.04	4.00	3.9
IVA	"	80	2.09	3.53	3.4
		8	1.0	3.41	6.8
		20	1.6	3.50	4.4
		80	1.5	2.72	3.6

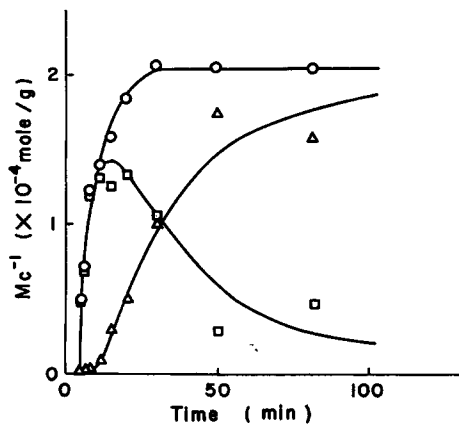


Fig. 6. Reaction time-conversion curves of various crosslinks for III at 160°C: (○) ν_T ; (□) ν_P ; (Δ) ν_M .

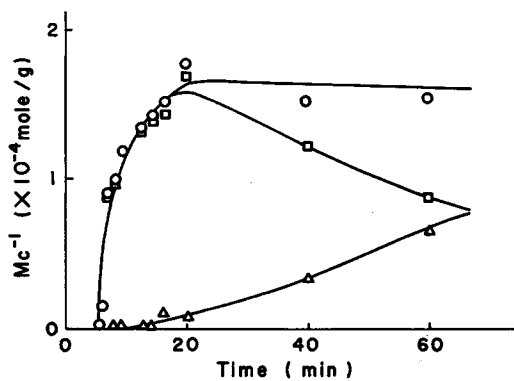


Fig. 7. Reaction time-conversion curves of various crosslinks for IVA at 160°C: (○) ν_T ; (□) ν_P ; (Δ) ν_M .

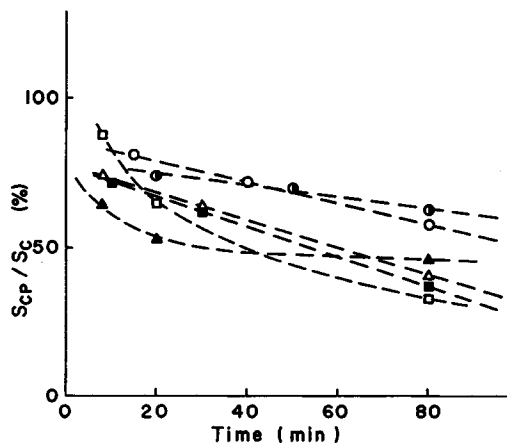


Fig. 8. Change in the amount of disulfuration in respect to portion thereof to the total organically combined sulfur: (○) IA; (●) IB; (□) IIA; (■) IIB; (Δ) III; (▲) IVA.

Crosslinking efficiencies of the present terpolymers seemed to be lower than that of natural rubber⁹ and subject to some differences. The efficiencies in dicyclopentadiene terpolymers were lower than in other terpolymers.

The ratio of the sulfur amount as removed by triphenylphosphine treatment to original sulfur content changed as shown in Figure 8. The conversion rates of the polysulfide to the mono and disulfide sulfurs differed with the sort of terpolymers and the magnitude of such rates seemed to be in order of: IV > II, III > I.

It was found that the larger was the decrease rate of polysulfide crosslink, the larger was the rate constant of crosslinking.

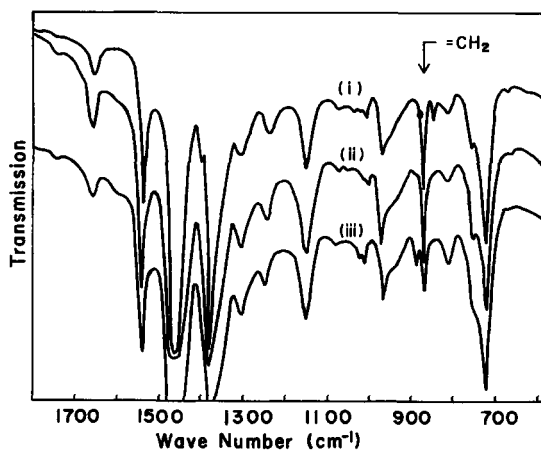


Fig. 9. Spectra for the samples of III in sulfur crosslinking system *a*: (i) sample sliced off from a compound; (ii) sample treated for 3 min at 130°C; (iii) crosslinked sample.

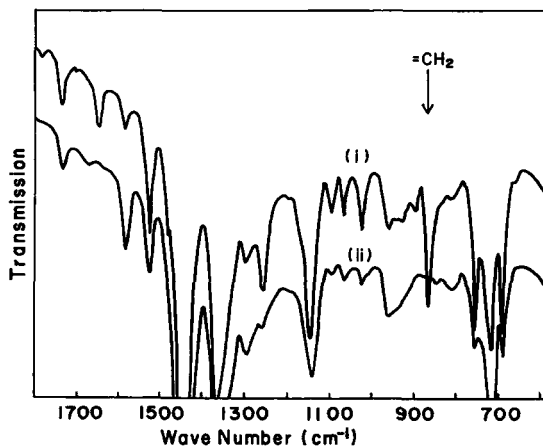


Fig. 10. Spectra for the samples of III in peroxide crosslinking system *e*: (i) sample treated for 3 min at 130°C; (ii) crosslinked sample.

Utilization of Double Bond

Spectra for the samples of methylene norbornene terpolymer are shown in Figures 9 and 10.

The absorption of double bond lowered as affected by crosslinking. The changes of absorption which were quantitatively investigated by heating a uniform film having been put between two plates of KBr and which were analyzed by the base line method are shown in Figure 11.

It was made clear that the absorption at 1150 cm^{-1} for propylene unit and at 720 cm^{-1} for ethylene block underwent no change except in the initial

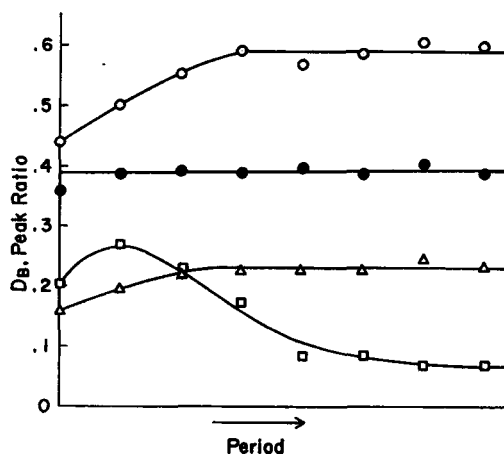


Fig. 11. Change in absorptions during crosslinking obtained from uniform sample of III in sulfur crosslinking system: (O) 720 cm^{-1} ; (□) 870 cm^{-1} ; (Δ) 1150 cm^{-1} ; (●) peak ratio between 1150 cm^{-1} and 720 cm^{-1} .

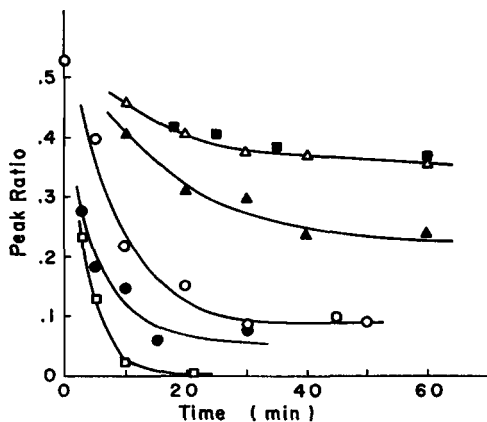


Fig. 12. The consumption curves of unsaturation for III: (Peak ratio: $870\text{ cm}^{-1}/720\text{ cm}^{-1}$): (O) Sample a; (●) Sample b; (Δ) Sample c; (▲) Sample d; (□) Sample e; (■) Sample f.

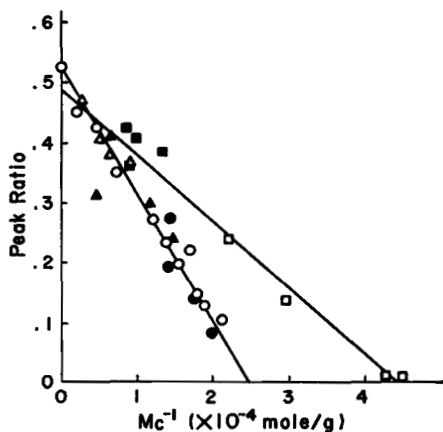


Fig. 13. Relation between consumption of unsaturation and crosslinking density for III (Peak ratio: $870\text{ cm}^{-1}/720\text{ cm}^{-1}$): (○) Sample a; (●) Sample b; (△) Sample c; (▲) Sample d; (□) Sample e; (■) Sample f.

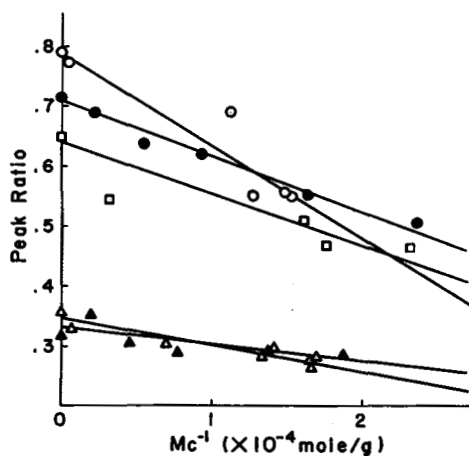


Fig. 14. Relation between consumption of unsaturation and crosslinking density for IC, IIA, and IIB (Peak ratio: $3035\text{ cm}^{-1}/720\text{ cm}^{-1}$ for IC, $966\text{ cm}^{-1}/720\text{ cm}^{-1}$ for IIA and IIB): (△) IC-Sample a; (▲) IC-Sample e; (○) IIA-Sample a; (●) IIA-Sample e; (□) IIB-Sample a.

period in which the sample was kept flowing. The peak ratio between the both cases of absorption was constant throughout the period. The changes of unsaturation during crosslinking were represented by the peak ratio of the absorption of double bond to the standard. The changes of peak ratio for each curing system are shown in Figure 12 in reference to the crosslinking of methylene norbornene terpolymer.

The linear relations were obtained between the crosslinking density, and consumption of double bond in all cases examined in this work are as shown in Figures 13 and 14.

TABLE V
Consumption of Double Bond

Polymer	Crosslinking agent	U ($\times 10^{-4}$ mole/g)	M_c^{-1} ($\times 10^{-4}$ mole/g)	$M_c^{-1}/\Delta U$
IC	Sulfur	7.2	7.6	1.1
	Peroxide		11	1.5
IIA	Sulfur	5.1	4.4	0.9
	Peroxide		7.7	1.5
IIB	Sulfur	3.7	5.5	1.5
III	Sulfur	4.0	2.5	0.6
	Peroxide		4.4	1.1

From the intercepts of these correlation lines with axis of abscissa (M_c^{-1}) and unsaturation of raw polymers (U), crosslinking efficiencies of double bond ($M_c^{-1}/\Delta U$) could be calculated. These values are summarized in Table V.

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