

# Isothermal Degradation of *cis*-1,4-Polyisoprene Vulcanizates

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## Synopsis

The isothermal degradation of high *cis*-1,4-polyisoprene vulcanizates having different crosslinking structures was investigated by a measurement of weight loss of sample, IR and NMR, gel permeation chromatography (GPC), and gas chromatography (GC). The degradation behavior of dicumyl peroxide-cured sample is similar to that of the uncrosslinked one. On the other hand, a sulfur-cured sample is very different from the other samples. At the initial stage of the degradation, weight loss in this sample is faster than that in an uncrosslinked one. Furthermore, a microstructural change in this polymer occurring by thermal degradation is also very much larger than microstructural changes in the others. This will be attributed to polythiyl radicals produced by the scission of polysulfide crosslinkages. Although the polyisoprene chain undergoes random scission along the main chain above 473 K under inert gas or *in vacuo*, a molecular weight distribution of the residue after thermal degradation was broadened as the degradation proceeded. That is to say, the fragments having enormous molecular weight increase together with the production of lower molecular weight compounds. This indicates the occurrence of crosslinking reaction and the addition of polymer radicals to carbon-carbon double bonds in another polymer molecule in the thermal degradation process. Such reactions are thought to take place in the crosslinked polymers, in particular the sulfur-cured polymer, in larger quantities. Thermal degradation mechanisms were discussed in some detail.

## INTRODUCTION

Studies of thermal degradation of rubbers have been carried out using (1) thermogravimetry (TG) and differential TG (DTG),<sup>1-5</sup> differential thermal analysis (DTA),<sup>6,7</sup> and differential scanning calorimetry (DSC),<sup>8,9</sup> (2) gas chromatography-mass spectroscopy (GC-MS),<sup>10-13</sup> and (3) infrared spectroscopy (IR) and nuclear magnetic resonance (NMR).<sup>14-16</sup> Most of the thermal degradation studies of rubbers have been made under the condition of temperature-program heating or flash heating in an inert atmosphere. Isothermal degradation of rubbers has been scarcely investigated.

Generally, the diene rubbers undergo random scission along the main chain above 473 K under inert gas or *in vacuo*.<sup>17,18</sup> However, few volatile products are obtained below 523 K. Probably the polymer radicals produced by main chain scissions are thought to react by addition to carbon-carbon double bonds, recombination, and/or disproportionation. Above 523 K, various low molecular weight compounds, mainly monomer and dimer, are produced. The microstructure of polymer residue also changes during the thermal degradation above 473 K.<sup>14-16</sup>

Degradation of rubber vulcanizates may be affected by crosslinking structures. In the present paper, we investigated the thermal degradation of *cis*-1,4-polyisoprene vulcanizates having different crosslinking structure in the temperature range of 523–623 K, using (1) the measurement of weight loss of samples, (2) IR and NMR spectroscopies, (3) gel permeation chromatography, and (4) GC.

## EXPERIMENTAL

**Samples.** High *cis*-1,4-polyisoprene (Nipol 2200, Nippon Zeon Co., Ltd.) was used in this work. The polymer was extracted with hot acetone for 48 h in nitrogen and dried *in vacuo*. Since this polymer had contained high gel fraction, only a sol fraction was concentrated by filtration and lyophilized. The molecular weight of this was measured by gel permeation chromatograph (GPC; Toyo Soda Manufacturing Co., Ltd.; HLC-802UR). To protect the purified polymer against oxidation, it was stored *in vacuo* in the dark. The polymer was dissolved with curing reagents in benzene-eliminated air and was lyophilized. Dicumyl peroxide (DCP) was recrystallized from ethanol. The commercial sulfur powder was used as a crosslinking reagent. The preparation of crosslinked polymers is described in Table I.

**Degradation in Nitrogen.** Sample weight loss was measured in nitrogen (99.99% N<sub>2</sub>) in the temperature range of 523–603 K, using the quartz spring balance constructed in our laboratory. Sample size was about 50 mg. This balance can weigh to a precision of 0.2 mg. From this measurement, the overall kinetic parameters of the formation of volatile low molecular weight compounds can be obtained.

**Degradation *in Vacuo*.** A diagram of apparatus used to decompose the rubbers *in vacuo* is shown in Figure 1. The pressure inside the vacuum line was about  $2 \times 10^{-4}$  Torr. The sample size was about 150 mg. Decomposition of rubbers was mainly carried out at 573 K for 1–3 h. The volatile products were trapped at the temperature of liquid nitrogen and the higher molecular weight compounds (viscous liquid ones) were trapped at room temperature, which were generated during heating. There was a residue in the furnace.

**Analysis of Degradation Products and Residue.** The mixture of volatile constituents produced was analyzed using conventional gas chromatography (GC; Shimadzu Co., Ltd., GC-4CPT). The column used is the stainless steel tubing (2m  $\times$  4mm o.d.) packed with silicone rubber (10% SE30) supported on an inert substrate (60/80 mesh Chromosorb AW-DMCS). The microstructural changes of the liquid products and the residues were investigated by the infrared (IR; Hitachi Co., Ltd., EPI-S2) and <sup>1</sup>H-NMR spectroscopies (Nippon Denshi Co., Ltd., JNM-C-60HL). The molecular weight of these products and the residue was measured by the gel permeation chromatography.

## RESULTS AND DISCUSSION

### Isothermal Degradation under Nitrogen

The weight loss of samples 1, 2, and 3 was measured in nitrogen in the temperature range of 523–603 K. Below 523 K, the weight loss did not appear in the observation time. The relative weight vs. time  $\{\log[W(t)/W(0)]$  vs.  $t$  of

TABLE I  
Preparation of *Cis*-1,4-Polyisoprene Vulcanizates

Sample no.	Curing ingredients	Curing time	Curing temp	Crosslinking structure	Crosslinking density <sup>c</sup>
1 <sup>a</sup>	—	—	—	—	—
2	DCP <sup>b</sup>	30 min	418 K	C—C	$2.14 \times 10^{-1}$ mol/dm <sup>3</sup>
3	sulfur	240 min	418 K	C—S <sub>x</sub> —C (x ≥ 1)	$1.24 \times 10^{-1}$ mol/dm <sup>3</sup>

<sup>a</sup> High *cis*-1,4-polyisoprene (98.5% *cis*: Nipol 2200, Nippon Zeon Co., Ltd.).

<sup>b</sup> Dicumyl peroxide.

<sup>c</sup> Estimated using statistical theory of rubberlike elasticity.

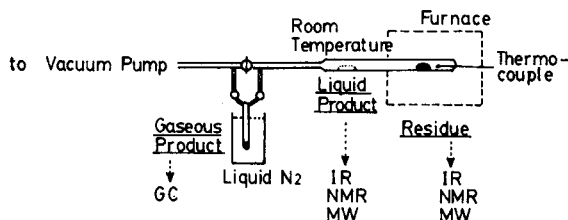


Fig. 1. Diagram of apparatus for thermal degradation of polymer *in vacuo*.

sample 2, for a typical example, is shown in Figure 2. It can be seen from the figure that all the weight loss curves linearly decay with time at the initial stage and then indicate a gradual departure from the straight lines at later stage. This degradation behavior suggests that the microstructural change in this sample occurs together with the production of volatile low molecular weight substrates. The weight loss of all the samples at 573 K is shown in Figure 3. The degradation of DCP-cured polyisoprene (no. 2) proceeds in a similar way to that of uncross-linked one (no. 1). This suggests that the presence of crosslinkages consisting of carbon-carbon bonds does not appreciably affect the weight loss of sample. On the other hand, the rate of weight loss of sulfur-cured polyisoprene (no. 3) is faster than that of the other samples at the initial stage, and a deviation from the straight line in  $\log[W(t)/W(0)]$  vs.  $t$  plots also appears at a comparatively early observation time. It has been known that the main chain of this sample is modified to some extent during the curing process.<sup>19</sup> Therefore, the thermal degradation behavior of sample 3 is thought to be different from the others.

The initial rate constant of the weight loss,  $\log k$  ( $\text{min}^{-1}$ ) was plotted against the reciprocal temperature,  $1/T$  ( $\text{K}^{-1}$ ) (Fig. 4). From the slope of the straight lines in the figure, apparent activation energies ( $F_a$ ) for the thermal degradation were estimated as about 210 kJ/mol for samples 1 and 2 and about 155 kJ/mol for sample 3, respectively. This means that the formation process of volatile compounds for sample 3 is different from that of the other samples.

The crosslinkage of sample 3, as is well known, consist of mono-, di-, and polysulfides. Polysulfides are thermally labile. Therefore, polythiyl radicals,

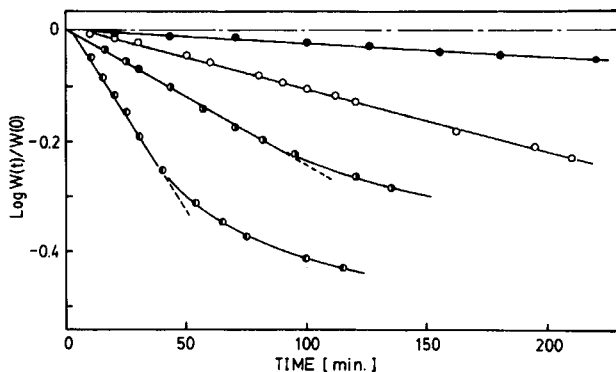


Fig. 2. Relative weight loss curves of DCP-cured rubber (sample 2) at various temperatures (K) under nitrogen: (●) 553; (○) 573; (●) 583; (●) 603.

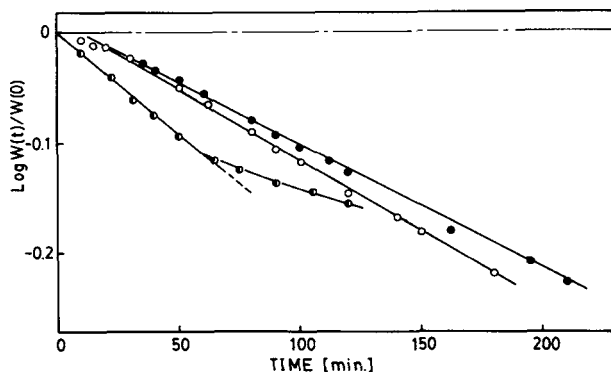


Fig. 3. Relative weight loss curves of various samples at 573 K under nitrogen: (O) uncrosslinked rubber (sample 1); (●) DCP-cured rubber (sample 2); (◐) sulfur-cured rubber (sample 3).

which will be produced by the thermal scission of the polysulfide crosslinkages at lower temperature, will influence the following reactions.

### Isothermal Degradation *in Vacuo*

#### *Molecular Weight of Viscous Liquid Products and Residue*

As mentioned above, during heating of the sample above 523 K, the volatile components, the viscous liquid ones, and the residue are produced. The residue after the degradation for 1 and 3 h at 573 K was weighed. Figure 5 shows the relations between  $\log[W(t)/W(0)]$  and  $t$ . Although these, because of approximate values, can not be directly compared with the results in nitrogen (Fig. 3), the liquid products seem to be formed about 10–20 wt % during the degradation for 3 h at 573 K. Since the fragments having higher molecular weight will not

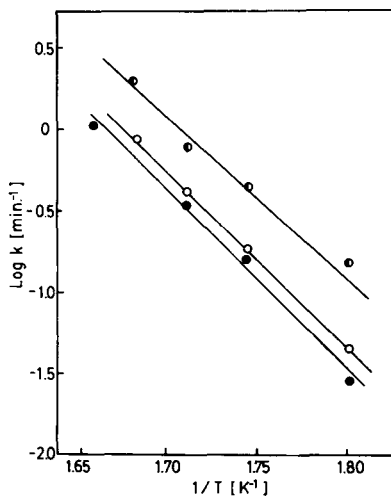


Fig. 4. Relation between initial rate constant ( $\log k$ ) of weight loss and reciprocal temperature ( $1/T$ ): (O) sample 1; (●) sample 2; (◐) sample 3.

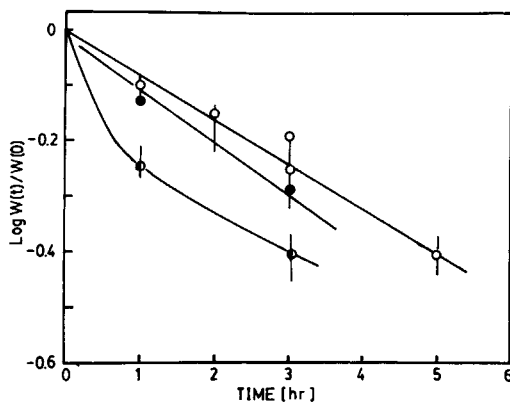


Fig. 5. Relative weight loss curves of various samples at 573 K *in vacuo*. Symbols as in Figure 3.

be able to be removed from the furnace during heating in nitrogen, the secondary products will be also contained in fairly large quantities. On the other hand, in the case of the degradation *in vacuo*, few secondary products will be formed, since both the volatile products and the liquid substances are almost immediately removed from the furnace.

The measurement of gel permeation chromatograph (GPC) was carried out for the liquid products and the residue. The residue of uncrosslinked sample (no. 1) did not contain the gel fraction. As the residue of crosslinked samples (nos. 2 and 3) has a large amount of gel fraction (about 30 wt %), it was eliminated by filtration before GPC measurement. Figure 6 shows the GPC profile of the liquid products for samples 1, 2, and 3. For all the samples, the number average molecular weight ( $M_n$ ), the weight average one ( $M_w$ ), and the distribution ( $M_w/M_n$ ) of the liquid products were estimated from the GPC data, as given in Table II. The  $M_w/M_n$  value for sample 1 seems to become progressively greater with degradation time. The estimates of  $M_n$  and  $M_w$  of liquid products for

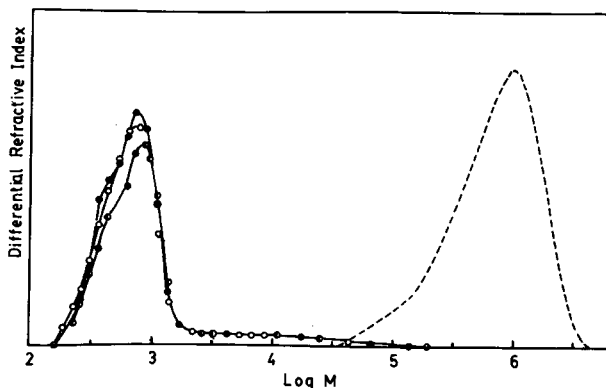


Fig. 6. GPC profiles of liquid products obtained by thermal degradation of various samples for 3 hr at 573 K: (---) uncrosslinked rubber before degradation (sample 1); (○) sample 1; (●) sample 2; (◐) sample 3.

TABLE II  
Molecular Weights and Molecular Weight Distribution of Liquid Products and Residue

Sample no.	Degradation time	Liquid product		Residue		
		$M_n$	$M_w$	$M_n$	$M_w$	
1	0			393,800	859,800	2.2
	1	540	1450	3500	9600	2.8
	3	560	1680	3400	39700	11.8
	5	550	1780	3300	52000	15.6
	3	560	2100	3900	16600	4.3
3	3	670	2110	3200	13300	4.1

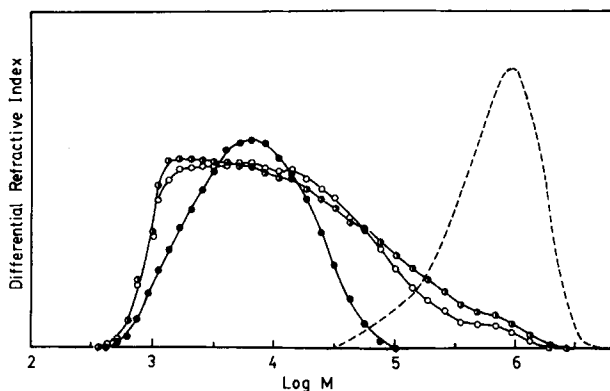


Fig. 7. GPC profiles of residue after thermal degradation of sample 1 for different times at 573 K: (---) uncrosslinked rubber before degradation (sample 1); (●) 1 h; (○) 3 h; (◐) 5 h.

samples 2 and 3 are somewhat higher compared with that for sample 1. However, it should be considered that the overall GPC profile of liquid products was not so largely affected by the conditions of degradation, e.g., temperature and time, and further even by the existence of crosslinkage. The  $M_n$  of the liquid product for sample 1 is about 560, corresponding to the octamer of isoprene.

The GPC profile of the residue for sample 1 is shown in Figure 7. From the figure, it is found that the average molecular weight values significantly decrease at the initial stage of degradation, while the distribution slightly increases, at least, during heating for 1 h at 573 K. The profile significantly changes from the initial one as the degradation proceeds. Interestingly, the fragments having higher molecular weight ( $M > 10^5$ ) are produced with degradation time together with lower molecular weight ones. Therefore, the number average molecular weight does not change with the degradation time, but the molecular weight distribution ( $M_w/M_n$ ), nevertheless, varies. The formation of fragments having higher molecular weight may be caused by the crosslinking, that is, recombination of polymer radicals and/or addition reaction of polymer radicals to carbon-carbon

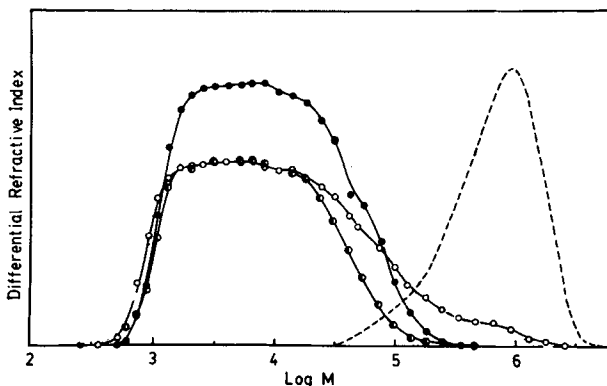


Fig. 8. GPC profiles of residue after thermal degradation of various samples for 3 h at 573 K. Symbols as in Figure 6.



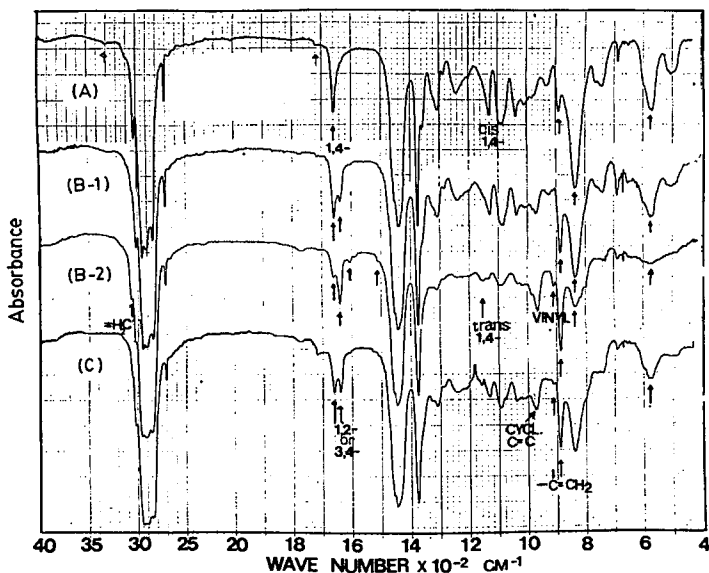


Fig. 9. IR spectra of sample 1 before and after thermal degradation at 573 K: (a) before degradation; (B-1) liquid products obtained during heating for 1 h; (B-2) liquid products obtained during heating for 3 h; (C) residue after heating for 3 h.

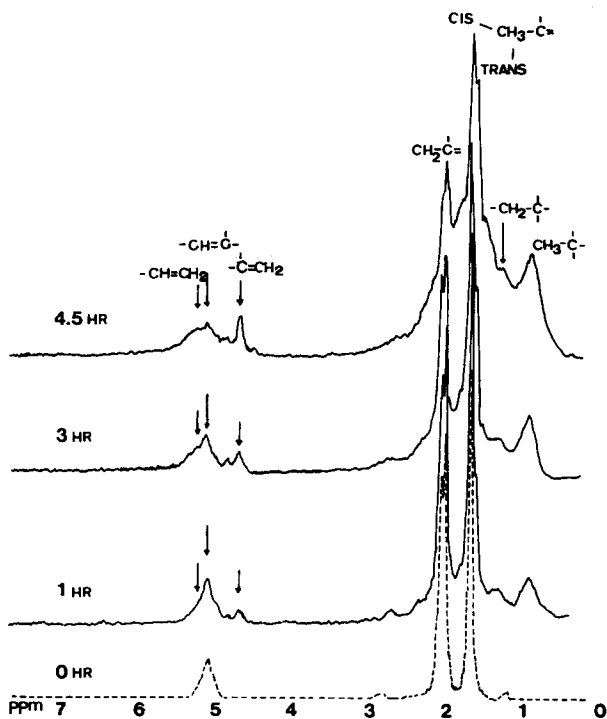


Fig. 10(a). NMR spectra of liquid products obtained by thermal degradation of sample 1 for different times at 573 K.

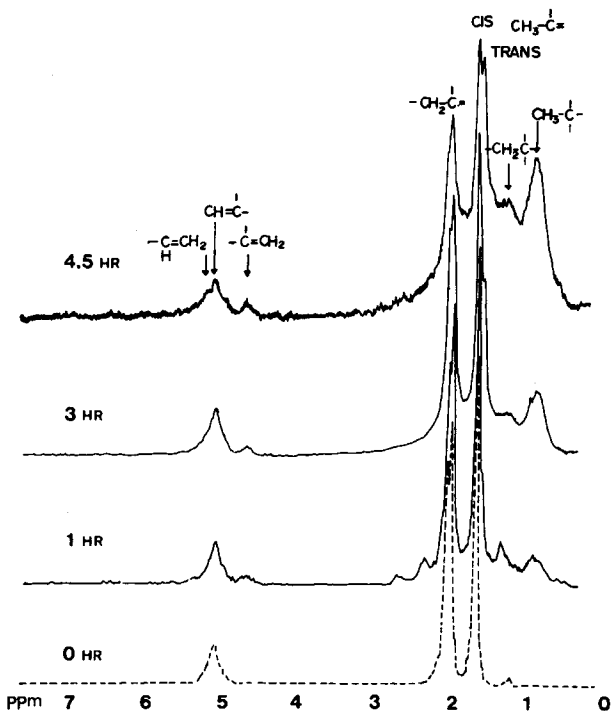


Fig. 10(b). NMR spectra of residue after thermal degradation of sample 1 for different times at 573 K.

double bonds on the other polymer chains. Figure 8 shows GPC profile of the residue for samples 1, 2, and 3 have heating at 573 K for 3 h. Although  $M_n$  values for all the samples are similar to each other, the molecular weight distributions ( $M_w/M_n$ ) for the crosslinked polymer (samples 2 and 3) are appreciably narrow compared with that for the uncrosslinked one (sample 1) (Table II). This is probably due to the fact that the partial fragments with enormous molecular weight are contained in the gel fraction.

#### *Microstructural Change of Liquid Products and Residue by Thermal Degradation*

The change of chemical structures was observed for the liquid products trapped at room temperature and the residue in the furnace. Figure 9 shows IR spectra for sample 1 before and after degradation at 573 K *in vacuo*. Figures 10(a) and (b) show NMR spectra of the liquid products and the residue for the sample 1, respectively. The change of microstructure becomes progressively greater as degradation proceeds. These results are very similar to Golub's observations<sup>14-16</sup> related to 1,4-polyisoprenes. He has investigated the microstructural changes of the various diene polymers due to the TGA type-thermal degradation using IR and NMR spectroscopies in detail. Both spectra of the residue and the liquid products are similar to each other, although the change for the latter appears to be larger. The results for samples 2 (DCP-cured) and 3 (sulfur-cured) are shown in Figures 11(a) and (b) and 12(a) and (b), respectively.

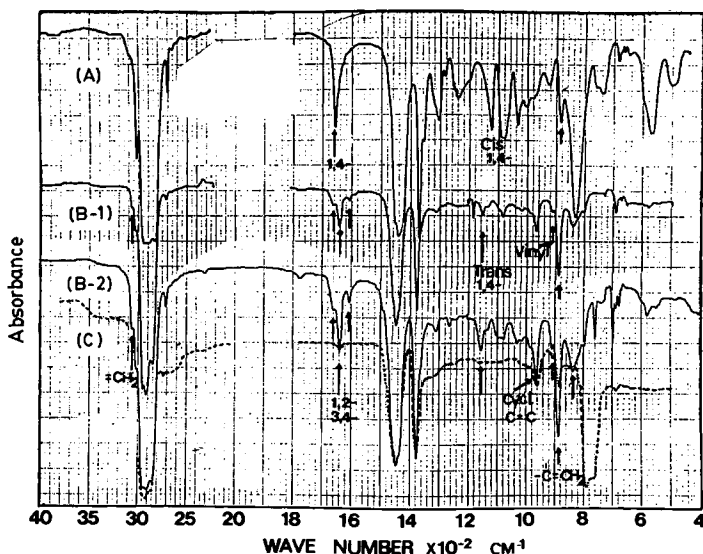


Fig. 11(a). IR spectra of sample 2 before and after thermal degradation at 573 K: (A) before degradation; (B-1) liquid products obtained during heating for 1 h; (B-2) liquid products obtained during heating for 3 h; (C) residue after heating for 3 h.

As can be seen from the comparison with Figures 9 and 10, the structural change of crosslinked polymers is larger than that of the uncrosslinked one (sample 1), and the change of the liquid degradation products, on the contrary to the case of sample 1, is smaller than that of the residue. Especially, in the spectra of these crosslinked polymers after heating for 3 h, the significant decrease of double bonds is observed. This means that the existence of crosslinks in the polymer effects the change of microstructure due to thermal degradation.

Although quantitative comparison is difficult, *cis/trans* isomerization, cyclization, and formation of 1,2 double bond for crosslinked polymers take place more quickly than those for the uncrosslinked one. This is remarkably observed in the spectra of sulfur-cured sample (no. 3). The residue of this sample is colored in brown. A further pronounced difference in the degradation behavior between uncrosslinked and crosslinked polymers is whether aromatic groups and/or conjugated double bonds are observed in the spectra of the residue and the liquid products. This is probably based on the fact that conjugated double bonds are first formed by the hydrogen abstraction from the polymer chain, followed by the production of aromatic compounds.

#### *Gas Chromatography of Low Molecular Weight Products Trapped at Temperature of Liquid Nitrogen*

Various gaseous fragments are generated by heating *in vacuo* or under an inert gas above 523 K. Figure 13 shows the gas chromatogram of volatile products, for samples 1, 2, and 3, elaborated during heating at 573 K for 3 h. Chromatograms are very complicated. A number of low molecular weight compounds are produced. The main products are isoprene monomer and dimers. The latter

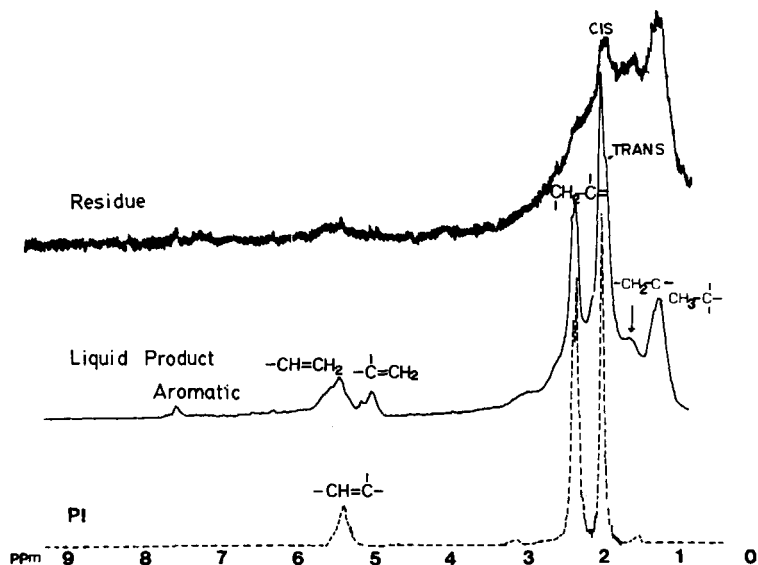


Fig. 11(b). NMR spectra of sample 2 after heating for 3 h at 573 K: (---) uncrosslinked rubber (sample 1) before degradation.

are formed in much larger quantities. The production of dimers progressively increases as the decomposition temperature is lowered. Dipentene is chiefly produced as cyclic dimers of isoprene, which has been identified by infrared and  $^1\text{H-NMR}$  spectra. In the case of sulfur-cured polyisoprene (sample 3), the relative quantity of benzene increases and that of  $\text{C}_7$  compounds, probably, 3-methylcyclohexene, decreases. This will be based on the formation of conjugated double bonds on the main chain. Such a structural change may have partially occurred in the process of crosslinking reaction of rubber,<sup>19,20</sup> although it cannot be observed in the infrared spectra.

The gas chromatogram of volatile degradation products of dicumyl peroxide-cured polyisoprene (sample 2) is somewhat different from that of the other samples. That is to say, isoprene, dipentene, and benzene are chiefly produced. Only a little of the other compounds produced by decomposition of samples 1 and 3 are obtained. This suggests that the presence of crosslinks affects the degradation mechanisms and/or the microstructure of main chain has been changed by the crosslinking reaction.

### Mechanisms of Thermal Degradation of *Cis*-1,4-Polyisoprene Vulcanizates

Generally, diene rubbers undergo thermally random scission along the main chain *in vacuo* or under an inert gas above 473 K.<sup>17,18,21</sup> The crosslinking site in the sulfur-cured sample (no. 3) is first cleaved at a moderately lower temperature, that is, the exchange reaction of polysulfide linkages takes place above 353 K<sup>22</sup> and the scission at or near mono- and disulfide crosslink sites occurs above 413 K.<sup>23</sup> Thus, polythiyl radicals are produced by such reactions (Scheme I below). However, the volatile compounds occur in negligibly small amounts

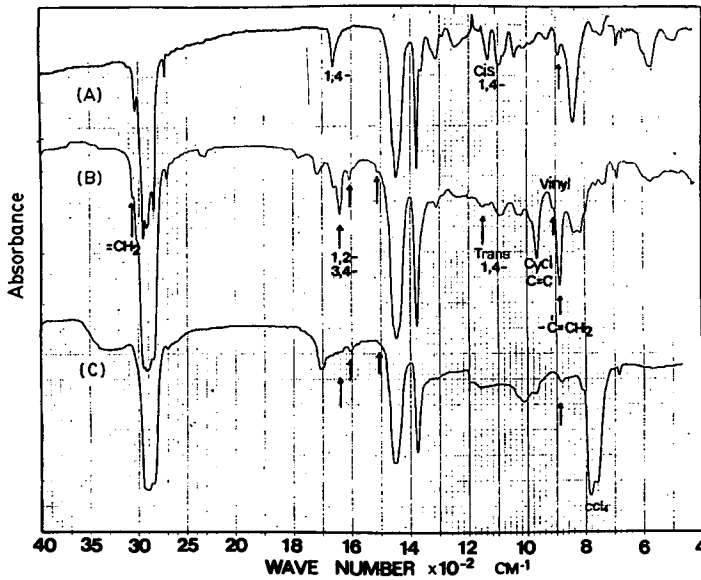


Fig. 12(a). IR spectra of sample 3 before and after thermal degradation for 3 h at 573 K: (A) before degradation; (B) liquid products; (C) residue.

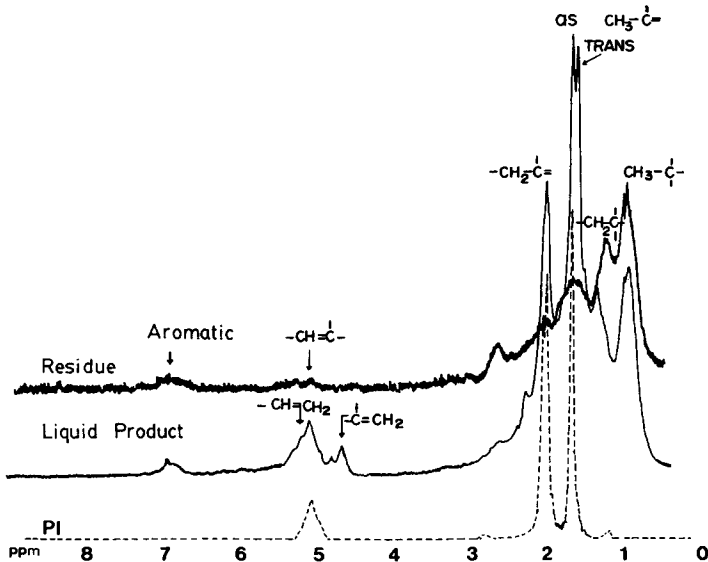
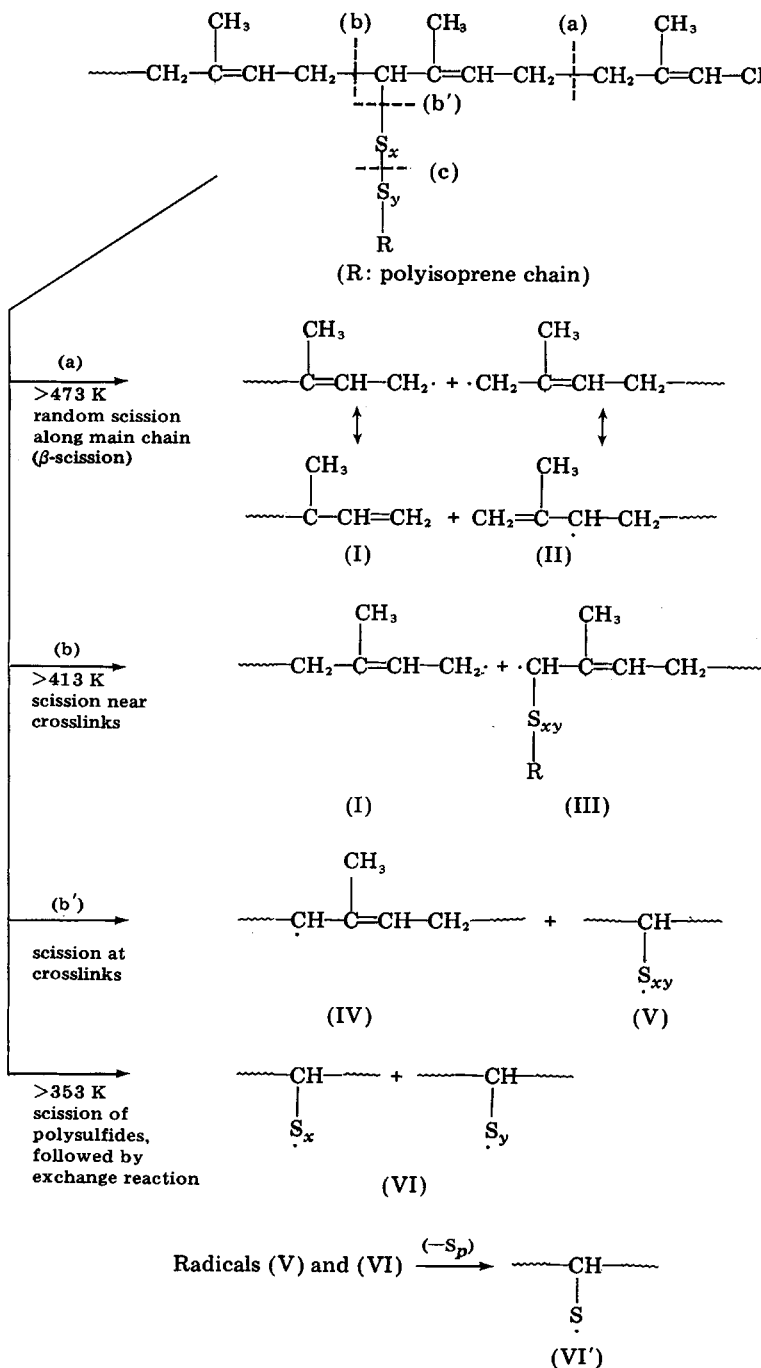


Fig. 12(b). NMR spectra of sample 3 before and after thermal degradation for 3 h at 573 K.

at temperatures below 523 K. A few percents of viscous liquid substances are formed. The polymer radicals produced by the above reactions will react by recombination, addition to carbon-carbon double bonds in the main chain, and disproportionation. Further, *cis/trans* isomerization and the formation of a 1,2 structure were observed in IR spectra for all the samples after heating above 473 K. Decrease of double bonds was scarcely observed.



Scheme I

As described above, at temperatures above 523 K, the various gaseous fragments, mainly isoprene monomer and cyclic dimer (dipentene) are also elaborated. At a comparatively lower temperature, for example, at 543 K, dipentene

is formed in fairly large quantities. The mechanism of formation of these volatile compounds has been well known in the literatures.<sup>14,24</sup> That is to say, isoprene and dipentene are produced by depolymerization from polymer radicals (I) and (II) occurring by  $\beta$ -scission to double bond (see Scheme I).

These radicals are liable to form six-membered rings, especially under mild degradation conditions. Therefore, dipentene is predominantly obtained at a lower temperature. Although the formation of various dimers may be enabled in the degradation process, dipentene has been known to be produced from 1,4-polyisoprene.<sup>14(b),25</sup> Golub and Sung<sup>14(b)</sup> and Galin<sup>25</sup> have investigated the relation between the various structures of polyisoprene and the type of dimers produced in detail.

During the thermal degradation of crosslinked rubbers, benzene is produced in somewhat quantity, while the production of C<sub>7</sub> compound, probably 3-methylcyclohexene, decreases. Although the formation mechanism of benzene and other aromatic compounds cannot be well accounted for, it will be attributed to the production of conjugated double bonds in the polymer chain during the degradation. Such a microstructural change of polymer chain may have already partially occurred in the process of crosslinking.<sup>19,20</sup> In particular, in the case of the sulfur-cured sample (no. 3), polythiyl radicals generated by the thermal scission of crosslinkages will act on the production of conjugated double bonds (Scheme II). Further, the weight loss of sample 3 in nitrogen proceeds more rapidly than that of the other samples (Figs. 3 and 4). The apparent activation energy of weight loss of this sample is also lower compared with the one of the other samples. Polythiyl radicals (III), (V), and (VI) and the other polymer

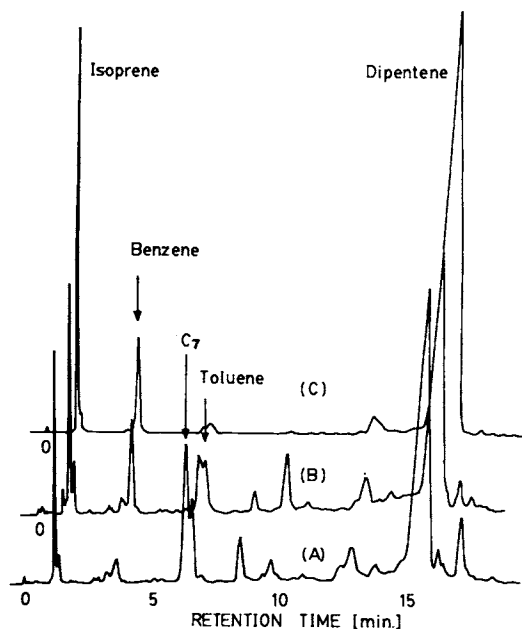
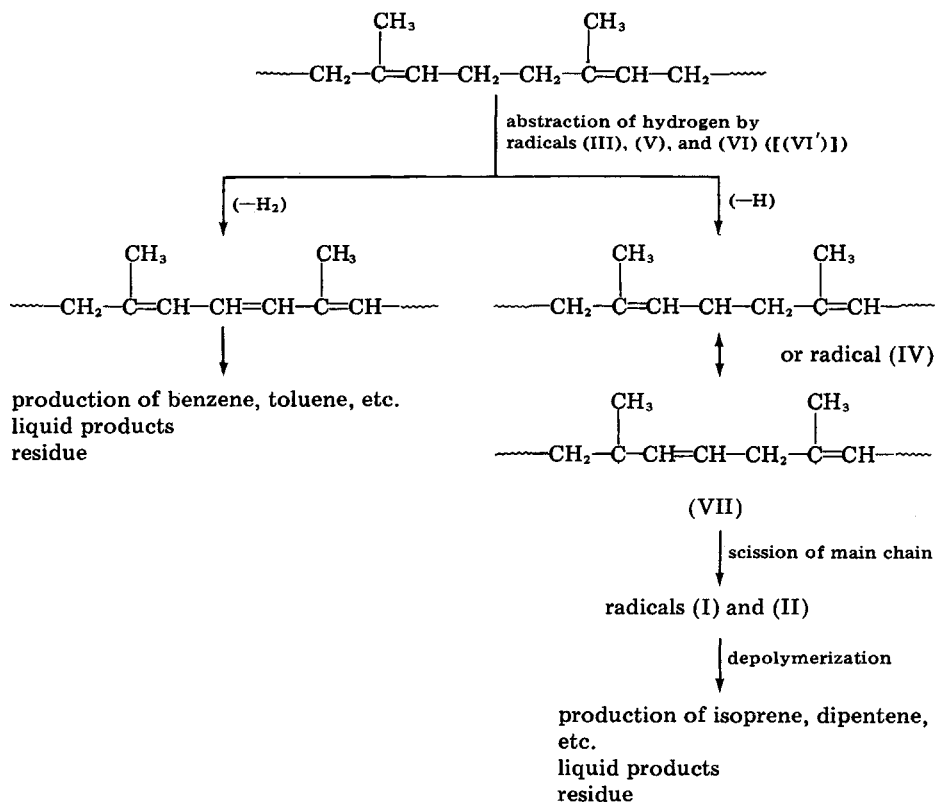


Fig. 13. Gas chromatogram of volatile products elaborated during thermal degradation of various samples for 3 h at 573 K: (A) sample 1; (B) sample 3; (C) sample 2.

radicals (I) produced by the scission near and at crosslinks will abstract allylic hydrogen in the polyisoprene at a relatively lower temperature, followed by the scission along the main chain and the production of isoprene and dipentene owing to the depolymerization.



Scheme II

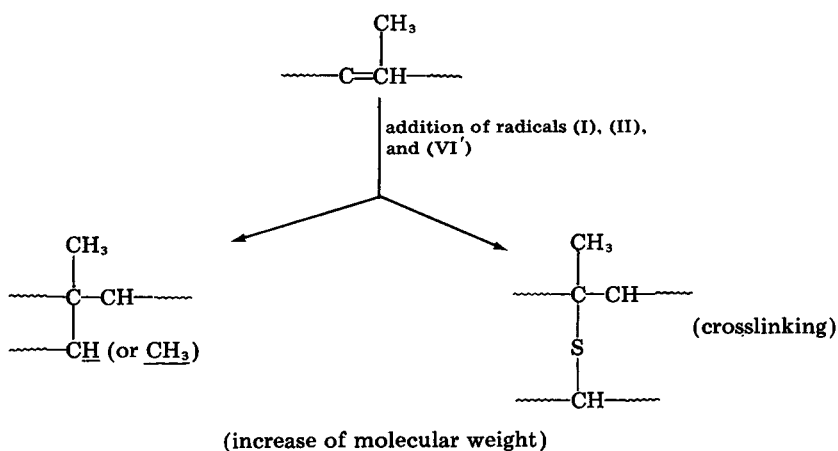
The mixture of relatively high molecular weight compounds (liquid products) is also produced to be trapped at room temperature. The average molecular weight of this mixture seems to be independent of the kind of samples and the degradation conditions. The microstructure of these products, however, has been remarkably changed from the original polyisoprene, as mentioned above, as the degradation proceeds. In the case of the DCP-cured sample (no. 2), IR and NMR spectra of liquid products are very similar to those of the uncrosslinked one (no. 1), without the appearance of peaks of aromatic and/or conjugated double bonds. The case of the sulfur-cured sample (no. 3) also generates fundamentally the similar spectral changes to sample 1. However, the rate of structural change of sample 3 is faster compared with the other samples.

The residue in the furnace after the degradation also has undergone large microstructural changes, that is, cis/trans isomerization, the formation of 1,2 double bonds and conjugated double bonds, cyclization, and the pronounced decrease of double bonds. Such structural changes are observed more signifi-



cantly for the results of the crosslinked samples (nos. 2 and 3) than for that of the uncrosslinked one (no. 1).

The number average molecular weight ( $M_n$ ) of the residue is independent on the kind of samples, but molecular weight distribution is very different among the uncrosslinked sample and the crosslinked ones (Table II). This will be due to that the insoluble fraction (gel) of the residue in solvent (tetrahydrofuran) is removed before being injected into GPC columns. In the case of sample 1, the broadening of distribution ( $M_w/M_n$ ), that is, the increase of weight average molecular weight ( $M_w$ ) is observed as the degradation proceeds (Table II and Figure 7). This obviously indicates that the recombination between the polymer radicals and the addition to carbon-carbon double bonds in another polymer take place together with the chain scission during heating. Addition reactions will also occur in the crosslinked rubbers. Especially, in sample 3, this will be pronouncedly caused by the polythiyl radical produced at lower temperature (Scheme III). The decrease of double bonds ought to arise from cyclization of the polymer chain.



Scheme III

The mechanism of thermal cyclization has been investigated by Golub and his co-workers in detail.<sup>14-16</sup>

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