Pyrolysis–Molecular Weight Chromatography–Vapor-Phase Infrared Spectrophotometry: An On-Line System for Analysis of Polymers. IV. Influence of *Cis/Trans* Ratio on the Thermal Degradation of 1,4-Polybutadienes

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Synopsis

The influence of the *cis/trans* ratio of 1,4-polybutadienes on the volatile products formed during temperature-programmed thermal degradation to 15% weight loss has been investigated using a mass chromatograph (a gas chromatograph which directly provides mass numbers of resolved components of a mixture) and an "on the fly" vapor-phase infrared spectrophotometer. In order of amounts, major volatile products were 4-vinyl-1-cyclohexene (dimer), 1,3-butadiene (monomer), cyclopentene, and 1,3-cyclohexadiene. With increasing trans content, the relative quantities of 4-vinyl-1-cyclohexene decreased strongly, cyclopentene increased strongly, 1,3-butadiene decreased moderately, and 1,3-cyclohexadiene increased moderately. For a high-trans polybutadiene, increasing the heating rate produced relatively more monomer and dimer but less cyclopentene. Mass chromatograms from 1,4-polybutadienes which had been heated to 15% weight loss in their prehistory were similar to those obtained from 1,2-polybutadiene, indicating that 1,4-polybutadiene undergoes isomerization prior to degradation. Mechanisms for the formation of the main volatile products of decomposition are discussed.

INTRODUCTION

The instrumentation used in the pyrolysis laboratory is discussed in part I of this series of papers.[1] It includes a programmable pyrolyzer in series with a thermal conductivity detector and a trap which permit monitoring of the formation of volatile effluents and their selective trapping, respectively. The products are released as a slug from the trap by rapid heating, this process being monitored by the same thermal conductivity cell. The slug of gases then passes either to a mass chromatograph, which separates the constituents and provides their mass numbers by means of a pair of gas density balance detectors, or to a conventional gas chromatograph in series with an "on the fly" vapor-phase infrared spectrophotometer, which provides spectra of separated constituents. Theoretical aspects of the mass chromatograph have been reported elsewhere[2]; earlier papers introduced the pyrolyzer–mass chromatograph technique.[3,4] Parts II and III of this series dealt with the thermal decomposition of polyolefins[5] and polyolefin sulfones,[6] respectively. Poly(methyl methacrylates),[7] poly(*tert*-butyl methacrylates),[7] and polystyrenes[6,8] have also been examined.

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The present communication deals with the thermal degradation under programmed heating conditions of 1,4-polybutadienes having different *cis/trans* ratios. There appears to be no detailed report in the literature on this subject. Most of the related studies[9-15] have been concerned with distinguishing between 1,4- and 1,2-structures using flash heating pyrolysis–gas chromatography and/or –mass spectrometry. Braun and Canji[16,17] have studied polybutadienes containing different amounts of 1,2-structure by flash heating to 600°C and examining the volatile C_1 to C_{12} products without identifying their chemical structures. In general, it seems that the complexity of flash pyrolysis arises from the many fragments that result in part from reactions of the initial products at high temperature.[9,14,17,18] Advantages of programmed-temperature thermal degradation include minimization of this problem and the ability to study regimes of degradation, the boundaries of which may be obtained with the aid of other techniques which include a thermal conductivity probe (TC), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The present report emphasizes thermal degradation in an initial stage (<15% weight loss), with some results being provided for more extensive degradation at higher temperatures. Some degradation mechanisms are also discussed.

EXPERIMENTAL

Polybutadienes

Table I provides a list of the polymers and characterization data. Nine of the samples (numbered 1–9) were high 1,4-structures with varying *cis/trans* ratios. One sample (numbered 10), of 83%–90% 1,2-structure with 17%–10% total 1,4-structure, was included for comparison of the degradation of the 1,4-structures with that of a 1,2-structure.

TABLE I
Characterization of Polybutadienes[a]

Sample no.	trans-1,4, %	1,2-vinyl, %	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Gel, %	T_{15},[b] °C
1	0	1–2	633,500	175,000	3.62	—	458
2	20	0	360,700	143,700	2.50	1.8	465
3	20	0	286,900	132,000	2.17	0	461
4	32	0	267,900	107,100	2.49	6.4	464
5	63	0	179,800	59,200	3.03	—	447
6	63	0	300,000	109,000	2.75	0	454
7	73	0	248,800	83,200	2.99	1.0	457
8	86	0	85,000	30,100	2.81	7.2	466
9	87	0	67,300	30,800	2.18	5.1	465
10	17–10[c]	83–90	177,000	107,000	1.66	—	—

[a] Source and molecular characterization of polymers: sample 1, The General Tire and Rubber Company, Akron, Ohio 44329; samples 2–9, The B. F. Goodrich Company, Brecksville, Ohio 44141; sample 10, Japan Synthetic Rubber Company, Tokyo, Japan (syndiotactic 1,2-polybutadiene 60%–70% syndiotactic).

[b] Temperature of 15% weight loss ($\Delta T/\Delta t = 20$°C/min).

[c] *Cis* and *trans* 1,4-structure.

Pyrolysis

As an example of preliminary procedures, Figure 1 includes complementary results of thermogravimetric analysis (TGA), differential thermal analysis (DTA), and the thermal conductivity detector (TC) response for sample 9 (87% trans) in the course of being heated at 20°C/min in an inert atmosphere. Three regions of activity are noted: the first involves negligible loss of weight from 300° to 400°C but is exothermic; the second involves about 15% weight loss by 465°C; the third involves complete and rapid loss of weight above 465°C. The corresponding DTA curve for sample 1 (0% trans) is included in Figure 1. Table I includes the temperature, T_{15}, by which 15% weight loss has occurred for samples under the above conditions.

Details of the pyrolyzer–trap–mass chromatograph and the pyrolyzer–trap–gas chromatograph–infrared spectrophotometer systems have been presented.[1] Polymer samples (ca. 30 mg) were heated in a stream of helium at a programmed rate of heating (generally 20°C/min) from room temperature to an appropriate upper limit (generally T_{15}). Volatiles formed between 300°C and this temperature were selectively trapped. After release from the trap, separation of the constituents was achieved in the mass chromatograph and in the conventional gas chromatograph using stainless steel tubing (15 ft × ⅛ in. O.D.) packed with polycarboranesiloxane (5% Dexsil 300) supported on an inert substrate (60/80 mesh Chromosorb W). The chromatographic columns were held at 30°C for 5 min before being program heated at 4°C/min to 300°c and were then held isothermally at 300°C.

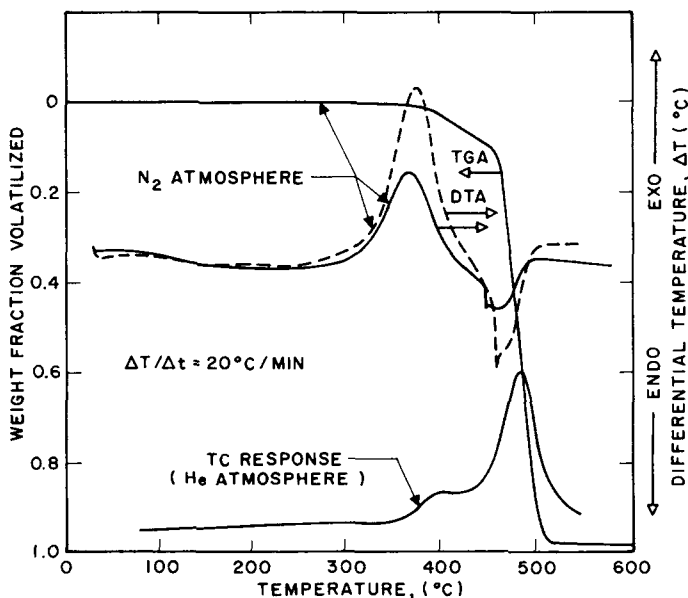In addition to providing mass numbers of resolved constituents, the mass

Fig. 1. Thermal history before and during pyrolysis of 1,4-polybutadienes: (—) sample 9 (87% trans); (- - -) sample 1 (0% trans).

chromatograph could be used to provide estimates of the weight amounts of each (W_i). This could be performed by comparing the areas on the CO_2 channel output of the mass chromatograph with those of peaks obtained under the same chromatographic conditions from a synthetic mixture containing known amounts of n-hydrocarbons. For compounds of the same molecular weight with similar retention times, responses of the gas density balance detector are directly proportional to their amounts.[8] The relative amount of a component (P_{wt}), as a weight percentage of those measured, was calculated using

$$P_{wt} = \frac{W_i}{\Sigma W_i} \times 100$$

Infrared spectra of the more abundant volatile products were obtained immediately after their elution from the conventional gas chromatograph. Four six-sec scans (2.5–15 μm) were computer-added and averaged.[8]

RESULTS AND DISCUSSION

Degradation to 15% Weight Loss

Mass chromatograms of the volatile products from a high-*cis* (sample 1) and from a high-*trans* (sample 9) 1,4-polybutadiene are shown in Figures 2 and 3, respectively. The numbered peaks designate those for which mass numbers could be assigned (i.e., Fig. 2, 1–11; Fig. 3, 1–13). The same numbers in different chromatograms are considered to be for the same compound. Table II includes a list of the assigned mass numbers. Mass numbers for a region of peaks designated C_{11}–C_{12} (Fig. 2, CO_2 channel) could not be estimated with discrimination because of the lack of sensitivity of gas density balances in the vicinity of the molecular weights of carrier gases (Freon-115, MW = 154.46); the general assignment C_{11}–C_{12} was made on the basis of a comparison with retention times of n-hydrocarbons. The C_{12} compounds are presumably trimers of butadiene. Smaller amounts of higher molecular weight materials are assigned C_{16}, C_{20}, and C_{24} on the basis of retention times of n-hydrocarbons (Fig. 2, CO_2 channel, vertical arrows).

The influence of the *cis/trans* ratio on the volatile degradation products formed in the initial region (to 15% weight loss) is apparent in the relative amounts of peaks 1, 2, and 9 and in the presence only in the volatile products from the high-*trans* 1,4-polymer of peaks 12 and 13.

Infrared spectra of some of the main volatile compounds from the high-*cis* 1,4-polymers (peaks 1, 2, and 9) and from high-*trans* 1,4-polymers (peaks 1, 2, 5, and 9) are shown in Figures 4 and 5, respectively. The spectrum for peak 1 matches literature spectra for 1,3-butadiene. Mass numbers, infrared spectra, and retention times for the compounds represented by peaks 2, 5, and 9 compare well with cyclopentene, 1,3-cyclohexadiene, and 4-vinyl-1-cyclohexene, respectively. Vibration assignments for the main absorption bands of the infrared spectra of material of peaks 1, 2, 5, and 9 are tabulated in Table II together with assignments of C-numbers for these and other mass-chromatographic peaks. The formation of 1,3-butadiene (monomer) and 4-vinyl-1-cyclohexene (dimer) as degradation products of poly-1,4-butadienes has been reported.[13,17] The present report of the formation of cyclopentene and 1,3-cyclohexadiene appears
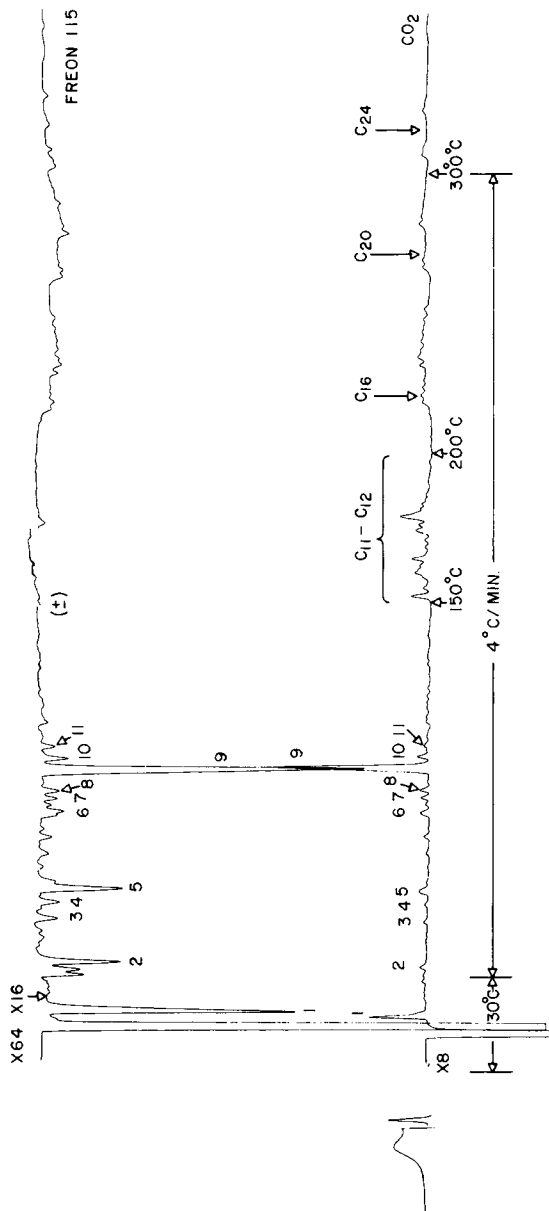
Fig. 2. Mass chromatogram of the pyrolysis products of high-*cis* 1,4-polybutadiene (sample 1, 0% *trans*) formed during 15% weight degradation; heating rate 20°C/min. Peak attenuations for the Freon-115 channel were ×64 for peak 1 and ×16 thereafter; that for the CO_2 channel was ×8 for all peaks. The symbol (±) indicates the location at which the polarity of the Freon-115 detector was reversed.
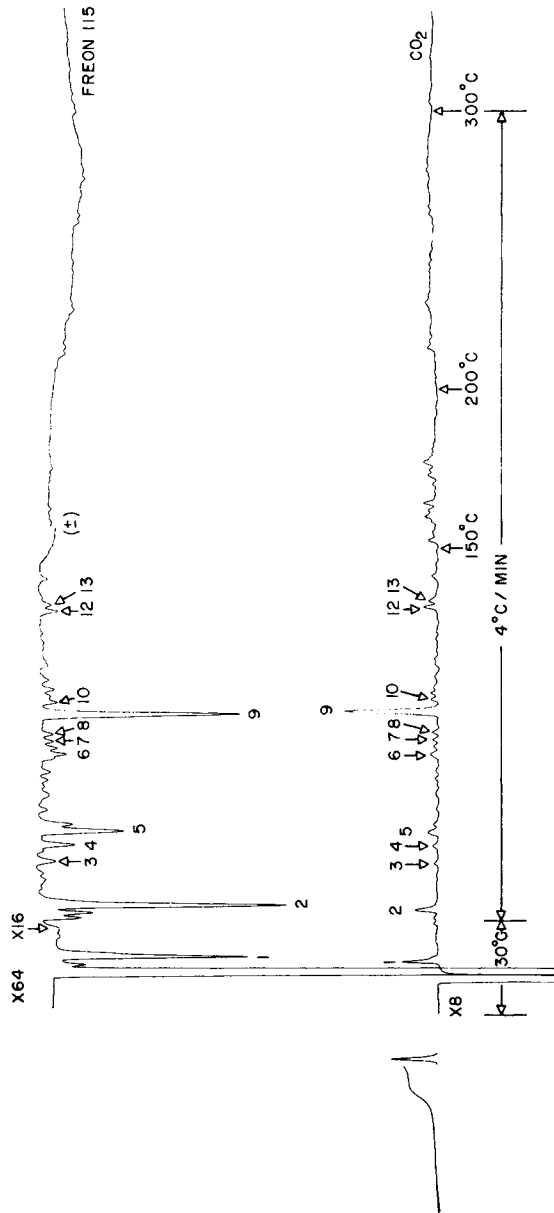
Fig. 3. Mass chromatogram of the pyrolysis products of high-*trans* 1,4-polybutadiene (sample 9, 87% *trans*) formed during 15% weight degradation; heating rate 20°C/min. Peak attenuations for the Freon-115 channel were ×64 for peak 1 and ×16 thereafter; that for the CO_2 channel was ×8 for all peaks. The symbol (±) indicates the location at which the polarity of the Freon-115 detector was reversed.

TABLE II

Identification of Volatile Degradation Products from 1,4-Polybutadienes (15% Weight Loss)

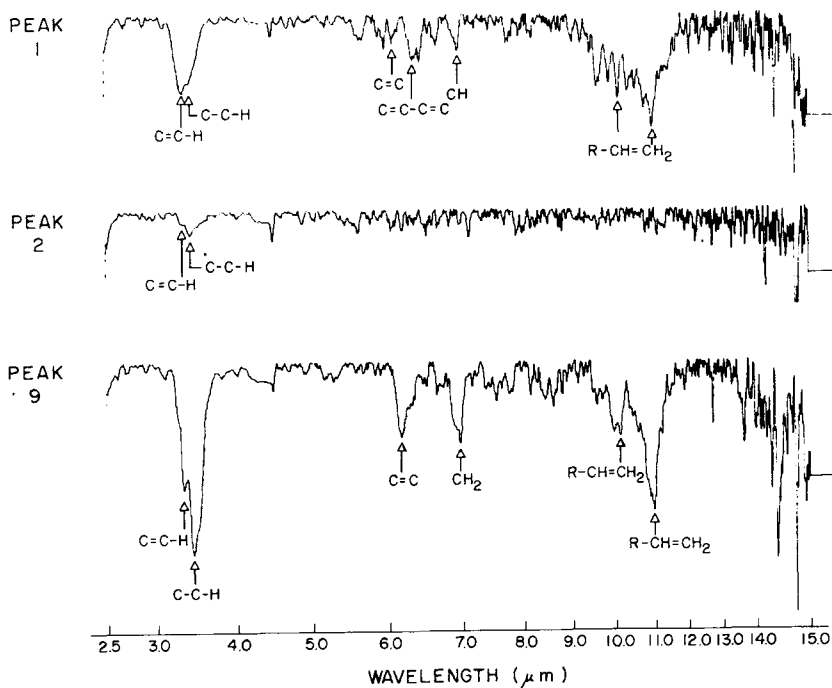| Mass-chromato-graphic peak number (Figs. 2 and 3)	MW (calculated)	Infrared spectra	Molecular structure (assigned)	MW (theoretical)
1	56.3	C=CH (3.35 μm), —CH (3.50 μm), conj. C=C (6.25–6.29 μm), CH$_2$ (6.95 μm), CH$_2$=CH— (10.15 and 11.0 μm)	1,3-butadiene	54.1
2	68.7	C=CH (330 μm), —CH (3.50 μm), nonconj. C=C (6.0–6.2 μm)	cyclopentene	68.1
3	84.4		1,3-hexadiene	82.1
4	81.7		2,4-hexadiene	82.1
5	77.2	C=CH (3.35 μm), —CH (3.50 μm), conj. C=C (6.25–6.29 μm)	1,3-cyclohexadiene	80.1
6	99.9		heptadiene	96.2
7	112.9		C$_8$ hydrocarbon	—
8	112.3		C$_8$ hydrocarbon	—
9	108.8	C=CH (3.35 μm), —CH (3.50 μm), nonconj. C=C (6.0–6.2 μm), CH$_2$ (6.95 μm), CH$_2$=CH— (10.15 and 11.0 μm)	4-vinyl-1-cyclo-hexene	108.2
10	106.3		styrene	104.1
11	107.1		ethylbenzene	106.1
12	117.5		C$_9$ hydrocarbon	—
13	119.8		C$_9$ hydrocarbon	—

Fig. 4. "On the fly" infrared spectra for peaks 1, 2, and 9 of the pyrogram (Fig. 2) of sample 1 (0% trans).

to be new; however, literature chromatograms of the flash pyrolysis of poly-1,4-butadienes appear to display peaks due to them.[10,13,17]

The relative amounts of each of the volatile products which formed during the first 15% weight loss of the nine 1,4-polybutadienes as determined from the mass chromatograms are provided in Table III. In decreasing order of quantity are 4-vinyl-1-cyclohexene (peak 9), 1,3-butadiene (peak 1), cyclopentene (peak 2), and 1,3-cyclohexadiene (peak 5). This order is observed, too, in the relative intensities of the infrared spectra (Figs. 4 and 5). The amounts of these products are related to the cis/trans ratios of the polymers in Figure 6. The quantity of 4-vinyl-1-cyclohexene decreases, whereas that of cyclopentene increases with increasing trans content, the sum of the two amounts being approximately constant (Fig. 6). The amounts of 1,3-butadiene and 1,3-cyclohexadiene are unaffected until high trans contents. Small amounts of C_9 hydrocarbons (peaks 12 and 13) are produced from samples with high trans contents (samples 6–9). The sum of 1,3-butadiene and the C_9 compounds is almost independent of trans content.

The above results differ from those obtained on flash pyrolysis.[11,17,19] In the latter, 1,3-butadiene is formed in most abundance and the ratio of the amounts of 4-vinyl-1-cyclohexene to 1,3-butadiene has been reported to be the same for high-cis 1,4- and high-trans 1,4-polybutadienes. Analogous results have been presented for the flash pyrolysis of 1,4-polyisoprenes from which isoprene and its dimers form.[20,21]

Comparison of the quantities of products formed during 15% weight loss (Fig. 6) with the amounts formed during 10% weight loss (Fig. 7) shows that relatively more 1,3-butadiene and 4-vinyl-1-cyclohexene form on initial degradation.
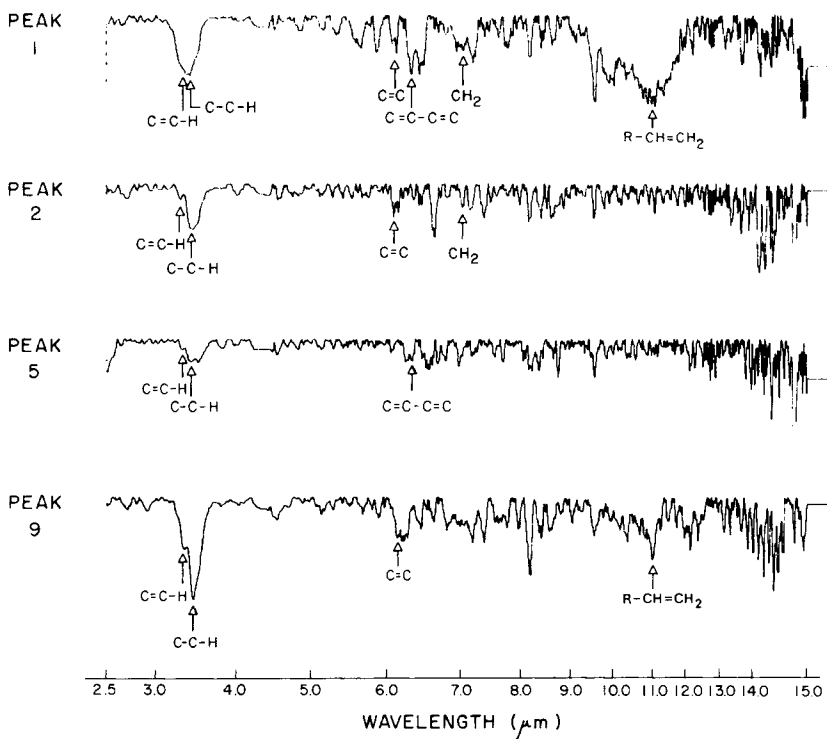
Fig. 5. "On the fly" infrared spectra for peaks 1, 2, 5, and 9 of the pyrogram (Fig. 3) of sample 9 (87% trans).

The effect of heating rate on the particular four main products of degradation formed during 15% weight loss is summarized in Figure 8.   In this study, all samples were heated to 300°C at 20°C/min (with negligible weight loss) prior to collecting volatile products which formed at higher temperatures at the selected heating rates (2°–20°C/min).   The common prehistory was given in an attempt to minimize differences in chemical structure that are thermally induced in the specimens.

Sample 9 (87% *trans*) was selected because the particular four main products had been most clearly displayed in the mass chromatogram (Fig. 3).   The amounts of 1,3-butadiene and 4-vinyl-1-cyclohexene increased linearly and cyclopentene decreased linearly, whereas 1,3-cyclohexadiene appeared to be unaffected by heating rate.   The sum of the amounts of 4-vinyl-1-cyclohexene and cyclopentene again appeared to be constant (compare Fig. 8 with Figs. 6 and 7). The increase in amount of monomer with heating rate is noteworthy; if depolymerization is favored at low temperatures, as is the case with polystyrene,[8] then the reverse is to be expected.   The unusual behavior of 1,4-polybutadienes is probably a consequence of an isomerization reaction which attempts to form polymer with 1,2-butadiene residues in competition with volatilization of degradation products (see below).   The formation of large amounts of monomer at higher heating rates is in accord with the results of flash pyrolysis.[11,17,19]

TABLE III
Amounts of Volatile Degradation Products from 1,4-Polybutadienes (15% Weight Loss)

Peak	Sample	Amount of product, wt-%							
no.	1	2	3	4	5	6	7	8	9
1[a]	32.0	29.8	29.0	31.2	30.0	27.5	26.6	24.6	27.4
2[b]	3.3	3.2	3.5	3.3	4.2	6.5	7.4	13.1	14.0
3	2.9	2.2	2.3	1.7	2.5	1.8	2.3	2.2	2.0
4	1.9	1.7	1.7	1.2	2.1	2.2	2.3	1.9	2.2
5[c]	2.9	3.1	4.1	3.0	3.0	3.2	3.0	4.5	4.8
6	3.5	3.3	3.6	2.6	2.6	2.8	3.0	2.8	2.6
7	2.6	2.5	2.8	2.4	2.5	2.6	2.5	2.2	2.5
8	3.0	3.0	3.3	2.7	2.7	2.8	3.1	2.3	2.5
9[d]	43.2	46.4	44.4	47.0	45.7	42.9	41.2	37.3	33.4
10	3.2	3.2	3.4	3.0	3.1	3.5	3.2	2.7	2.2
11	1.5	1.6	1.9	1.9	1.6	1.8	1.8	trace	trace
12	—	—	—	—	—	1.6	2.5	4.2	3.9
13	—	—	—	—	—	0.8	1.1	2.2	2.5

[a] 1,3-Butadiene.
[b] Cyclopentene.
[c] 1,3-Cyclohexadiene.
[d] 4-Vinyl-1-cyclohexene.

Fig. 6. Amounts of main products vs trans content at 15% weight loss: (●) 1,3-butadiene; (◑) cyclopentene; (◒) 1,3-cyclohexadiene; (○) 4-vinyl-1-cyclohexene; (- - △ - -) cyclopentene + 4-vinyl-1-cyclohexene. Numbers identify samples.

Degradation After 15% Weight Loss

Figure 9 displays the mass chromatogram of the volatile products formed after 15% weight loss on heating high-*trans* 1,4-polybutadiene (sample 9, 87% *trans*) at 20°C/min to 550°C in helium. The complexity of it prevented mass numbers being assigned other than by comparison with the retention times (Fig. 3) of products formed from the same polybutadiene during decomposition to 15%
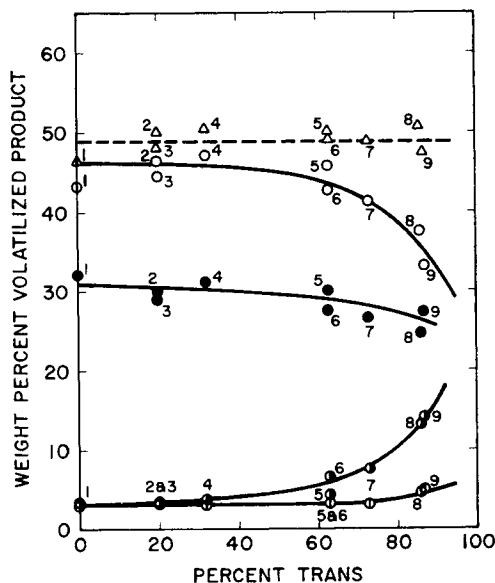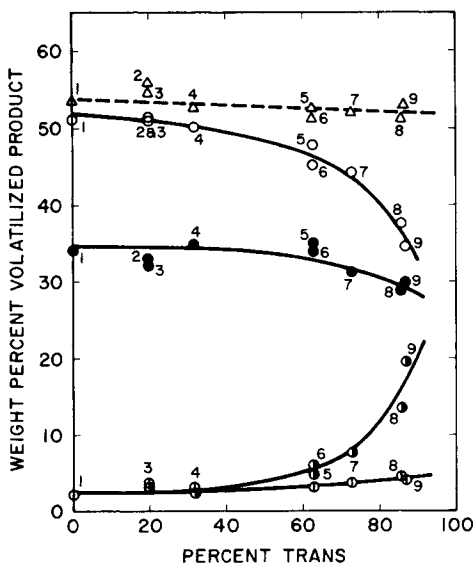
Fig. 7. Amounts of main products vs trans content at 10% weight loss: (●) 1,3-butadiene; (◐) cyclopentene; (Φ) 1,3-cyclohexadiene; (○) 4-vinyl-1-cyclohexene; (- - △ - -) cyclopentene + 4-vinyl-1-cyclohexene. Numbers identify samples.
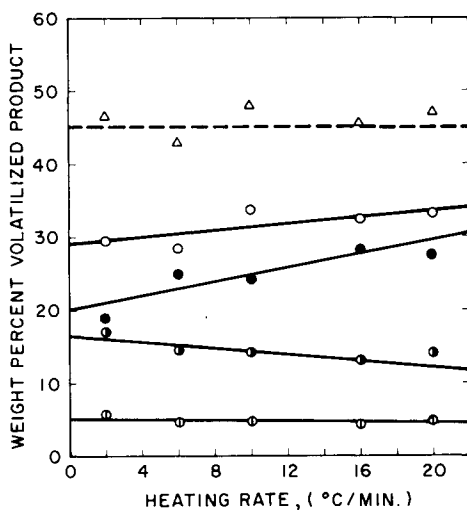
Fig. 8. Effect of heating rate on the amounts of the main products formed during 15% weight loss for sample 9 (87% trans): (●) 1,3-butadiene; (◐) cyclopentene; (Φ) 1,3-cyclohexadiene; (○) 4-vinyl-1-cyclohexene; (- - △ - -) cyclopentene + 4-vinyl-1-cyclohexene.

weight loss. 4-Vinyl-1-cyclohexene (peak 9) and 1,3-cyclohexadiene (peak 5) are only minor products of further decomposition (Fig. 9).

Figure 10 displays the corresponding pyrogram for high-*cis* 1,4-polybutadiene (sample 1, 0% trans). The similarity to that for the high-trans 1,4-polybutadiene (Fig. 9) is striking, the main differences being in the relative amounts of the components (e.g., cyclopentene; Figs. 9 and 10, peak 2).

For comparison, the mass chromatogram of 1,2-vinyl-polybutadiene (Table I, sample 10) is presented in Figure 11. This reveals volatile products which
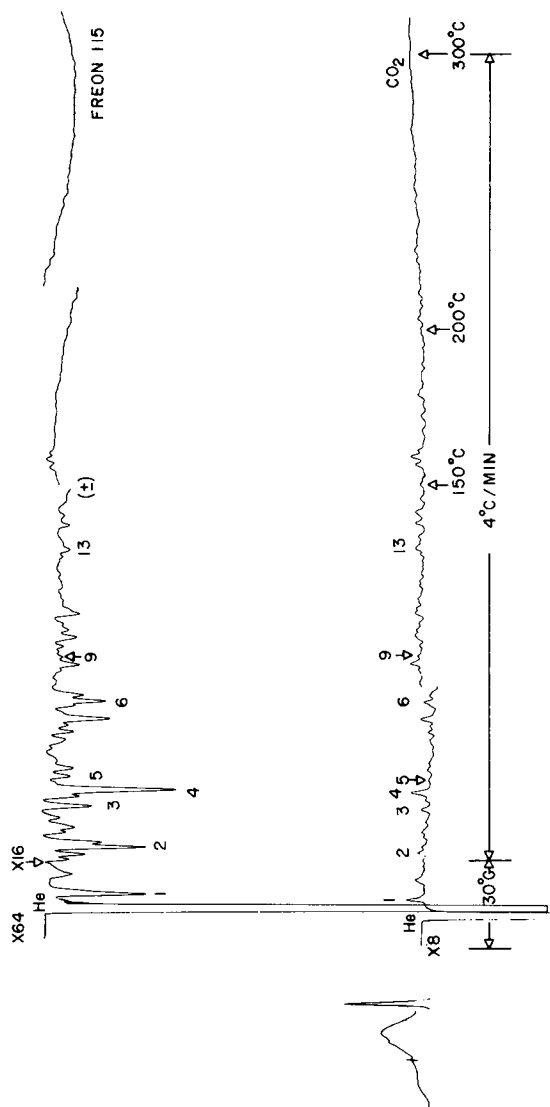
Fig. 9. Mass chromatogram of the pyrolysis products of high-*trans* 1,4-polybutadiene (sample 9; 87% *trans*) formed during 15% to 100% weight loss; heating rate 20°C/min. Peak attenuations of the Freon-115 channel were ×64 for peak 1 and ×16 thereafter; that for the CO_2 channel was ×8 for all peaks. The symbol (±) indicates the location at which the polarity of the Freon-115 detector was reversed. The numbers indicate retention times of pyrolysis products formed during the first 15% weight loss of 1,4-polybutadienes.

Fig. 10. Mass chromatogram of the pyrolysis products of high-*cis* 1,4-polybutadiene (sample 1, 0% *trans*) formed during 15% to 100% weight loss; heating rate 20°C/min. Peak attenuations of the Freon-115 channel were ×64 for peak 1 and ×16 thereafter; that of the CO_2 channel was ×8 for all peaks. The symbol (±) indicates the location at which the polarity of the Freon-115 detector was reversed. The numbers indicate the retention times of pyrolysis products formed during the first 15% weight loss of 1,4-polybutadienes.

formed on heating at 20°C/minute between 300°C (0 percent weight loss) and 550°C in helium. (It is noted that whereas 1,4-polybutadienes underwent a two-step weight loss, the 1,2-vinyl polybutadiene underwent a single-step loss in weight on programmed temperature heating.) Striking similarities between the pyrograms of all the products of pyrolysis for the 1,2-vinyl polybutadiene (Fig. 11) and those from pyrolysis above 15% weight loss for 1,4-polybutadienes (Figs. 9 and 10) are apparent. The similarity suggests that a considerable part of the 1,4-structure underwent isomerization to the 1,2-structure in the course of being heated to 15% weight loss.

Mechanisms of Degradation

The DTA experiments show that reactions proceed before the onset of measured weight loss. Chain scission and competitive crosslinking reactions are held responsible for the reported stress relaxation and higher intermittent moduli which occur in crosslinked *cis* 1,4-polybutadienes at temperatures between 200° and 270°C.[22,23] However, the present results do not contribute to an understanding of degradation prior to loss of weight. Some consideration will be given to the formation of 1,3-butadiene (monomer), cyclopentene, 1,3-cyclohexadiene, and 4-vinyl-1-cyclohexene (dimer) which together account for 90% of the measured volatile products of the first 10% weight loss and for 80% of the measured volatile products of the first 15% weight loss.

ESR studies have concluded that free radicals form on the irradiation of 1,4-polybutadienes[24] and 1,4-polyisoprene[25] with UV under vacuum at low temperatures; for polybutadiene, the following radicals were suggested:

$$\sim CH_2 - CH{=}CH - \dot{C}H_2 \leftrightarrow \sim CH_2-\dot{C}H- CH{=}CH_2 \text{ (major)}$$
$$\text{I}$$

$$\sim CH{=}CH-\dot{C}H-CH_2\sim \text{ (minor)}$$
$$\text{II}$$
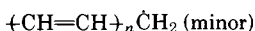
$$\text{+}CH{=}CH\text{+}_n\dot{C}H_2 \text{ (minor)}$$
$$\text{III}$$

Radical I arises from chain β scission to double bonds and is expected to be the precursor to the major products. Radical II, which arises from the abstraction of a hydrogen atom by another radical, accounts for crosslinking by coupling reactions. Radical III accounts for induced coloration noticeable in the residue after 15% loss of weight.

1,2-Vinyl residues can form from radical I by recombination,

$$\sim CH_2{-}CH{=}CH{-}\dot{C}H_2 + \sim CH_2{-}\dot{C}H{-}CH{=}CH_2 \longrightarrow$$
$$\text{I} \qquad\qquad \text{I}$$

$$\sim CH_2{-}CH{=}CH{-}CH_2{-}\underset{\underset{\overset{\|}{CH_2}}{\overset{|}{CH}}}{CH}{-}CH_2\sim$$

1,4-residue 1,2-residue
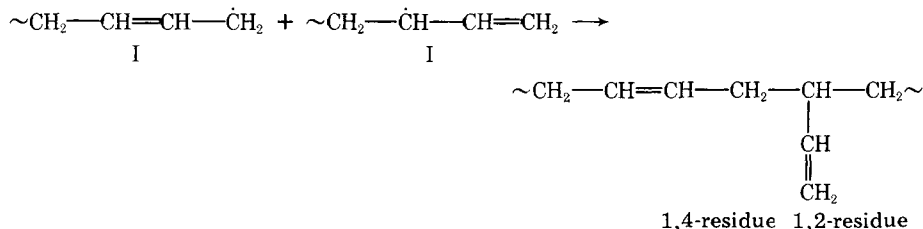
This mechanism accounts for the similarity of the pyrograms of the volatile products from 1,2-vinyl polybutadiene and of the volatile products formed after 15% weight loss from 1,4-polybutadienes.
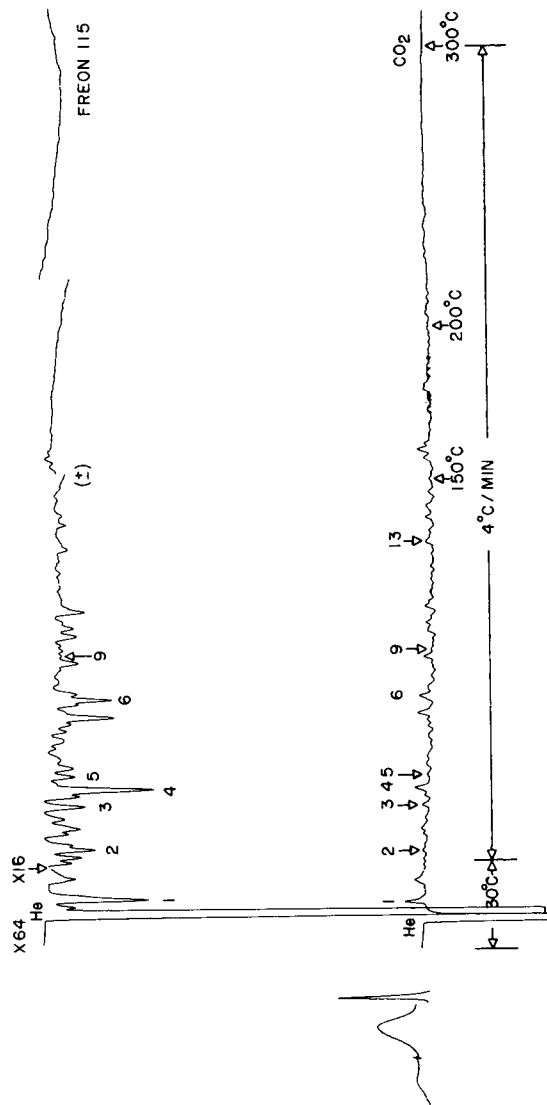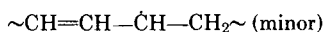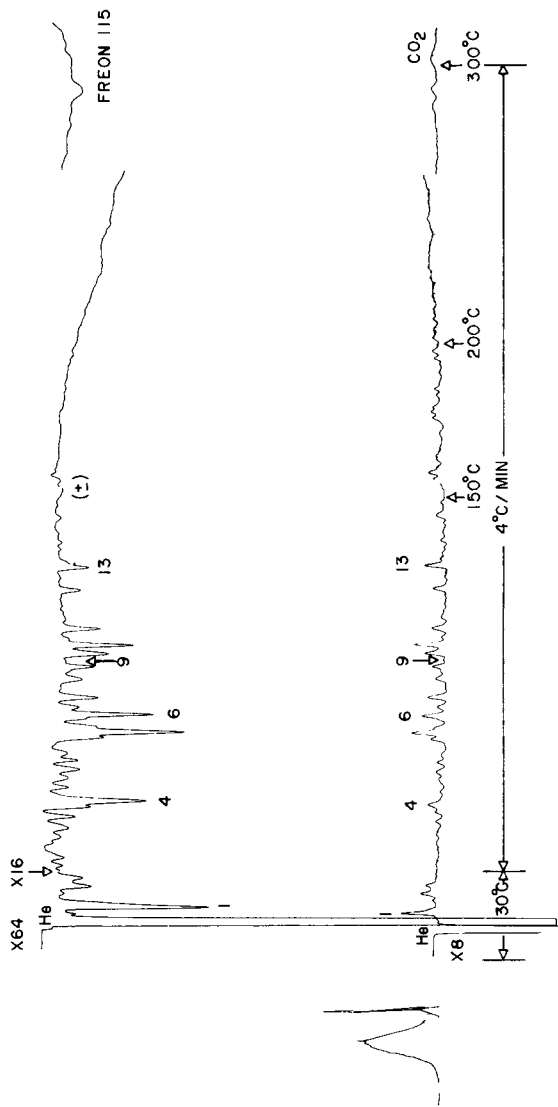
Fig. 11. Mass chromatogram of the pyrolysis products of syndiotactic 1,2-polybutadiene (sample 10, 1,2-structure 83–90%) formed during 100% weight loss; heating rate 20°C/min. Peak attenuations for the Freon-115 channel were ×64 for peak 1 and ×16 thereafter; that for the CO_2 channel was ×8 for all peaks. The symbol (±) indicates the location at which the polarity of the Freon-115 detector was reversed. The numbers indicate retention times of the pyrolysis products which formed during the first 15% weight loss of 1,4-polybutadienes.

Cis/trans isomerization[26-29] can arise from radical I:
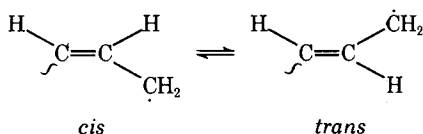
However, since the amounts of the individual compounds formed to 15% weight loss vary with the *cis/trans* ratio of the starting 1,4-polybutadiene, this reaction is limited.

1,3-Butadiene (monomer) arises from radical I as follows:

$\sim CH_2{-}CH_2{-}CH{=}CH{-}\dot{C}H_2 \leftrightarrow \sim CH_2{-}CH_2{-}\dot{C}H{-}CH{=}CH_2$

$$\xrightarrow{\beta\text{-scission}} \sim\dot{C}H_2 + CH_2{=}CH{-}CH{=}CH_2$$
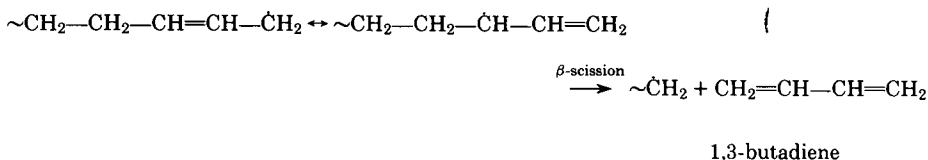
1,3-butadiene

On the basis of the amount of 1,3-butadiene formed, the process is not appreciably affected by the *cis/trans* ratio.

4-Vinyl-1-cyclohexene arises[19,30] from radical I by the following mechanism:

$\sim CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}\dot{C}H_2 \longleftrightarrow$

$\sim CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \longrightarrow$

4-vinyl-1-cyclohexene
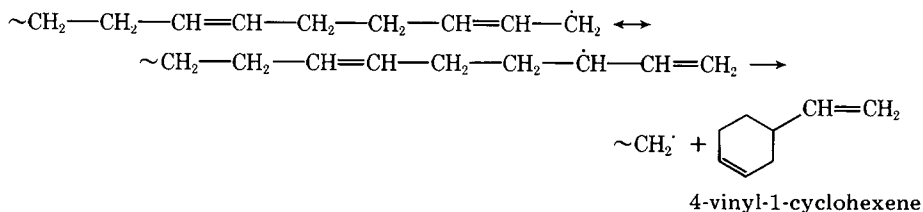
This product would be expected to be favored by a high-*cis* 1,4-structure as is indicated by
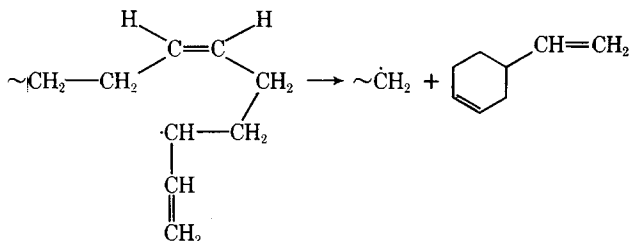
This mechanism is similar to that recognized for the thermal degradation of 1,4-polyisoprene.[20,21] The experimental results (Figs. 6 and 7) are in accord with the mechanism in that the isomerization of *trans* 1,4-structures to *cis* 1,4-structures is necessary for the formation of 4-vinyl-1-cyclohexene from *trans* 1,4-polybutadiene. Since *cis/trans* isomerization is limited, the amount of 4-vinyl-1-cyclohexene will decrease with increasing *trans* content.

The larger quantities of 4-vinyl-1-cyclohexene than butadiene which form at relatively low temperatures (Table III, Figs. 6 and 7) concur with calculations of activation energies for the analogous formation of dipentene (42 kcal/mole) and isoprene (52 kcal/mole) from *cis* 1,4-polyisoprene.[30]

Dimers of butadiene can form if monomer is not removed rapidly from the

reaction zone.[31-33] These include

$CH=CH_2$ ·

4-vinyl-1-cyclohexene

$CH=CH_2$
$CH=CH_2$

trans-1,2-vinylcyclobutane

1,5-cyclooctadiene

Trans-1,2-vinyl-cyclobutane is usually the main product. Its absence as a product in the first stage of pyrolysis of 1,4-polybutadienes, and the presumed absence of it and of 4-vinyl-1-cyclohexene in spite of the presence of butadiene in the last stages of pyrolysis, indicate that dimerization of monomer was not significant in the presently reported pyrolysis experiments.

A speculative mechanism for the formation of cyclopentene and 1,3-cyclohexadiene follows from homolytic scission of the single bond at the site other than β to a double bond:

$\sim CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2\sim$

$\rightarrow \sim CH_2-CH=\dot{C}H + \dot{C}H_2-CH_2-CH=CH-CH_2\sim$

IV   V

This process is energetically more difficult than the formation of radical I by β-scission to a double bond. However, since increasing trans 1,4-content decreases the competitive route of radical I to 4-vinyl-1-cyclohexene, products arise via radicals IV and V for high-trans polymers.

Cyclopentene may be formed thus:

$\sim CH_2-CH=CH-CH_2-|-CH_2-CH=CH-CH_2-\dot{C}H_2 \rightarrow$

V

$\sim CH_2-CH=CH-\dot{C}H_2 +$

cyclopentene

1,3-Cyclohexadiene may be formed thus:

$\sim CH_2-|-CH=CH-CH_2-CH_2-CH=\dot{C}H \rightarrow \sim \dot{C}H_2 +$

1,3-cyclohexadiene

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