# Pyrolysis Paths of Polybutadiene Depending on Pyrolysis Temperature

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**Abstract:** Polybutadiene (BR) was pyrolyzed at 540-860 °C and the effect of pyrolysis temperature on variations in the relative abundance of the major pyrolysis products (C4-, C5-, C6-, C7-, and C8-species) was investigated. Formation of the C4-, C5-, C6-, and C7-species competed with that of the C8-species. Relative intensity of the C8-species decreased with increasing pyrolysis temperature, while that of the C5-, C6-, and C7-species increased. Pyrolysis paths were became more complicated with increasing pyrolysis temperature. We suggested the operation of double bond migration and succeeding rearrangements for the formation of the C5- and C7-species and various rearrangements, including a double bond, for the formation of the C6-species at high temperature. The activation energies for the pyrolysis product ratios of (C5+C6+C7)/C4 and C8/C4 were used to explain the competition reactions to form the pyrolysis products.

*Keywords:* polybutadiene, pyrolysis path, mechanism, pyrolysis temperature.

## Introduction

Polybutadiene (BR) is one of commonly used rubbers. BR has different microstructures depending on the monomer insertion in the polymer chain and there are three different sequences, cis-1,4-, trans-1,4-, and 1,2-units. Pyrolysis has been used extensively to characterize polymeric materials.[1-5] Pyrolysis-gas chromatography (Py-GC), pyrolysis-mass spectrometry (Py-MS), and Py-GC/MS have been used for decades to elucidate the structures of rubbers.[6-12] Pyrolysis of BR has been studied by many researchers using Py-GC or Py-GC/MS.[1,10,13,14]

The major volatile products formed from BR by pyrolysis are butadiene (C4-species), cyclopentene (C5-species), cyclohexene and cyclohexadiene (C6-species), 1,4-cycloheptadiene (C7-species), and 4-vinylcyclohexene (C8-species).[1,11,13,15,16] Kinds and relative abundances of pyrolysis products of polymers are varied with the pyrolysis temperature.[17,18] Relative abundances of the major pyrolysis products of BR will be varied with the pyrolysis temperature. In the present work, we studied variation of the relative abundances of the major pyrolysis products of BR with the pyrolysis temperature and suggested plausible pyrolysis paths depending on the pyrolysis temperature. Pyrolysis temperature is a very important factor not only for proper and efficient analysis of polymeric materials but also for recycling of scrap polymeric materials.[17,19,20]

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## Experimental

KBR01 (cis-1,4-unit content=98%) of Korea Kumho Petroleum Co. was used as BR. Analysis of the pyrolysis products was performed with Py-GC. The Py-GC chromatograms were acquired with Pyroprobe 2000 of CDS Analytical Inc. and ACME 6000 gas chromatograph of Younglin Co. The sample (0.3±0.1 mg) was preheated at 200 °C for 10 sec and pyrolyzed at 540-860 °C for 5 sec under $N_2$ atmosphere. HP-5 capillary column (length 21 m) was used. The temperatures of the injector and detector of the GC were 200 °C. The GC oven temperature program was as follows. (1) The initial temperature was 60 °C and was maintained for 3 min. (2) The temperature was then increased from 60 to 160 °C at a rate of 8 °C/min.

## Results and Discussion

Figure 1 shows the pyrograms obtained from Py-GC analysis at 560 and 760 °C. Relative abundances of pyrolysis products are varied with the pyrolysis temperature. The major pyrolysis products are peaks at 1.97, 2.16, 2.68, 3.58, and 4.58 min assigned to C4-species (butadiene), C5-species (cyclopentene), C6-species (cyclohexene and cyclohexadiene), C7-species (cycloheptadiene), and C8-species (4-vinylcyclohexene), respectively. The most abundant product is the butadiene and the second one is the butadiene dimer (4-vinylcyclohexene). The pyrogram at 560 °C shows a simple

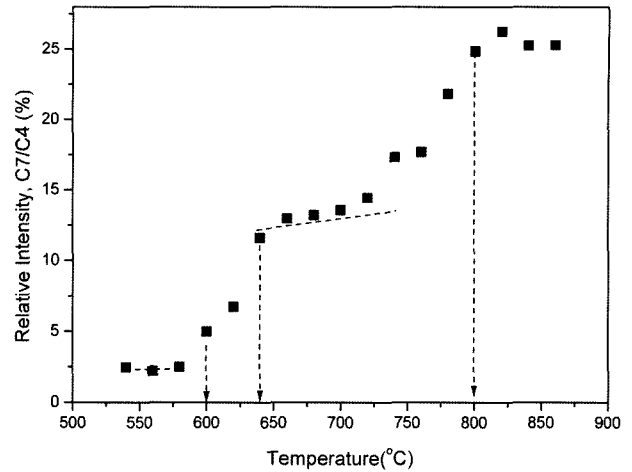Figure 1. Pyrolysis-GC chromatograms of the BR at 560 °C (a) and 760 °C (b).



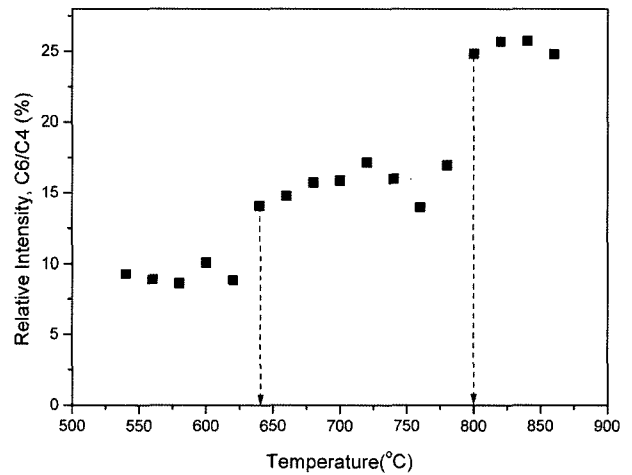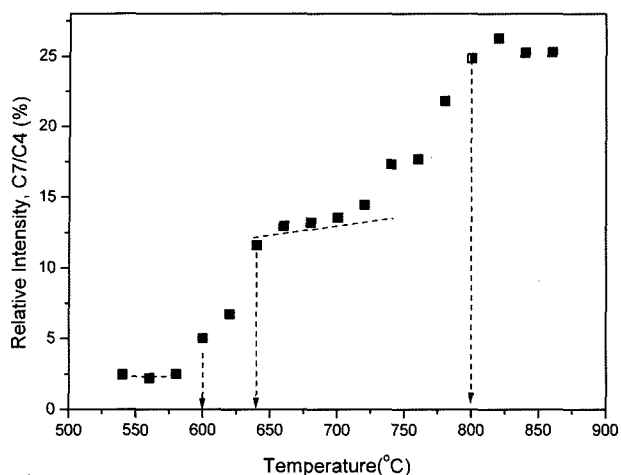Figure 2. Variation of the relative intensity of C5-species as a function of the pyrolysis temperature.



Figure 3. Variation of the relative intensity of C6-species as a function of the pyrolysis temperature.

peak distribution of the C4- and C8-species, while the pyrogram at 760 °C shows many peaks of the C4-, C5-, C6-, C7-, and C8-species. The BR was pyrolyzed at 540-860 °C and variation of the pyrolysis products with the pyrolysis temperature was investigated.

Figures 2-5 give variations of the relative abundances of the major pyrolysis products of BR with the pyrolysis temperature. The relative intensities were calculated by letting the abundance of butadiene be 100%. In general, the most important and abundant one of pyrolysis products of a polymeric material is its repeat unit. The butadiene is the repeat unit of BR. Since the absolute abundances of pyrolysis products are varied with the experimental conditions such as the sample weight and the pyrolysis temperature and time, the experimental results were analyzed with the relative abundances not the absolute ones. Relative intensities of the C5-, C6-, and C7-species, on the whole, increase with increase of the pyrolysis temperature, while the C8-species decreases. This implies that the formation of C8-species needs less energy than those of C5-, C6-, and C7-species and the formations of C5-, C6-, and C7-species will be competitive with that of C8-species. Relative intensity of the C8-species

decreases continuously with increase of the pyrolysis temperature (Figure 5). Below 540 °C, the peak intensity of C8-species is higher than that of C4-species. Chen and Qian[18] also reported that the C8-species was more abundant at 491 -530 °C than the C4-species. The variations of relative intensities of the C5-, C6-, and C7-species with the pyrolysis temperature show some specific regions. For the C5-species, the relative intensity increases suddenly at 620 and 680 °C (Figure 2). For the C6-species, the relative intensity increases suddenly at 640 and 800 °C (Figure 3). For the C7-species, the relative intensity also increases suddenly at 640 and 800 °C (Figure 4). These break points imply that pyrolysis reactions are activated at the temperatures or new pyrolysis reactions occur.

At low temperature, pyrolysis of BR is started by dissociating the C-C single bond. The radical formed by the C-C

Figure 4. Variation of the relative intensity of C7-species as a function of the pyrolysis temperature.
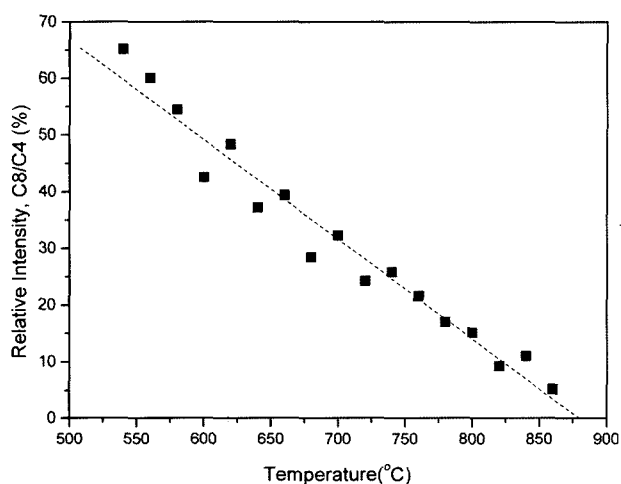


Figure 5. Variation of the relative intensity of C8-species as a function of the pyrolysis temperature. The curve fitting equation is $y=-0.176x+154.7$ ($r=-0.980$).

**Scheme I**



**Scheme II**



cleavage is rearranged and butadiene and 4-vinylcyclohexene are generated as shown in Scheme I. This path is less energy-required route. The pyrogram at low temperature of 560 °C shows the big peaks of butadiene and 4-vinylcyclohexene and the other products are trace as shown in Figure 1(a). Steep increases of the relative intensities of C5-, C6-, and C7-species around 660 °C can be explained with another pyrolysis path. Migration of hydrogen atom to a C=C double bond can occur at high temperature.[21] The diradical structure is formed by the 1,2-hydrogen shifts and the long single bond sequence can be formed by the 1,5-hydrogen shift as shown in Scheme II. The single bond sequence of ~C-C-C-C~ can be easily dissociated to form various radicals through the paths (1), (2), and (3). The radical formed from the path (1) cleavage is rearranged to form C6-species, while the radical
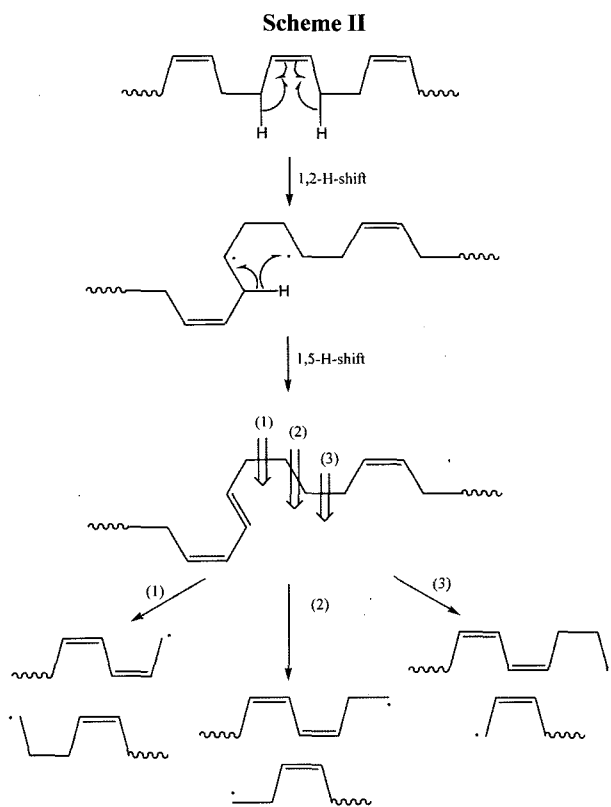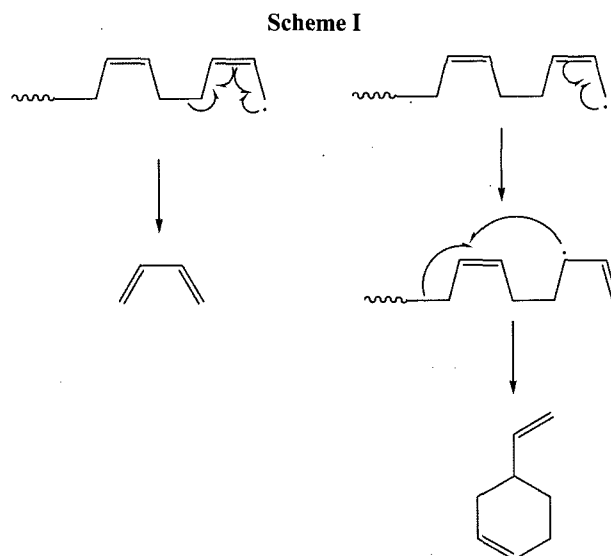
formed from the path (2) cleavage is rearranged to form C5- and C7-species (Scheme III).

The relative intensities of C6- and C7-species steeply increase again around 800 °C. This can be also explained with another pyrolysis path of Scheme IV. The radical formed from the C-C single bond cleavage can be rearranged involving the second C=C double bond to form cyclohexenyl group. The C6-species can be formed through β-hydrogen atom migration. At high temperature the radical formed from

**Scheme III**

(1)

(2)

(3)
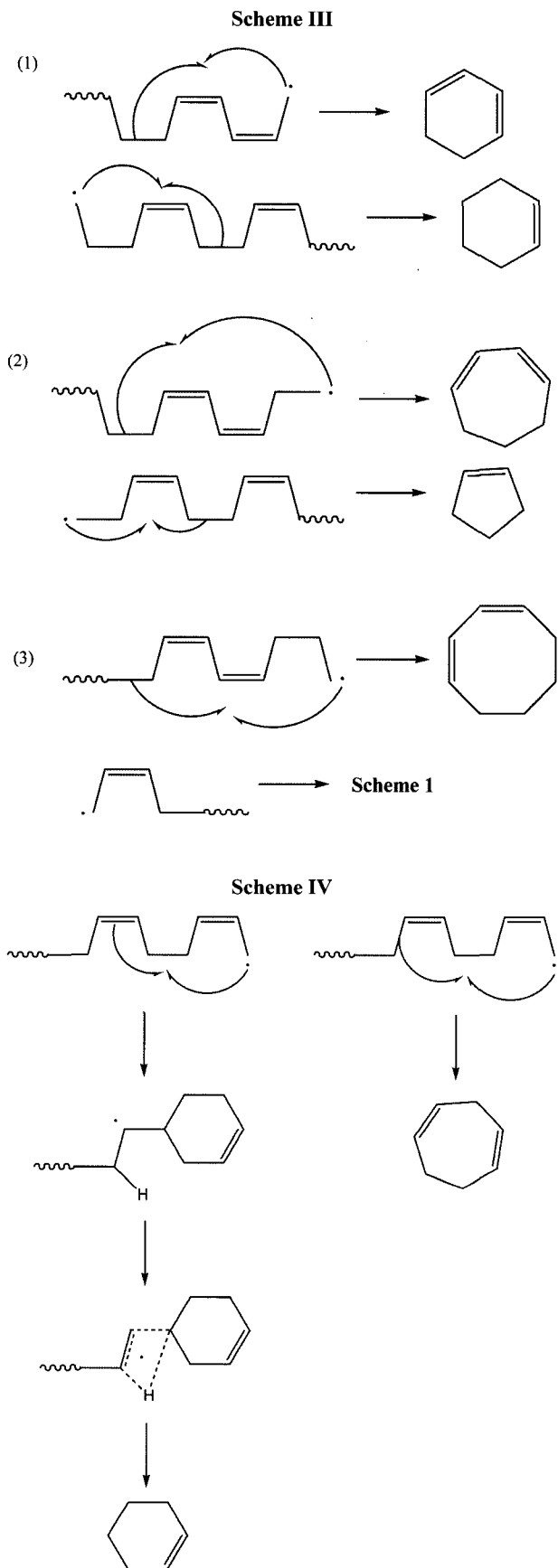
Scheme 1

**Scheme IV**

C-C single bond cleavage can be also rearranged involving the C-C single bond next to the double bond ($\sim$-C-C=C$\sim$) to form 1,4-cycloheptadiene as shown in Scheme IV. Bond strength of the C-C single bond in the $\sim$-C-C=C$\sim$ is much stronger than that in $\sim$-C-C-C$\sim$. Thus, the rearrangement involving the $\sim$-C-C=C$\sim$ can occur only when the pyrolysis temperature is enough high.

Figure 6 shows variation of the sum of relative abundances of the C5-, C6-, and C7-species with the pyrolysis temperature. The (C5+C6+C7)/C4 ratio increases by 2.23% every 10 °C increase (Figure 6), whereas the C8/C4 ratio decreases by 1.76% every 10 °C increase (Figure 5). Arrhenius plots of $1/T$ vs ln$k$ for the (C5+C6+C7)/C4 and C8/C4 ratios were performed to obtain the activation energies as shown in Figure 7. The $k_s$ are the (C5+C6+C7)/C4 and C8/C4 ratios. Activation energy for the (C5+C6+C7)/C4 ratio is 50.79 kJ/mol, whereas that for the C8/C4 ratio is -50.36
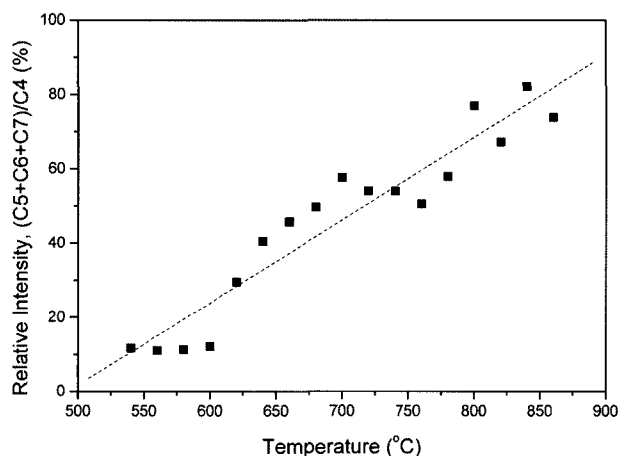


**Figure 6.** Variation of the sum of relative intensities of the C5-, C6-, and C7-species as a function of the pyrolysis temperature. The curve fitting equation is $y=0.223x-109.7$ ($r=0.950$).
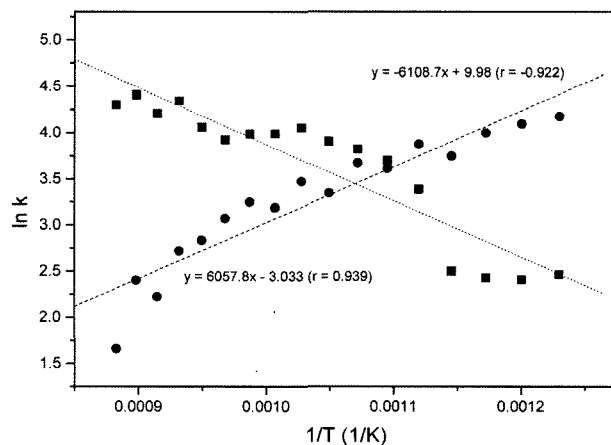


**Figure 7.** Arrhenius plots for the (C5+C6+C7)/C4 (squares) and C8/C4 (circles).

kJ/mol. The negative value of activation energy for the C8/C4 ratio is because of the decreased C8/C4 ratio with increase of the pyrolysis. Absolute values of the activation energies of the (C5+C6+C7)/C4 and C8/C4 ratios (50.79 and 50.36, respectively) are nearly the same. Thus, we can say that formations of the C5-, C6-, and C7-species and formation of the C8-species are competition reactions, and the C5-, C6-, and C7-species increase as much as the C8-species decreases by increasing the pyrolysis temperature.

## Conclusions

Relative abundances of the pyrolysis products of BR were varied with the pyrolysis temperature. Relative abundances of the C5-, C6-, and C7-species increased as the pyrolysis temperature increased, while that of the C8-species decreased. By increasing the pyrolysis temperature, new pyrolysis paths to form the C5-, C6-, and C7-species were involved, which leads to the increases of their relative abundances. Absolute values for the activation energies for the (C5+C6+C7)/C4 and C8/C4 ratios were nearly the same and the signs (+ or −) were opposite.

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