

Thermal Crosslinking of *cis*-1,4-polybutadiene at Ultrahigh Pressures

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ABSTRACT: *cis*-1,4-Polybutadiene (BR) samples, in the absence of crosslinking agents, were simultaneously compressed by ultrahigh pressures (>4.0 GPa) and annealed between 25 and 180°C. The BR samples were crosslinked when the annealing temperatures were above 100°C. The Vickers microhardness of the treated BR increased and the extent of swelling decreased rapidly as the annealing temperature increased, indicating that the crosslinking density increased. Solid-state carbon-13 nuclear magnetic resonance and Fourier transform infrared spectroscopy results showed that some C=C bonds in the BR were opened to form the crosslinking network structures with C—C linkages and that a partial *cis*–*trans* isomerization took place during the treatments. Differential scanning calorimetry studies revealed that the glass transition temperature increased and the crystallinity decreased as the annealing temperature increased. When the annealing temperature exceeded 140°C, the treated BR samples lost their rubbery elastic characteristics completely and became brittle materials. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2131–2140, 1998

Key words: *cis*-1,4-polybutadiene; ultrahigh pressure; crosslinking; microhardness; solid-state ¹³C-NMR

INTRODUCTION

cis-1,4-polybutadiene, commonly called butadiene rubber (BR), is a synthetic rubber whose production ranks only after natural rubber (NR) and styrene–butadiene rubber (SBR).¹ Crosslinked BR has excellent abrasion resistance,^{1–3} good low-temperature flexibility, and high resilience.^{1,2} It is widely used in tires, shoe soles, transmission belts, shock absorber pads, children's toys, and so on.^{1,2} Like most of the common rubbers such as

NR and SBR, BR can be crosslinked by crosslinking agents such as sulfur and peroxides^{2,4,5} or by high-energy radiation.^{2,6} Many research results^{4–10} indicate that the crosslinking reaction mechanisms and the structures and properties of the crosslinked rubbers were very different when different crosslinking agents were used or when the crosslinking conditions were different.

Temperature and pressure are two of the most important factors affecting the crosslinking reactions and the structures and properties of the crosslinked rubbers. BR is generally crosslinked at a temperature lower than 160°C^{4,9–11} under a pressure lower than 100 MPa.^{9–12} However, rubbers are sometimes processed or used under high temperatures and high pressures, or even ultrahigh pressures in some industrial applications and scientific experiments, especially in aerospace applications. Some studies^{13–17} have shown that the structures and properties of some poly-

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mers, including rubbers and organic materials containing unsaturated bonds, would change remarkably under high pressures at certain temperatures. For examples, Sasuga and Takehisa¹⁶ found that high pressures could remarkably accelerate the radiation-induced crosslinking rates of unsaturated polymers such as *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene; and Frenkin and colleagues¹⁷ were able to increase the thermal crosslinking rates of polybutadiene at high pressures. However, their applied pressures were below 1.0 GPa so that a long time (ca. 3 h) was required to produce samples of moderate crosslinking densities even at a high temperature of 290°C. In this work, BR samples, with no added crosslinking agents, were subjected to ultrahigh pressures (>4.0 GPa) between room temperature and 180°C; the molecular structures and physical properties of the treated BR were studied by various characterization techniques. It was found that the BR samples were crosslinked when the temperatures applied were at or above 100°C. These results not only help to develop the theory for the structure–property relationships of polymers, but also provide important experimental data for the applicability of BR under the extreme conditions of high pressures and high temperatures.

MATERIALS AND METHODS

Annealing *cis*-1,4-Polybutadiene Samples under Ultrahigh Pressures

The BR material (BR 9000) was obtained from the Balin Petroleum Company of Hunan, China, synthesized by the Ni(Naph)₂-BF₃·OEt₂-Al(*i*-Bu)₃ catalyst system (a complex compound composed of nickel naphthenate, trifluoroboron diethyl ether, and triisobutyl aluminium), and had the following properties: Mooney viscosity ML₁₊₄^{100°C} = 46; volatile matter = 0.12 wt %; ash content = 0.05 wt %; antioxidant 264 (2,6-di-*tert*-butyl-*p*-cresol) = 0.74 wt %. Relative amounts of *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, and 1,2-polybutadiene structures were 97.3, 1.1, and 1.6 wt %, respectively. The simultaneous high-pressure compression and medium-temperature annealing of the BR samples were carried out at the Institute of Geochemistry, Academia Sinica, Guizhou, China. A schematic diagram of the setup is shown in Figure 1. Simply described, a 0.05-mm-thick and 30-mm-wide stainless-steel sheet was rolled into a triple-walled hollow cylinder of 8-mm inner diameter and 30-mm height. A

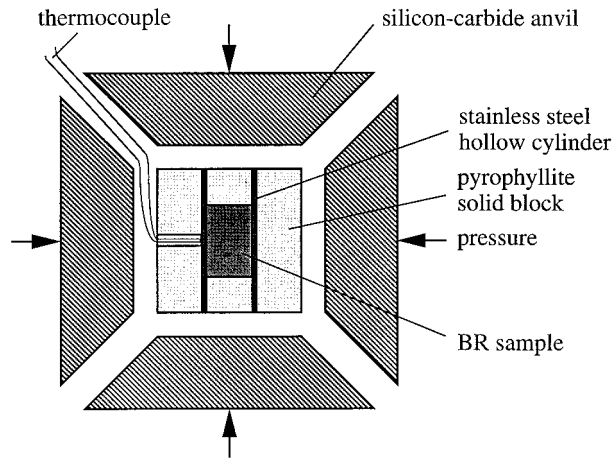


Figure 1 Schematic diagram of the setup used to treat BR samples at different pressures and temperatures.

BR sample was placed at the center of this hollow cylinder. The two ends of the cylinder were filled with pyrophyllite powders and pressed firmly. This structure was then inserted into the cavity of a prefabricated pyrophyllite solid block, which had the shape of a regular hexahedron with a lateral length of 35 mm. The entire hexahedron block was compressed with a six-platen press constructed by the Institute of Geochemistry. The applied pressure could be adjusted according to different requirements and a pressure gauge provided the readings of the actual pressures being exerted on the samples. Moreover, the samples were annealed simultaneously by passing an electric current between the two ends of the hollow cylinder during the compression process. The annealing temperature (T_a) was controlled by changing the current intensity and was measured with a thermocouple adhered to the surface of the stainless-steel cylinder. After the BR sample was treated at the required temperature and pressure for 10 min, the pressure was relieved. The sample was cooled to room temperature and removed for material characterization. The treatment conditions for various BR samples are shown in Table I.

Vickers Microhardness Measurements

The Vickers microhardness measurements (H_v) were carried out by a Zeiss MHT-4 Microhardness Tester with Video Measuring System. A load of 0.49 N was applied to the BR specimens for 60 s at room temperature. The specimens were disks, about 8 mm diameter and 3 mm thick, which were

Table I Compression and Annealing Conditions for Various BR Samples

Conditions	BR-0	BR-1	BR-2	BR-3	BR-4	BR-5	BR-6
Pressure (GPa)	—	5.0	4.0	4.0	4.0	4.0	4.0
Annealing Temperature T_a (°C)	—	25	100	120	140	160	180

All samples were treated for 10 min. BR-0 is the untreated sample.

cut out of the treated BR samples with a South Bay Technology 660 Diamond Wheel Saw and polished on a South Bay Technology 180 Hand Polisher using 10–15 μm abrasive.

Swelling Experiments

For the swelling experiments, circular specimens of 8-mm diameter and 3-mm thickness were cut from the treated BR samples. Each specimen was immersed in 70 mL of toluene (reagent grade; Fisher Chemical, U.S.A.) at room temperature, in which it was swollen to equilibrium. The weight of the swollen specimen was measured with an electronic balance at specific time intervals until a constant weight (W_c) was reached (i.e., after about 48 h). Finally, the swollen specimen was dried under a dynamic vacuum at 70°C for 36 h and the weight of the deswollen specimen was recorded as the original weight (W_o) of the specimen. The extent of swelling (Q) was given by

$$Q = \frac{W_c - W_o}{W_o}$$

Solid-State Carbon-13 Nuclear Magnetic Resonance Spectroscopy

The solid-state carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectroscopy was performed on a JEOL JNM-EX400 FT-NMR System operating at 400 MHz for ^1H . Cross-polarization magic angle spinning (CPMAS) technique was employed to obtain all NMR spectra. The BR samples were ground with an agate mortar and placed inside the zirconia rotor of the NMR spectrometer. All samples were spun between 4.0 and 4.5 kHz at a temperature of 23°C. The chemical shifts were referenced to tetramethylsilane by assigning the upfield peak of adamantane (the external standard) to 29.5 ppm. A total of 500 transients was collected for all CPMAS spectra of the BR samples.

Fourier-Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed on a Perkin-Elmer 16 PC FT-IR Spectrometer. The specimens were compressed KBr pellets in which BR was dispersed by grinding together in an agate mortar. All spectra were taken with 4 cm^{-1} spectral resolution.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC 2910 Differential Scanning Calorimeter between -130 and 220°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a constant nitrogen purge. For each test, about 8 mg of the BR sample was encapsulated in an aluminum pan while an empty aluminum pan was used as an internal reference.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) micrographs were obtained with a JEOL JSM-6300F Scanning Electron Microscope operating at 2 keV accelerating voltage. The fracture surfaces of the elastic samples (BR-0, BR-2, and BR-3) were obtained by tearing while the fracture surfaces of the brittle samples (BR-4, BR-5, and BR-6) were obtained by hammering at room temperature. All fracture surfaces were coated with a thin conducting layer of gold to prevent charging by the electron beam during the SEM observation.

RESULTS AND DISCUSSION

Microhardness and Swelling Behavior

Microhardness is directly related to the microstructures, mechanical properties, and some viscoelastic parameters of a material. It can be used to study the morphology, crosslinking, molecular chain orientation, and some microscopic mechanical properties of polymeric materials, including

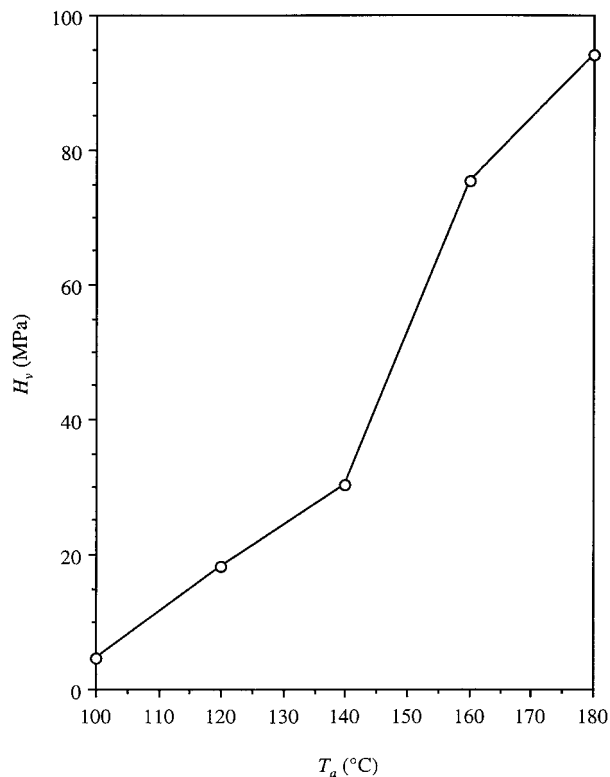


Figure 2 Effect of annealing temperature (T_a) on Vickers microhardness (H_v) of BR compressed at 4.0 GPa.

rubbers.^{18–20} Figure 2 illustrates the H_v of the BR samples (BR-2–BR-6) which had been compressed isobarically at 4.0 GPa at different T_a . As T_a increased, H_v increased rapidly. The H_v of BR-6 that had been annealed at 180°C was 94.1 MPa, which is greater than that of polyethylene (ca. 80 MPa).¹⁸ Figure 3 shows the effect of T_a on the Q of the compressed BR samples. Q decreased rapidly as T_a increased. Furthermore, it was also found that BR-1, which had been compressed at 5.0 GPa at room temperature, dissolved completely in toluene and its microhardness was too low to be measured. These results illustrate that the BR samples were rapidly crosslinked at 4.0 GPa when T_a was above 100°C and the crosslinking density increased as the T_a increased. In particular, when T_a exceeded 160°C, Q was very small (<0.10) and H_v was very high (>75 MPa), indicating that the crosslinking density was very high.

NMR Spectra

The solid-state ^{13}C -NMR spectra of various BR samples are shown in Figure 4. As shown in Figure 4(a), the original BR sample (BR-0) had two strong resonance peaks, at 28.5 and 130.3 ppm,

and a weak resonance peak at 33.6 ppm. They are attributed to the resonances of the *cis*-aliphatic, *cis*-olefinic, and *trans*-aliphatic carbons, respectively.^{4,6,21} The very low intensity of the peak at 33.6 ppm indicates that the amount of *trans* structural units in the BR sample was very small. The spectra of the BR samples which had been compressed at 100 and 120°C (i.e., BR-2 and BR-3) were very similar to that of BR-0, indicating that the crosslinking densities of these two samples were small. This was also reflected by their smaller microhardness and larger extent of swelling.

When T_a exceeded 140°C, there were great changes in the NMR spectra [Figure 4(d–f)]. In addition to the two main peaks at 28.5 and 130.3 ppm, a new broad resonance band was observed between 30 and 50 ppm (including the major peaks at 30.5, 33.6, 39.5, 42.5, 47.3 ppm, etc.) and its intensity increased as T_a increased. These peaks are very similar to those of BR crosslinked by γ -radiation⁶ or by using peroxides as crosslinking agents.⁴ Patterson and Koenig⁴ and O'Donnell and Whittaker⁶ assigned the broad band to the resonances of the crosslinking network structures, which were mainly due to the *trans* CH_2 —, the CH_2 — adjacent to the crosslinkages, and the

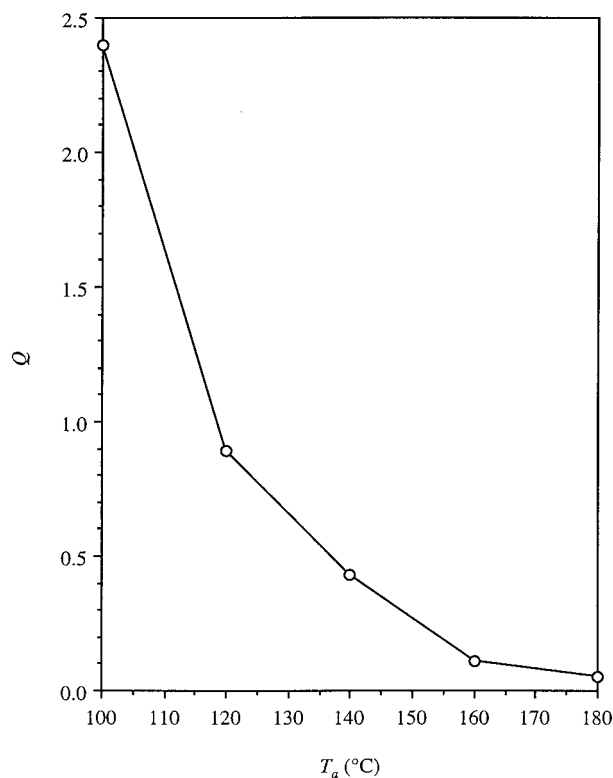


Figure 3 Effect of annealing temperature (T_a) on extent of swelling (Q) of BR compressed at 4.0 GPa.

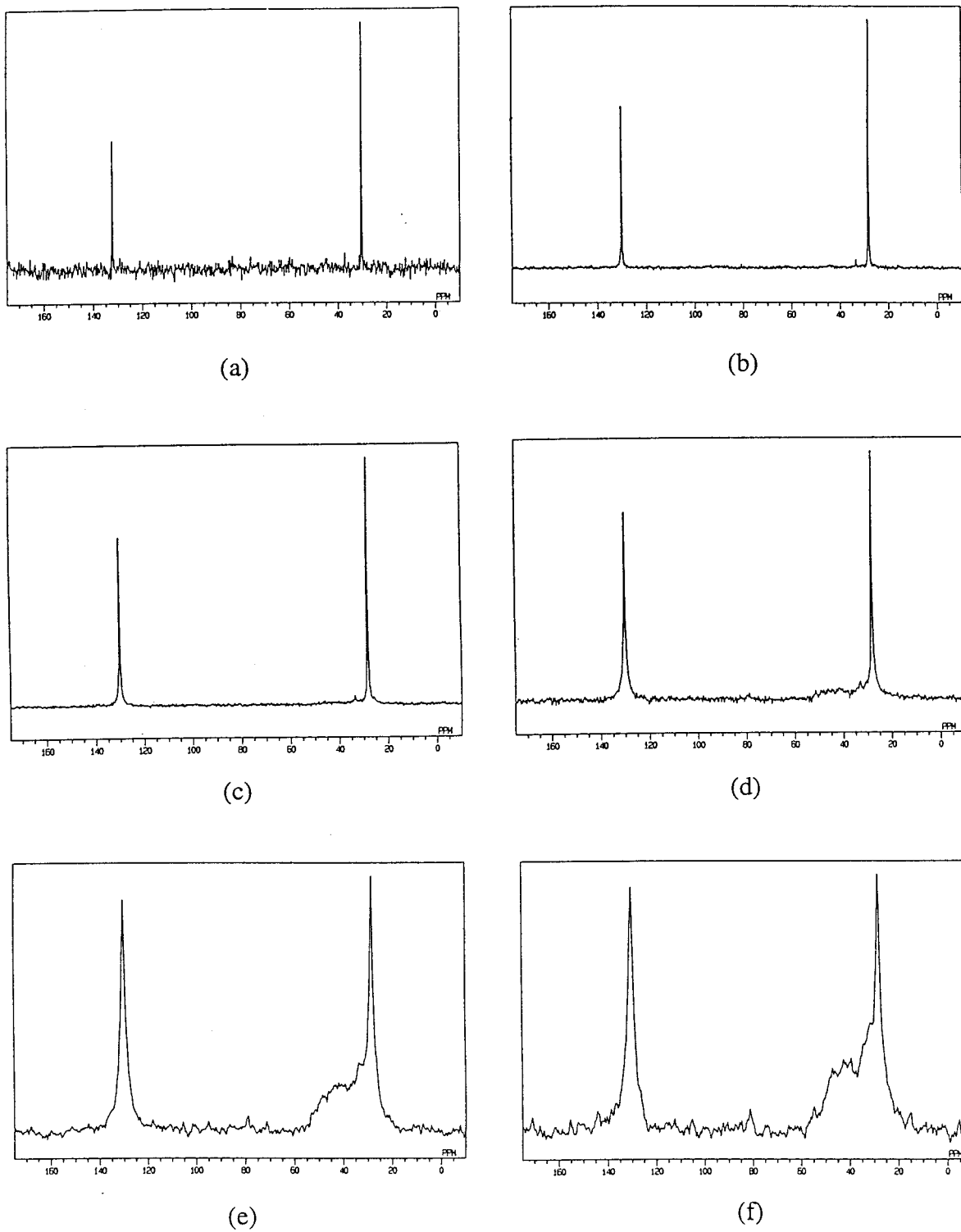


Figure 4 Solid-state ^{13}C -NMR spectra of various BR samples: (a) BR-0, (b) BR-2, (c) BR-3, (d) BR-4, (e) BR-5, and (f) BR-6.

Table II Full-Width-at-Half-Maximum (H_w) of the NMR Resonance Peaks at 28.5 and 130.3 ppm

Samples	H_w (Hz) of NMR Resonance Peaks at	
	28.5 ppm	130.3 ppm
BR-0	35.1	31.7
BR-2	41.3	39.9
BR-3	44.2	45.7
BR-4	47.5	50.8
BR-5	185.5	205.1
BR-6	361.3	322.3

CH— at the crosslinkages. As shown in Figure 4, the new resonance band is very complicated, illustrating the complexity of the crosslinking network structures. As T_a increased, an increase in the intensity of the resonance band indicated an increase in the crosslinking density. Moreover, the intensity of the peak centered at 33.6 ppm increased as T_a increased, indicating that a partial *cis-trans* isomerization took place during the crosslinking process. It is similar to the situations of crosslinking by γ -radiation⁶ or using sulfur and peroxides as crosslinking agents.^{4,21} The network structures and the precise assignments of various NMR peaks in the resonance band will be further studied.

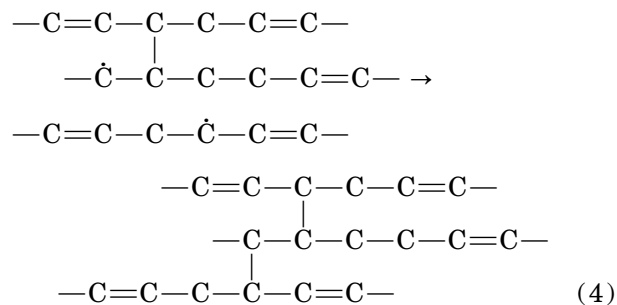
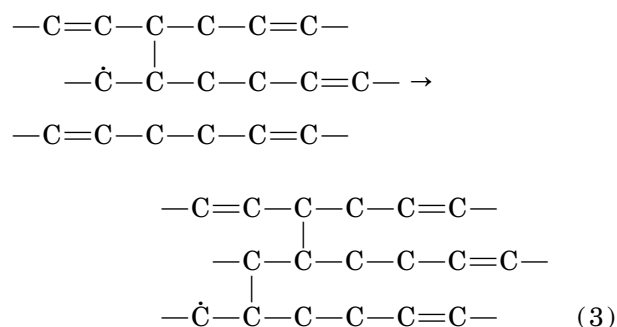
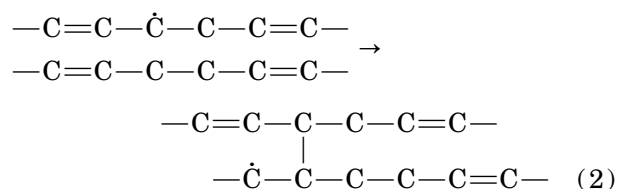
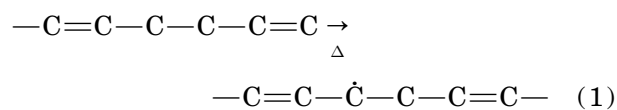
Table II shows the full-width-at-half-maximum (H_w) of the NMR resonance peaks at 28.5 and 130.3 ppm for BR-0 and BR-2–BR-6. H_w increased as T_a increased, indicating that the crosslinks decreased the molecular mobility.^{4,6,21} The greater was the crosslinking density, the more rigid was the network structure. Hence, the smaller was the molecular mobility. This result is in agreement with those of an increase in microhardness and a decrease in extent of swelling as T_a increased.

FTIR Spectra

Figure 5 shows the FTIR spectra of BR-0–BR-6. In the spectrum of the untreated sample BR-0, a strong, broad peak at 738 cm^{-1} was attributed to the out-of-plane bending vibration of the olefinic C—H.^{4,22,23} The two strong peaks at 2942 and 3008 cm^{-1} were attributed to the aliphatic C—H stretching and olefinic C—H stretching vibrations, respectively.²⁰ On the other hand, the peaks at 965 and 994 cm^{-1} , attributed to *trans* C—H bending and vinyl pendant group characteristic vibration, respectively,^{4,22,23} were very weak. The

spectrum of BR-1 was very similar to that of BR-0. It showed that BR-1 was not crosslinked and that its molecular structure was very similar to that of BR-0.

As shown in Figure 5, there were great changes in the spectra of BR-2–BR-6 when compared with the spectrum of BR-0. The relative intensities of the peaks at 738 and 3008 cm^{-1} (732 and 3006 cm^{-1} for BR-6) decreased as T_a increased. They showed that the amounts of the unsaturated structural units in BR decreased after being compressed at those temperatures. Combining our FTIR and NMR with Sasuga's results for radiation-induced crosslinking of doubly bonded polymers at high pressures (max. 900 MPa),¹⁶ the crosslinking mechanisms of *cis*-1,4-polybutadiene annealed at high pressures can be postulated as follows:



A polymer radical was generated by the thermal energy when the BR sample was annealed [reaction (1)]. The radical attacked a C=C bond in

the BR chain. As a result, the C=C bond was opened to form a crosslinking structure while the radical was regenerated within the new polymer structure [reactions (2) and (3)]. The propagation reaction might be terminated by a recombination of radicals [reaction (4)].

High pressures would reduce the free volumes of polymers and the segmental motions of polymer chains. In general, reactions (2) and (3) did not require a long-range migration of the radical to meet a double bond. And, at high pressures, the distance between the molecular chains decreased and the molecular chain interactions increased. Consequently, reactions (2) and (3) were accelerated. On the other hand, the termination reaction of the radicals [(4)] required a long-range migration of one polymer radical to meet another radical. Therefore, the probability of reaction (4) was reduced when high pressures restricted the segmental motions of polymer chains. Both contributions accelerated high-pressure crosslinking reactions. Frenkin and associates¹⁷ showed that the

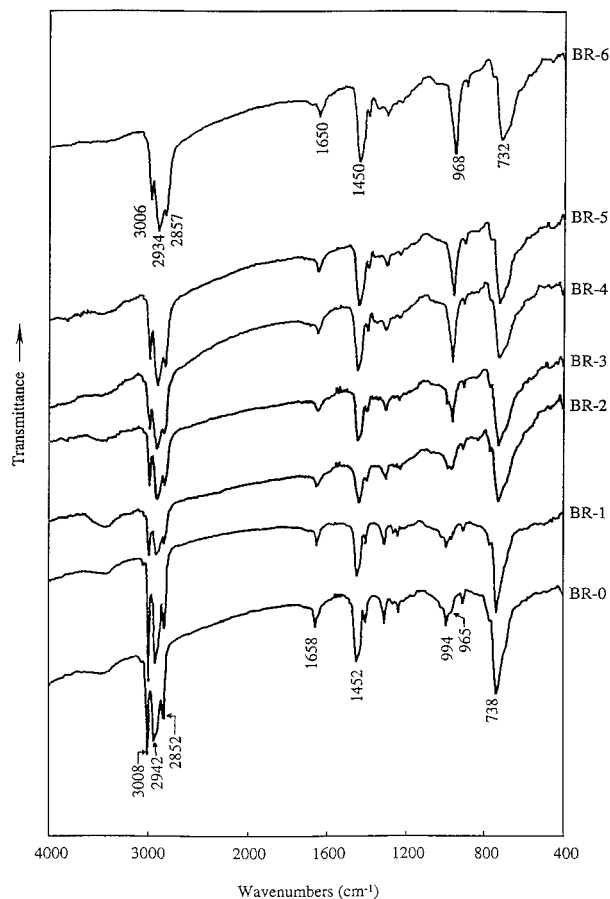


Figure 5 FTIR spectra of various BR samples.

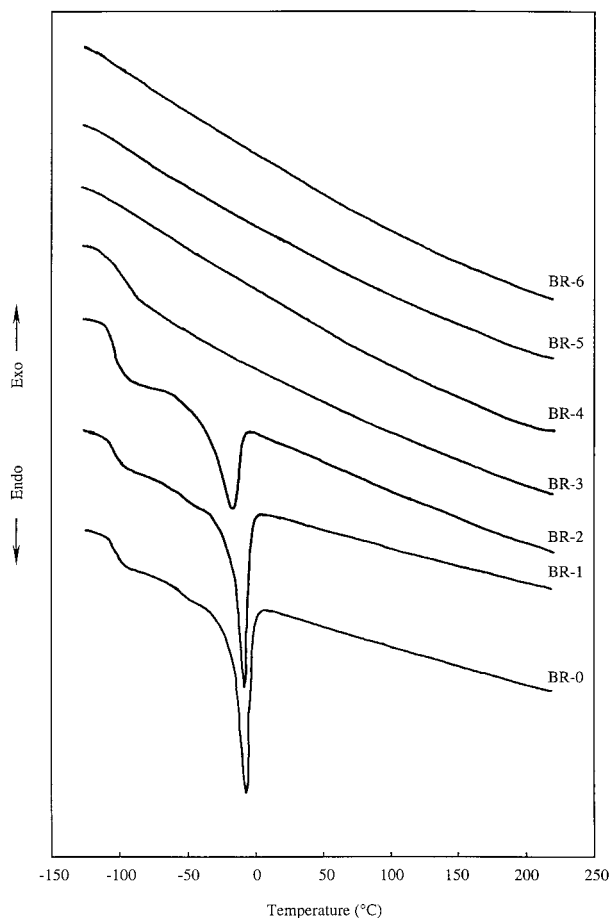


Figure 6 DSC thermograms of various BR samples.

crosslinking rate was extremely low at 200°C when the pressure was below 300 MPa. Furthermore, when T_a increased, reaction (1) was accelerated. The number of radicals and therefore the crosslinking density would increase in the BR samples. Conversely, reaction (1) hardly occurred at room temperature, so the concentration of polymer radicals was very low. As a result, crosslinking reactions did not occur in BR-1.

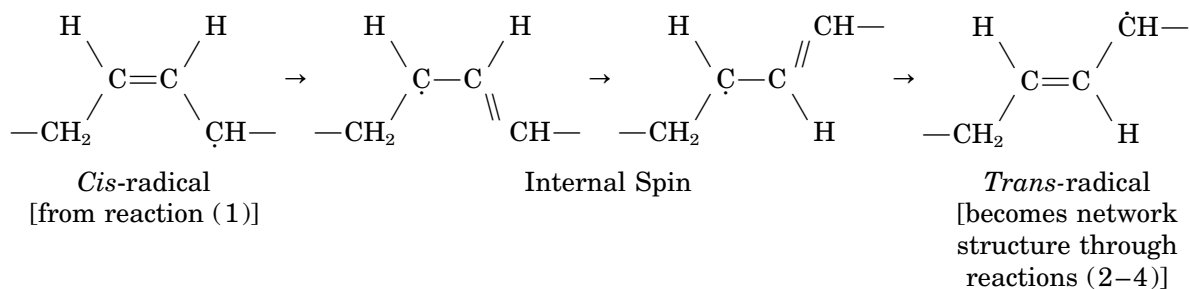
Also shown in Figure 5, the intensity of the peaks at 965 cm^{-1} (968 cm^{-1} for BR-6) increased remarkably as T_a increased. This indicates that a partial

Table III DSC Results of BR-0, BR-1, BR-2, and BR-3 Samples

Results	BR-0	BR-1	BR-2	BR-3
T_g (°C)	-102.9	-102.8	-102.9	-96.1
T_m (°C)	-6.9	-8.3	-17.6	—
ΔH_f (J/g)	50.2	46.9	20.9	—

cis-trans isomerization took place during the cross-linking process, a result consistent with those ob-

tained by NMR spectroscopy. The mechanisms for the *cis-trans* isomerization are shown below:



DSC Thermograms

Figure 6 shows the DSC heating curves of various BR samples; the analytical results appear in Table III. The untreated sample BR-0 had a melting point (T_m) of -6.9°C and a heat of fusion (ΔH_f) of 50.2 J/g . However, the T_m and ΔH_f of the lightly

crosslinked sample BR-2 decreased to -17.6°C and 20.9 J/g , respectively, indicating that its crystallinity decreased. Probably, the crosslinks reduced the chemical regularities of the BR molecular chains.^{22,24} As the crosslinking density became higher in BR-3–BR-6, there were no melting

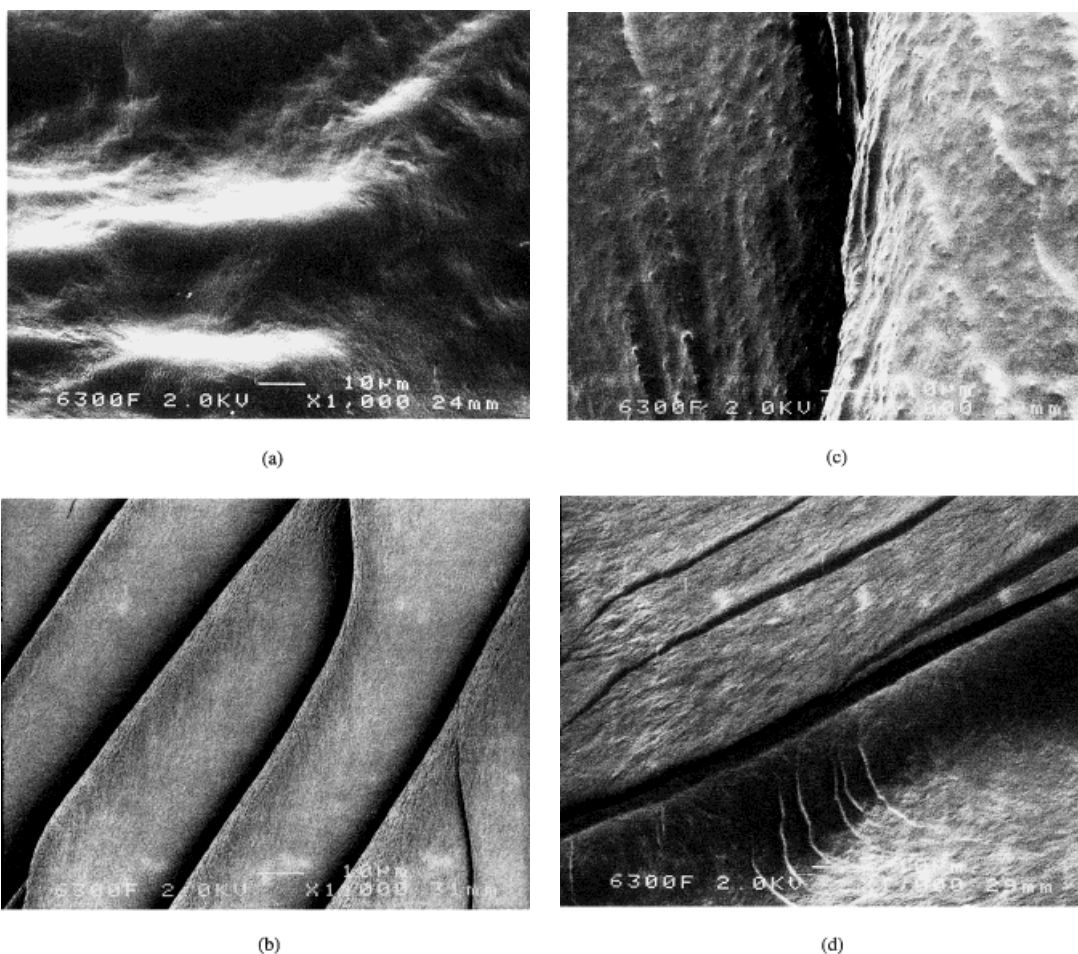


Figure 7 SEM micrographs of various BR samples: (a) BR-0, (b) BR-2, (c) BR-3, (d) BR-4, (e) BR-5, and (f) BR-6; (a–c) tear-fractured surfaces; (d–f) hammer-fractured surfaces.

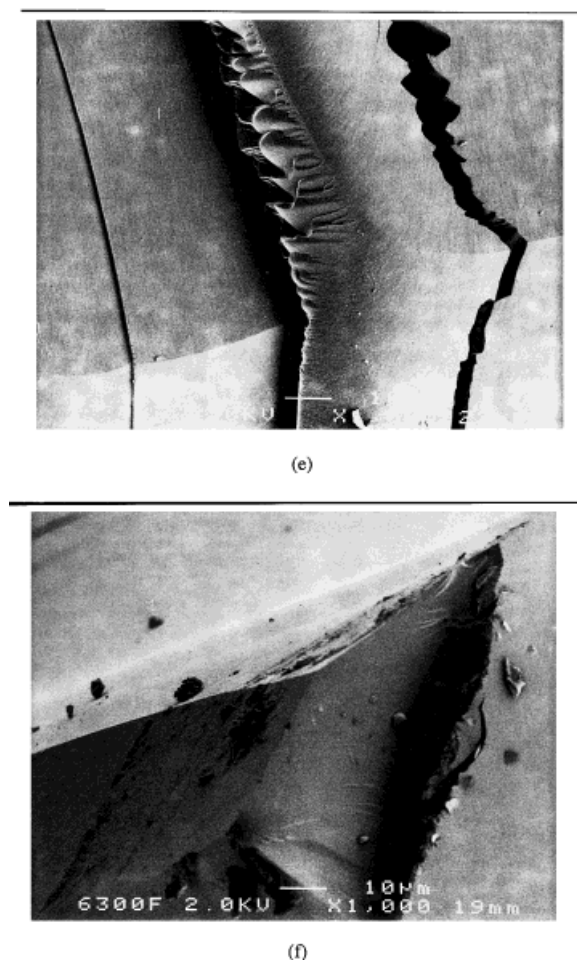


Figure 7 (Continued from the previous page)

peaks observed in their DSC curves, indicating that they were amorphous.

As shown in Figure 6 and Table III, the lightly crosslinked BR-2 had the same glass transition temperature ($T_g = -102.9^\circ\text{C}$) as that of the non-crosslinked BR-0. As BR-3 had a higher crosslinking density, its T_g also increased to -96.1°C . Finally, no glass transitions were observed in BR-4–BR-6 within the DSC experimental temperature range from -130 to 220°C , revealing that their network structures were very rigid.

It was interesting to note that the T_m and ΔH_f of BR-1, which had been compressed at 5.0 GPa and 25°C , were slightly lower than those of BR-0. In addition, the viscosity of BR-1 was greater than that of BR-0, and no cold-flow was exhibited in BR-1 at room temperature. However, FTIR and swelling experimental results did not show crosslinking in BR-1.

SEM Micrographs

Figure 7 shows the SEM micrographs of the fracture surfaces of all BR samples except BR-1. The

untreated BR material (BR-0) was highly viscoelastic at room temperature. A well-defined fracture surface could not be created because the sample was highly elastic and macroscopic surface restructuring occurred when the sample was fractured by tearing [Fig. 7(a)]. Samples BR-2–BR-6 had been treated at 4.0 GPa and 100 – 180°C for 10 min. Figures 7(b) and (c) show that the fracture surfaces of BR-2 and BR-3 were rough. Because of their low crosslinking densities, these two samples were elastic at room temperature and could be fractured only by tearing. The SEM micrographs also show that there were many microcavitations formed on the fracture surfaces—probably due to their weak mechanical properties because the samples contained no reinforcing agents.

The crosslinking density of the samples increased as the T_a increased. As a result, their hammering-induced fracture surfaces were quite smooth in comparison, particularly those of BR-5 and BR-6 [Fig. 7(e, f)], revealing that they had been broken typically in the brittle mode and had completely lost the rubbery elasticity. Hence, *cis*-1,4-polybutadiene has limited usage as rubbery materials at high pressures and high temperatures.

CONCLUSIONS

BR samples containing no crosslinking agents were rapidly crosslinked under a high pressure of 4.0 GPa when a temperature above 100°C was applied simultaneously. The crosslinking density and the H_v of the treated BR samples increased but the extent of swelling decreased as the T_a increased. Solid-state ^{13}C -NMR and FTIR results showed that some of the $\text{C}=\text{C}$ bonds in the BR samples were opened to form the crosslinking network structures with the $\text{C}-\text{C}$ linkages. A partial *cis-trans* isomerization took place during the compression process. Because crosslinking reduced the chemical regularities of the BR molecular chains, the crystallinity and melting points of the treated BR samples decreased as the treatment temperature increased. When the treatment temperatures were above 120°C , the treated BR samples became amorphous materials. In addition, the T_g of the treated BR increased as the treatment temperature increased. When the T_a exceeded 140°C , the compressed BR samples lost their original rubbery elasticity completely and no glass transitions were observed between -130 and 220°C . Therefore, BR has limited usage as a

rubbery material under a high pressure at a high temperature. Nevertheless, it is interesting to note a possibly new method of crosslinking by applying high pressures.

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