

Devulcanization of Nitrile Butadiene Rubber in Nitrobenzene

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ABSTRACT: Sulfur-crosslinked nitrile butadiene rubber (s-NBR) was found to be devulcanized when it was heated with nitrobenzene at 200°C for 3 h. The tetrahydrofuran (THF)-soluble fraction from s-NBR heated with nitrobenzene was purified by reprecipitation with THF/*n*-hexane, chloroform/*n*-hexane, and THF/*n*-hexane systems and was then characterized by means of Fourier transform infrared (FTIR) spectroscopy, ¹H-NMR, gel permeation chromatography, dynamic thermogravimetry/differential thermal analysis (DTA), and differential scanning calorimetry (DSC). FTIR and ¹H-NMR results revealed that the THF-soluble fraction contained aromatic rings derived from nitrobenzene. Furthermore, the molecular weight of the THF-soluble fraction was much lower than that of the parent noncrosslinked poly(acrylonitrile-*co*-butadiene). Although the weight loss of THF-soluble fraction began at a lower temperature than that of the nonheated original nitrile butadiene rubber, the residual weight at 700°C tended to be higher for the former. This tendency became more marked with increasing time of heat treatment with nitrobenzene. The DSC-determined glass-transition temperature of the THF-soluble fraction was higher than that of the original s-

NBR. To elucidate the devulcanization mechanism, we investigated two types of model reactions; one was the reaction of diphenyl disulfide with nitrobenzene, and the other was the reaction of polybutadiene with nitrobenzene. The former reaction, carried out at 250°C in diphenyl ether, yielded diphenyl sulfide with a loss of diphenyl disulfide and nitrobenzene. The use of a higher molar ratio of nitrobenzene to diphenyl disulfide resulted in a depression of diphenyl sulfide formation. The reaction of *p*-chloronitrobenzene with diphenyl disulfide also gave diphenyl sulfide. The reaction of polybutadiene with nitrobenzene at 200°C resulted in the backbone scission of the polymer. The THF-soluble solid product of the latter model reaction was found by FTIR and ¹H-NMR to contain aromatic rings derived from nitrobenzene. The devulcanization mechanism is discussed on the basis of a comparison of the results of the model reactions with those of the s-NBR devulcanization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3342–3353, 2004

Key words: polybutadiene; devulcanization; nitrobenzene; rubber; networks

INTRODUCTION

Vulcanized rubbers with three-dimensional chemical networks are infusible and insoluble in organic solvents. The presence of these networks causes a serious problem in rubber recycling. There are two main approaches to rubber recycling. One approach is mechanical methods (e.g., thermomechanical, cryomechanical). Recently, ultrasonic technology^{1–7} was reported to be effective for waste vulcanized rubbers as a mechanical processing method. The other approach is chemical processing,⁸ which is a possible method for reversing the crosslinked network through the use of chemical agents⁹ that attack carbon–sulfur or sulfur–sulfur bonds.

In the rubber industry, nitrile butadiene rubber (NBR) is widely used because of its oil-resistance char-

acteristics (e.g., O rings, packings, rotary shaft lip seals). NBR is a crosslinked rubber of poly(acrylonitrile-*co*-butadiene) (AB copolymer). Recently, we found that sulfur-crosslinked nitrile butadiene rubber (s-NBR) was easily devulcanized when it was heated with nitrobenzene at 200°C for several hours to give tetrahydrofuran (THF)-soluble solid products. To our knowledge, there have been no reports on the devulcanization of s-NBR by such an approach. This led us to investigate the devulcanization mechanism of s-NBR by heating with nitrobenzene.

This article describes the results of the devulcanization of s-NBR by heating with nitrobenzene. To elucidate the devulcanization mechanism, two types of the model reactions were investigated. One was the reaction of diphenyl disulfide with nitrobenzene at 250°C in diphenyl ether, and the other was the reaction of polybutadiene with nitrobenzene at 200°C.

EXPERIMENTAL

Measurements

Fourier transform infrared (FTIR) spectra of the reaction products were obtained with a Jeol JIR-6500 spec-

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TABLE I
Rubber Compound Recipe for the Experiments

Ingredient	Amount (phr) ^a
Copolymer	100 ^b
Stearic acid	1
Zinc oxide	5
Sulfur	0.3
Accelerator A (thiazoles)	2
Accelerator B (thiurams)	1.8
Accelerator C (thiurams)	1.7

^a phr-parts per hundred parts of rubber.

^b Poly(acrylonitrile-*co*-butadiene).

trometer. Gel permeation chromatography (GPC) was performed at 38°C with a Toso-HLC 802A chromatograph with THF as an eluent. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were estimated from the GPC results by calibration with polystyrene standards. ¹H-NMR and ¹³C-NMR spectra were obtained with a Jeol EX-400 (400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR). Dynamic thermogravimetry (TG) was performed in a nitrogen atmosphere (flow rate = 200 mL/min) with a Seiko Instruments, Inc., TG/DTA 6300 thermogravimeter at a heating rate of 10°C/min. Differential scanning calorimetry (DSC; Seiko Instruments, Inc., DSC 6200) was also used for the analysis of the thermal behaviors of s-NBR and its parent copolymer before and after they were heated with nitrobenzene (heating rate = 10°C/min). The conversions of the reactants and the yield of the reaction product were estimated by gas chromatography (GC; Hewlett Packard 5890 series). The reaction products were identified by gas chromatography mass spectrometry (GC-MS; Shimadzu Co., Ltd., QP-5050A).

Materials and compounding recipe

s-NBR was prepared as follows: AB copolymer [Nipol DN2835, supplied by Nihon Zeon (acrylonitrile content = 29 wt % by elemental analysis, $M_n = 7.83 \times 10^4$, $M_w = 2.65 \times 10^5$, $M_w/M_n = 3.38$ by GPC)] was refluxed with methanol (MeOH) before vulcanization. The purified AB copolymer was masticated by a milling mill and was mixed with several compounding ingredients. Table I shows the rubber compounding recipe for this study.

Diphenyl sulfide, nitrobenzene, *p*-chloronitrobenzene, di-2-ethylhexylphthalate (DOP), and diphenyl ether as guaranteed-grade reagents were used as received. The organic solvents, such as *n*-hexane and THF, were distilled before use.

Vulcanization conditions

A mixture of the AB copolymer and the compounding ingredients was heated at 170°C for 3 min by compression molding.

The s-NBR sheet obtained from compression molding (hardness A = 48 ± 1 JIS K 6253⁻¹⁹⁹⁷, tensile strength = 2.12 MPa, elongation at break = 610% JIS K 6251⁻¹⁹⁹³) was cut into pieces (5 × 5 mm) and was washed with MeOH before use.

Heating with aromatic solvents

A weighed sample (~2.5 g) of AB copolymer or s-NBR and an aromatic solvent (35 mL), such as nitrobenzene or DOP, were placed separately in a three-necked, 100-mL, round-bottom flask equipped with a thermometer, a condenser, and a nitrogen inlet pipette. Each mixture of AB copolymer or s-NBR with aromatic solvents was heated at 200°C for 3 or 8 h in an oil bath. During heating, a stream of nitrogen was bubbled into the flask through a pipette. After being heated, the reaction mixture was cooled to room temperature and was poured into 150 mL of THF. The resulting solution in THF was filtered, the filtrate was evaporated, and the residue was poured into a large amount of *n*-hexane to obtain the THF-soluble fraction as a black solid. The THF-soluble fraction thus obtained from the AB copolymer or s-NBR heated with an aromatic solvent was purified by reprecipitation with the THF/*n*-hexane, chloroform/*n*-hexane, and THF/*n*-hexane systems. The THF-soluble fraction thus obtained was subjected to characterization.

Model reaction of diphenyl disulfide with nitrobenzene

A mixture of nitrobenzene [1.23 g (10 mmol), 2.46 g (20 mmol), and 3.69 g (30 mmol)] and diphenyl disulfide [4.37 g (20 mmol)], which was adjusted to 20.0 g with diphenyl ether as a solvent, was placed in a three-necked, 100-mL, round-bottom flask equipped with a thermometer, a condenser, and a nitrogen inlet pipette. The reaction solution was held at about 250°C for 10 h. During the reaction, a stream of nitrogen was bubbled into the solution through a pipette. At a prescribed time interval (0.5 or 1 h), the reaction mixture was cooled to room temperature with a water bath, and a 0.05-g aliquot of the reaction mixture was taken out into 50 mL of *n*-hexane. Dimethyl phthalate as an internal standard (1500 ppm in a 5-mL *n*-hexane solution) was added and was further diluted with *n*-hexane. The resulting *n*-hexane solution was used to monitor the conversions of diphenyl disulfide and nitrobenzene and the product yield by GC. The reaction products were analyzed by GC-MS.

Model reaction of polybutadiene with nitrobenzene

Polybutadiene, supplied by Aldrich ($M_w \approx 4.2 \times 10^5$ by GPC; 36.0% cis, 54.3% trans, and 9.7% 1,2 addition

TABLE II
Soxhlet Extraction with Various Organic Solvents^a

Solvent	Extract yield (%)
Acetone	13.3
THF	9.2
Methylene chloride	10.2
MeOH	4.6
Chloroform	5.5
<i>n</i> -Hexane	0.9
Benzene	13.1
Toluene	12.3
Nitrobenzene	≥90 ^b

^a Refluxed for 8h.

^b As THF-soluble fraction.

by NMR), was reprecipitated from a THF/MeOH system before use. The purified polybutadiene 2.5 g was heated with nitrobenzene (35 mL) at 200°C for 3 or 8 h in the three-necked flask described previously. After it was heated, the reaction mixture was cooled to room temperature and poured into in 150 mL of THF. The resulting solution in THF was filtered, and the filtrate was evaporated. The residue was poured into a large amount of *n*-hexane, which yielded a black solid product. The purification of the THF-soluble fraction as a black solid was carried out according to the aforementioned procedure for the AB copolymer and s-NBR. The obtained THF-soluble fraction was subjected to characterization.

RESULTS AND DISCUSSION

Soxhlet extraction of s-NBR with various organic solvents

s-NBR was subjected to Soxhlet extraction for 8 h with various solvents. The solvents used were acetone, chloroform, methylene chloride, THF, MeOH, benzene, toluene, *n*-hexane, and nitrobenzene. The obtained results are listed in Table II. Among these solvents, only nitrobenzene was observed to extract most of s-NBR to yield

a black solution, suggesting that s-NBR was devulcanized by heating with nitrobenzene.

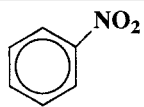
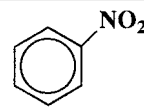
To confirm the devulcanization of s-NBR by nitrobenzene, s-NBR was heated with nitrobenzene at 200°C for 3 and 8 h. For comparison, DOP as a high-boiling-point solvent was also used to heat s-NBR and the AB copolymer at 200°C for 3 h. The results are shown in Table III. Thus, most of s-NBR became soluble when heated with nitrobenzene, whereas only a small amount of the THF-soluble fraction was obtained when it was heated with DOP. These findings led us to conclude that the heat treatment with nitrobenzene devulcanized s-NBR to give THF-soluble solid products. The AB copolymer heated in DOP was swollen but was no longer soluble in THF, although the nonheated one was soluble in THF, indicating that the AB copolymer was crosslinked during heating in DOP.

Characterization of THF-soluble fractions of s-NBR and the AB copolymer heated with nitrobenzene

Figure 1 shows the FTIR spectra of s-NBR before [Fig. 1(a)] and after [Fig. 1(b)] heating with nitrobenzene. The absorptions at 2237, 970, and 910 cm⁻¹ in the spectrum of nonheated s-NBR were assignable to nitrile (—CN), 1,4-butadiene (mainly trans), and 1,2-butadiene units, respectively. However, the spectrum [shown in Fig. 1(b)] of the THF-soluble fraction from the heated s-NBR showed a new peak near 1600 cm⁻¹ due to the stretching vibration of the C—H bonds on the aromatic ring, in addition to the aforementioned absorptions for the AB copolymer.

Figure 2 show the ¹H-NMR spectra of the THF-soluble fractions of s-NBRs after heating with nitrobenzene for 3 h [Fig. 2(a)] and 8 h [Fig. 2(b)]. The broad absorption observed at 6–7 ppm in both of the spectra was assignable to the aromatic ring hydrogen. We concluded from these FTIR and ¹H-NMR results that s-NBR was devulcanized by the reaction with nitrobenzene to yield a THF-soluble

TABLE III
THF-Soluble Fractions of AB Copolymers and s-NBRs After Heating with Nitrobenzene or DOP at 200°C for 3 h^a

	Sample			
	AB copolymer		s-NBR	
	DOP		DOP	
Initial sample weight (g)	2.55	2.53	2.55	2.51
THF-soluble weight (g)	~0	2.4	0.17	2.4
THF-insoluble weight (g)	2.55≥	0.05	2.39	0.27

^a Nitrobenzene and DOP (25mL).

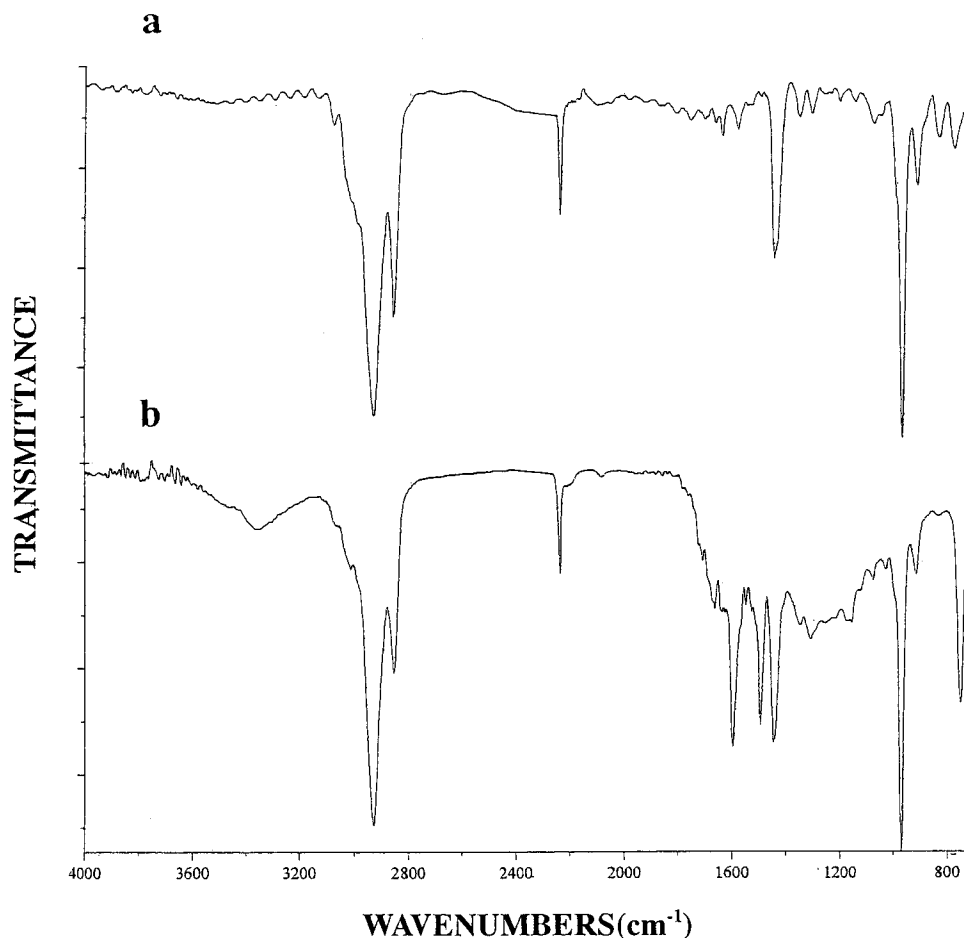


Figure 1 FTIR spectra of (a) the original s-NBR and (b) the THF-soluble fraction of s-NBR heated with nitrobenzene at 200°C for 3 h.

part containing aromatic rings derived from nitrobenzene.

Table IV summarizes the molecular weights of the AB copolymer and s-NBR before and after heating with nitrobenzene at 200°C for 3 and 8 h. The M_n values of the THF-soluble fractions of the AB copolymers after heating for 3 and 8 h were much lower, by a factor of about 30 and 40, than that of the nonheated original AB copolymer.

Similarly, the M_n values of the THF-soluble fractions of s-NBRs after heating with nitrobenzene for 3 and 8 h were about 1/40 and 1/60 compared to that of the parent noncrosslinked AB copolymer. Thus, the main-chain scission of s-NBR occurred during devulcanization by heating with nitrobenzene.

Table V shows the microstructures of the AB copolymer and s-NBR before and after heating with nitrobenzene. Microstructures (1,4- and 1,2-butadiene units) were estimated by means of FTIR¹⁰ and ¹H-NMR.¹¹ The microstructures of the AB copolymer before and after shearing by mechanical processing (mastication) are also listed in Table V. Thus, the microstructures of the AB copolymer before and after

shearing hardly changed. Further, the microstructures of the AB copolymer and s-NBR, even after heating with nitrobenzene, showed almost no change from those of the original AB copolymer.

In conclusion, the sulfur vulcanization of the AB copolymer by compression molding and also the devulcanization of s-NBR by heating with nitrobenzene did not cause significant changes in their microstructures.

Figure 3 shows the TG analysis curves of s-NBR before and after heating with nitrobenzene. As shown in Figure 3, the weight loss of the THF-soluble fraction began at a lower temperature than the nonheated original s-NBR, whereas the residual weight at 700°C tended to be higher for the former. This tendency became more marked with increasing time of heat treatment with nitrobenzene. Figure 4 shows the TG analysis curves of the AB copolymer before and after heating with nitrobenzene. The thermal behaviors of the AB copolymers were similar to the those of s-NBRs. These results also supported the previous conclusion that s-NBR reacted with nitrobenzene during devulcanization.

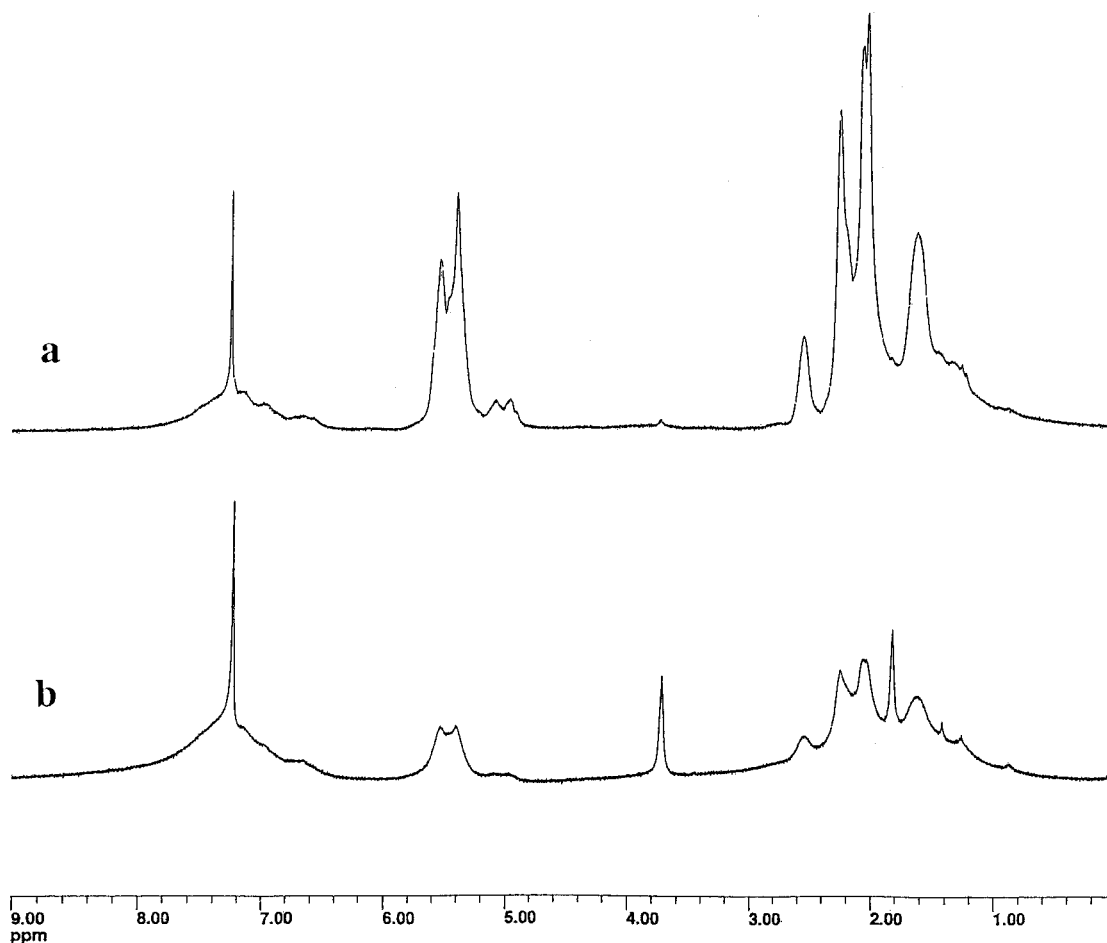


Figure 2 $^1\text{H-NMR}$ spectra of the THF-soluble fractions of s-NBRs heated with nitrobenzene for (a) 3 and (b) 8 h.

Figure 5 shows the DSC curves of the original s-NBR and the s-NBRs heated with nitrobenzene at 200°C for 3 and 8 h. The heated s-NBRs showed higher glass-transition temperatures (T_g 's) compared to that of nonheated one. Figure 6 illustrates DSC curves of the AB copolymers before and after heating with nitrobenzene. Similar to s-NBR, the AB copolymers after heating with nitrobenzene for 3 and 8 h showed higher T_g 's than the original one. Such differences in T_g observed here supported the occurrence of the reaction of s-NBR with nitrobenzene during devulcanization.

From these results, the devulcanization was considered to be caused by scissions of S—S bonds and also the main chain of s-NBR by heating with nitrobenzene. So, two types of model reactions were examined, the reactions of both diphenyl disulfide and polybutadiene with nitrobenzene.

Reaction of diphenyl disulfide with nitrobenzene in diphenyl ether

The reaction of diphenyl disulfide with nitrobenzene as a model reaction was carried out in diphenyl ether

TABLE IV
Molecular Weights of THF-Soluble Fractions of AB Copolymers and s-NBRs Before and After Heating with Nitrobenzene at 200°C for 3 and 8 h^a

Heating time (h)	s-NBR			AB-copolymer		
	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
0	—	—	—	7.83	2.65	3.38
3	0.20	0.13	6.32	0.25	0.13	5.02
8	0.14	0.08	5.64	0.19	0.12	6.09

^a Nitrobenzene (35 mL).

TABLE V
Microstructures [1,4- and 1,2-Butadiene (Bd)] of AB Copolymers and s-NBRs Before and After Heating with Nitrobenzene at 200°C for 3 h

Sample	FTIR		¹ H-NMR	
	1,4-Bd	1,2-Bd	1,4-Bd	1,2-Bd
AB copolymer (original)	0.85	0.16	0.894	0.106
AB copolymer (after shearing)	0.86	0.15	0.906	0.100
AB copolymer (THF-soluble fraction)	0.84	0.16	0.889	0.111
s-NBR (THF-soluble fraction)	0.83	0.17	0.909	0.091

with several molar ratios. Diphenyl sulfide identified by GC-MS was formed with a loss of diphenyl disulfide and nitrobenzene. A considerable amount of black solid products was also obtained as an *n*-hexane insoluble fraction.

Figure 7 shows the time-conversion curves of nitrobenzene at 250°C with various molar ratios of diphenyl disulfide to nitrobenzene. Thus, the conversion of nitrobenzene increased with time. The use of a higher molar ratio of diphenyl disulfide caused a higher con-

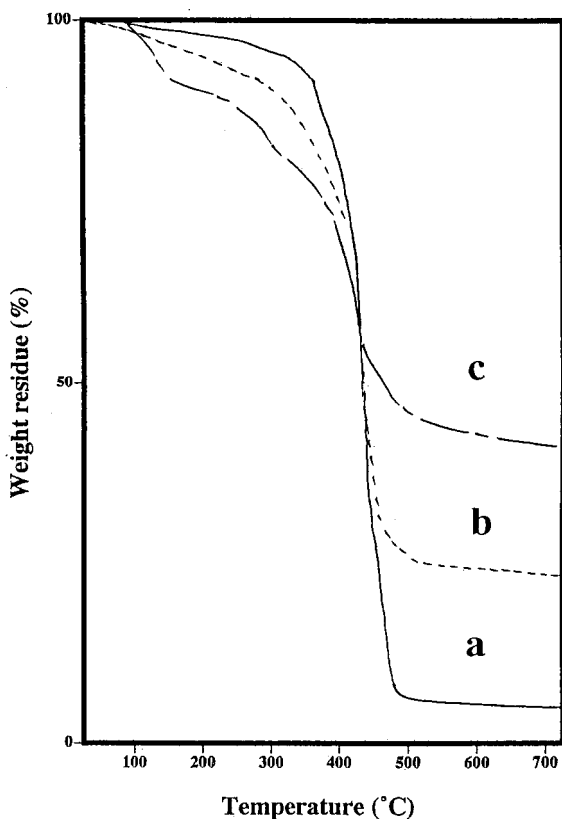


Figure 3 TG analysis curves of (a) the original s-NBR and the THF-soluble fractions of s-NBRs heated with nitrobenzene at 200°C for (b) 3 and (c) 8 h.

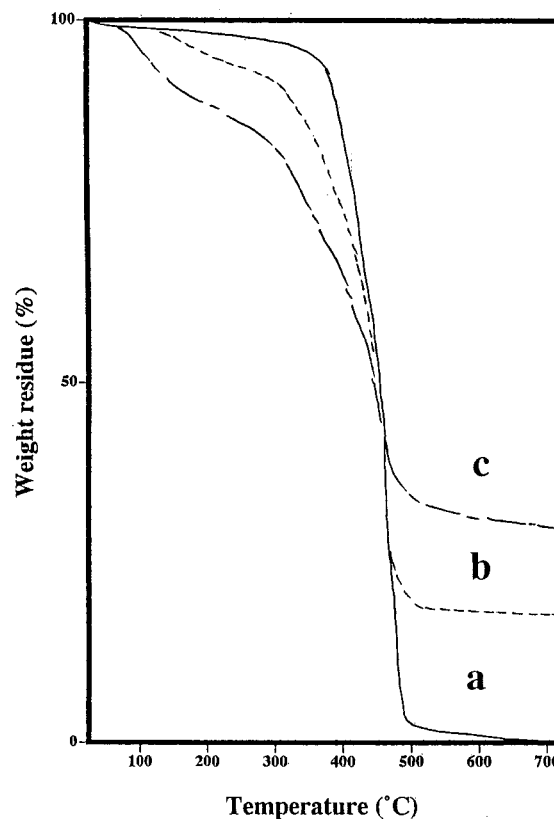


Figure 4 TG analysis curves of (a) the original AB copolymer and the THF-soluble fractions of AB copolymers heated with nitrobenzene at 200°C for (b) 3 and (c) 8 h.

version of nitrobenzene. Nitrobenzene hardly reacted in the absence of diphenyl disulfide.

Figure 8 presents the time-conversion curves of diphenyl disulfide observed at 250°C when the nitrobenzene concentration was changed. Although the conversion of diphenyl disulfide increased with time, the time-conversion curve depended slightly on the amount of nitrobenzene added.

Figure 9 presents the influence of the molar ratio of nitrobenzene to diphenyl disulfide on the diphenyl sulfide formation at 250°C. The reaction mixture showed almost no color change in the absence of nitrobenzene, whereas the reaction mixture in its presence became gradually black during heating. Diphenyl sulfide was formed even in the absence of nitrobenzene. The use of a higher molar ratio resulted rather in a depression of diphenyl sulfide formation.

Figure 10 shows the effect of temperature on diphenyl sulfide formation at an equimolar ratio of nitrobenzene and diphenyl disulfide. Thus, diphenyl sulfide was hardly formed below 200°C, and the yield of diphenyl sulfide increased with rising temperature.

In the place of nitrobenzene, *p*-chloronitrobenzene was also allowed to react with diphenyl disulfide at 250°C in diphenyl ether. Diphenyl sulfide was similarly formed with a loss of diphenyl disulfide and

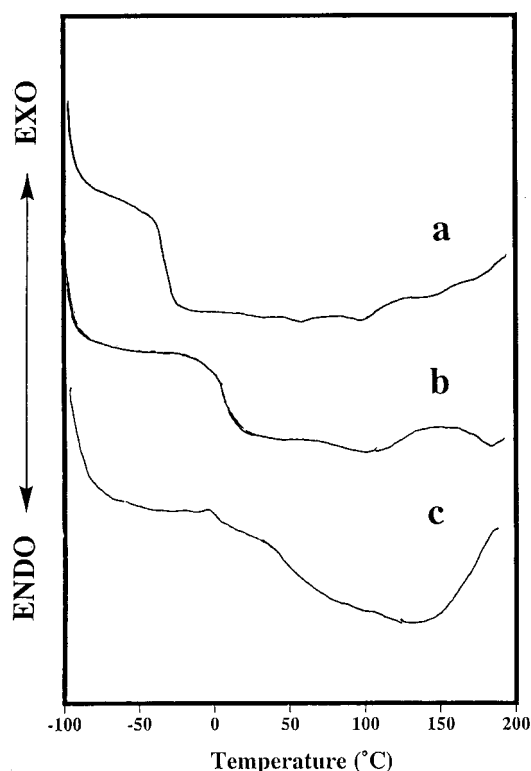


Figure 5 DSC curves of (a) the original s-NBR and the THF-soluble fractions of s-NBRs heated with nitrobenzene at 200°C for (b) 3 and (c) 8 h.

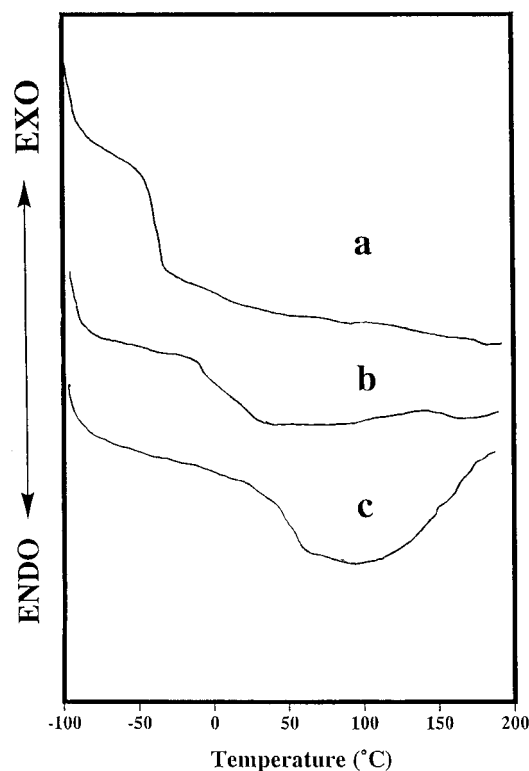


Figure 6 DSC curves of (a) the original AB copolymer and the THF-soluble fractions of AB copolymers heated with nitrobenzene at 200°C for (b) 3 and (c) 8 h.

p-chloronitrobenzene. As described previously, diphenyl sulfide was formed with a loss of diphenyl disulfide, even in the absence of nitrobenzene. These results indicated that the diphenyl sulfide formation was independent of nitrobenzene and derived probably from the homolysis of diphenyl disulfide by heating.

Diaryl disulfides are known to give diaryl sulfide by desulfurization by heating [eq. (1)] or by reaction with aryl halides such as iodobenzene and bromobenzene [eq. (2)].^{12,13} These reactions are considered to proceed via arylthiyl radicals formed by the thermolysis of diaryl disulfides.^{14,15} As shown in eq. (2), an ipso substitution of aryl iodide by arylthiyl radical produces an unsymmetrical diaryl sulfide and an iodine radical, which is converted to I₂.^{13,16} Similar ipso substitution of a diaryl thioether moiety by arylthiyl radical was proposed in the radical ring-opening polymerizations of macrocyclic aryl ether thioether ketone oligomers and related cyclic oligomers where arylthiyl radicals are expelled.^{17–20}

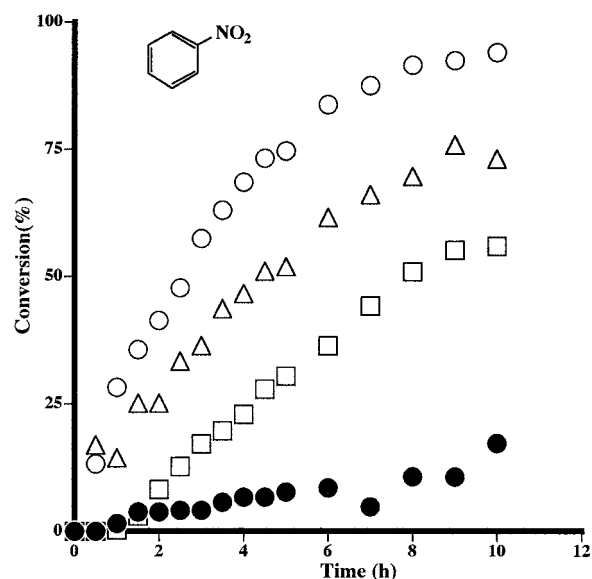
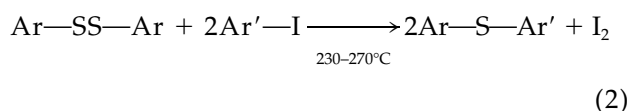
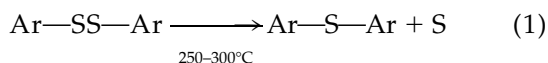


Figure 7 Time-conversion curves of nitrobenzene in the reaction of diphenyl disulfide with nitrobenzene at 250°C in diphenyl ether, (●) no diphenyl disulfide, 20 mmol of nitrobenzene, 20 mmol of diphenyl disulfide, and (○) 10, (△) 20, or (□) 30 mmol of nitrobenzene.

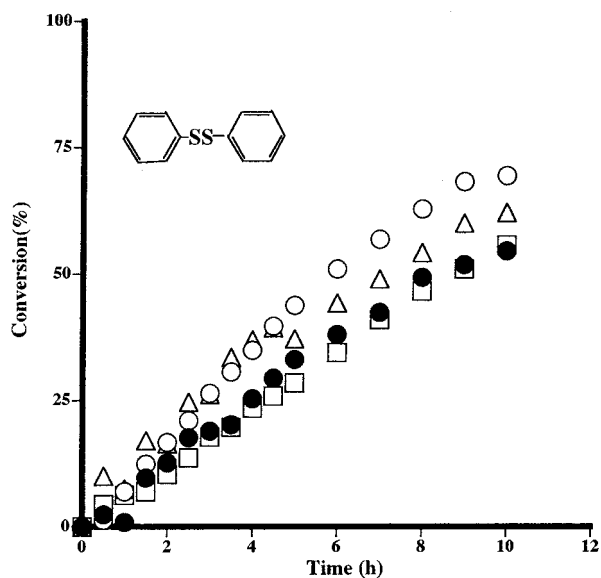


Figure 8 Time-conversion curves of diphenyl disulfide in the reaction of diphenyl disulfide with nitrobenzene at 250°C in diphenyl ether, 20 mmol of diphenyl disulfide, and (●) no nitrobenzene or (○)10, (△) 20, or (□) 30 mmol of nitrobenzene.

As described earlier, both nitrobenzene and *p*-chloronitrobenzene gave diphenyl sulfide in the reaction with diphenyl disulfide, and diphenyl sulfide was likewise formed even in the absence of nitrobenzene. These findings exclude the formation of diphenyl sul-

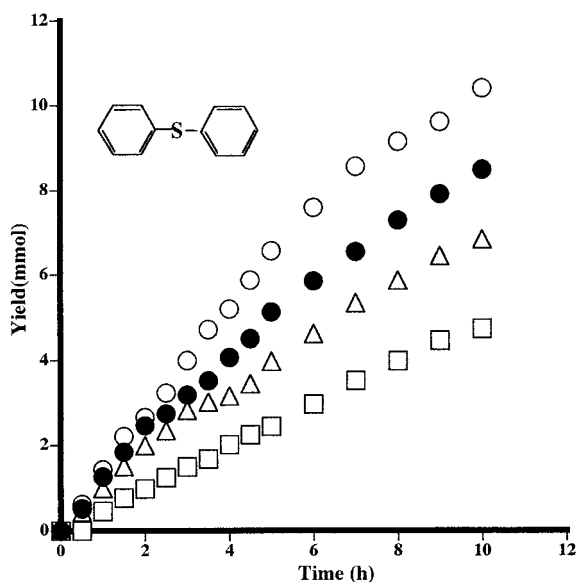


Figure 9 Influence of the molar ratio of nitrobenzene to diphenyl disulfide on diphenyl sulfide formation in the reaction of diphenyl disulfide with nitrobenzene at 250°C in diphenyl ether, 20 mmol of diphenyl disulfide, and (●) no nitrobenzene or (○)10, (△) 20, or (□) 30 mmol of nitrobenzene.

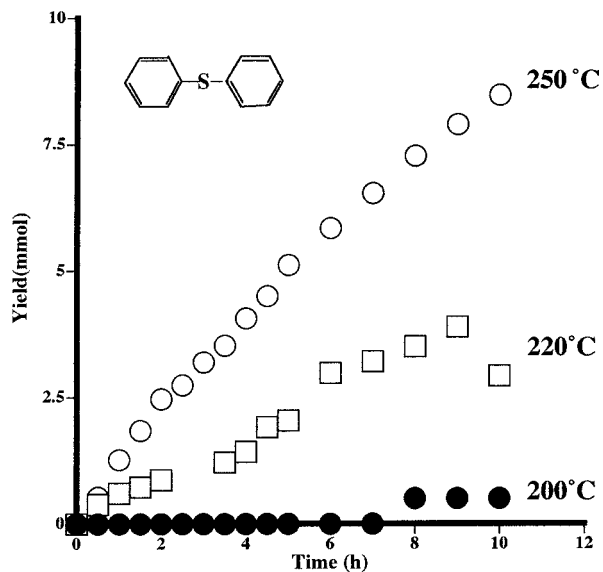
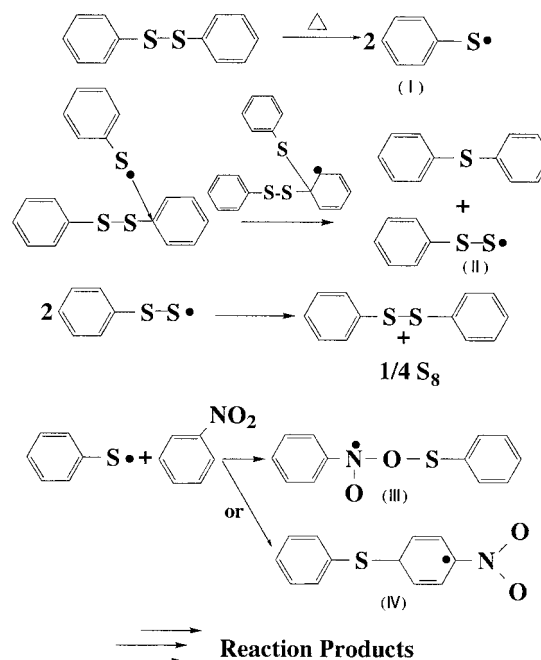


Figure 10 Effect of temperature on diphenyl sulfide formation in the reaction of diphenyl disulfide with nitrobenzene in diphenyl ether, 20 mmol of diphenyl disulfide, and 20 mmol of nitrobenzene at (●) 200, (□) 220, and (○) 250°C.

fide by the ipso substitution of nitrobenzene by the phenylthiyl radical.

Diphenyl sulfide and other reaction products were formed in the reaction of diphenyl sulfide with nitrobenzene, as proposed in Scheme 1. Diphenyl disulfide decomposed homolytically to yield the phenylthiyl radical (I). The generated thiyl radical attacked the benzene



Scheme 1 Reaction of diphenyl disulfide with nitrobenzene.

TABLE VI
Molecular Weights of Polybutadienes Before and After Heating with Nitrobenzene at 200°C for 3 and 8 h^a

Heating time (h)	Initial weight (g)	Fraction weight (g)		Molecular weight			Nitrogen content (%)
		THF soluble	THF insoluble	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	
0	—	—	—	20.0	42.8	2.14	—
3	2.53	2.39	~0	0.36	0.89	2.45	4.22
8	2.52	4.46	~0	0.08	0.28	3.76	6.67

^a Nitrobenzene (35mL).

ring of diphenyl disulfide to undergo ipso substitution. The resulting phenylthiothiyl radical (II) reacted itself to give diphenyl disulfide and elemental sulfur.

The phenylthiyl radical also reacted with nitrobenzene through addition to a benzene ring or nitro group.²¹ The resulting radicals (III and IV) further reacted with other radicals or themselves to yield nitrogen-containing products. As a result, the use of a higher amount of nitrobenzene resulted in a decrease in the diphenyl sulfide yield.

The reaction of diphenyl disulfide with nitrobenzene (molar ratio, 1:1) at 250°C for 10 h gave an *n*-hexane insoluble fraction as a black solid in a yield of 38 wt % on the basis of the initial amounts of the reactants. Furthermore, the *n*-hexane insoluble fraction contained nitrogen (5.4% by elemental analysis), indicating that the *n*-hexane insoluble fraction was derived from nitrobenzene, probably via intermediate radicals III and IV.

Reaction of polybutadiene with nitrobenzene

Polybutadiene was heated with nitrobenzene at 200°C for 3 or 8 h. As shown in Table VI, almost all of the portion of heated polybutadiene was soluble in THF. The THF solution of the reaction mixture was concentrated and poured into a large excess of *n*-hexane, and then, the precipitated black solid product was filtered. The filtrate, as *n*-hexane solution, was evaporated and poured into a large amount of MeOH. However, no precipitation was observed, although the original polybutadiene was soluble in *n*-hexane and insoluble in MeOH. Interestingly, the THF-soluble and *n*-hexane insoluble fraction obtained as a black solid when heated for 8 h was about 1.8 times as large as the initial polybutadiene by weight. These results indicate that the THF-soluble fraction as a black solid was derived from polybutadiene and nitrobenzene.

Table VI also presents the molecular weight of the polybutadiene before and after heating with nitrobenzene. The M_n values of the polybutadienes heated with nitrobenzene for 3 and 8 h were about 1/55 and 1/266, respectively, that of the nonheated polybutadiene. The nitrogen contents of the polybutadienes heated with nitrobenzene for 3 and 8 h were 4.22 and

6.67%, respectively. These results again indicated that the reaction between polybutadiene and nitrobenzene occurred during heating.

Figure 11 shows the FTIR spectra of the polybutadiene before [Fig. 11(a)] and after heating with nitrobenzene for 3 h [Fig. 11(b)] and 8 h [Fig. 11(c)]. The absorptions at 966, 912, and 727 cm^{-1} in the spectrum [Fig. 11(a)] of the nonheated polybutadiene were due to the 1,4-*trans*, 1,2-, and 1,4-*cis*, respectively. As shown in Figure 11(b), the absorptions at 970 and 912 cm^{-1} were significantly weakened compared to those of the initial polybutadiene. Furthermore, as shown in Figure 11(c), the absorptions at 970 and 912 cm^{-1} almost vanished. However, new absorptions appeared near 1600, 1500, 750, and 690 cm^{-1} and tended to be stronger with increasing time of heat treatment with nitrobenzene. These absorptions seemed due to the aromatic rings derived from nitrobenzene.

Figure 12 shows the ¹H-NMR spectra of the polybutadiene before [Fig. 12(a)] and after heating with nitrobenzene for 3 h [Fig. 12(b)] and 8 h [Fig. 12(c)]. The broad absorptions observed at 6–7 ppm in Figures 12(b) and 12(c) were due to the aromatic ring hydrogens.

We concluded from the aforementioned GPC, FTIR, and ¹H-NMR results that the main-chain breakdown of polybutadiene was caused by the reaction with nitrobenzene to yield the THF-soluble part containing aromatic rings derived from nitrobenzene.

A main-chain scission mechanism of polybutadiene is proposed in Scheme 2. At first, nitrobenzene underwent an ene reaction with an allyl-type unit in polybutadiene. Polybutadiene was reported to be modified by ene reactions with triazolinedione derivatives, in which the N=N bond participated in the ene reaction.²² Carbonyl (C=O),²³ nitroso (N=O),²⁴ and even Se⁺—O[−] groups²³ have also been described to participate in the ene reaction.

The N—C bond of the resulting polymer (V) was homolytically severed to yield a stable allyl-type polymer radical (VI) and a nitrogen-centered radical (VII), being resonance stabilized by a phenyl group and the lone-pair electrons of two oxygens. β -Scission of the allyl-type polymer radical led to the breakdown of the polybutadiene backbone. Further reactions of the nitro-

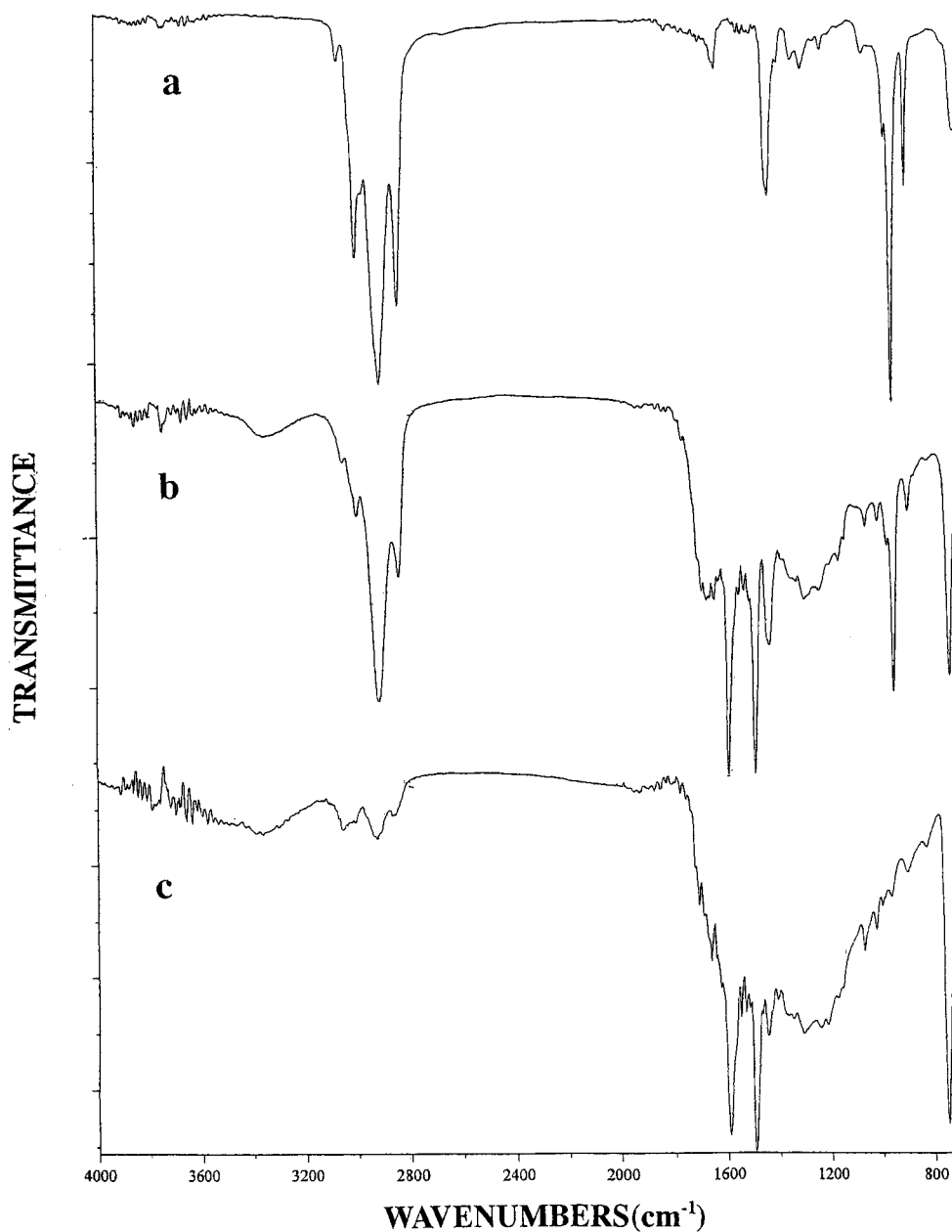


Figure 11 FTIR spectra of (a) the original polybutadiene and the polybutadienes heated with nitrobenzene at 200°C for (b) 3 and (c) 8 h.

gen-centered radical resulted in the formation of nitrogen-containing products.

Devulcanization mechanism of *s*-NBR with nitrobenzene

On the basis of the results of the two model reactions mentioned previously, the devulcanization of *s*-NBR proceeded as follows: at elevated temperatures, disulfide and polysulfide bonds as weak bonds in *s*-NBR repeatedly underwent scission and reformation.²⁵ The thiyl radicals formed from the scission of such sulfur-sulfur bonds were scavenged by nitrobenzene to pre-

vent relinking, which led to the devulcanization of *s*-NBR. The main chain of *s*-NBR was also broken into shreds by an ene reaction with nitrobenzene followed by the homolytic scission of the N—C bond in the side chains of the resulting polymer and subsequently by β -scission of the polymer radical.

CONCLUSIONS

s-NBR was devulcanized by heating with nitrobenzene at 200°C for 3 h. The THF-soluble fraction from *s*-NBR heated with nitrobenzene contained aromatic

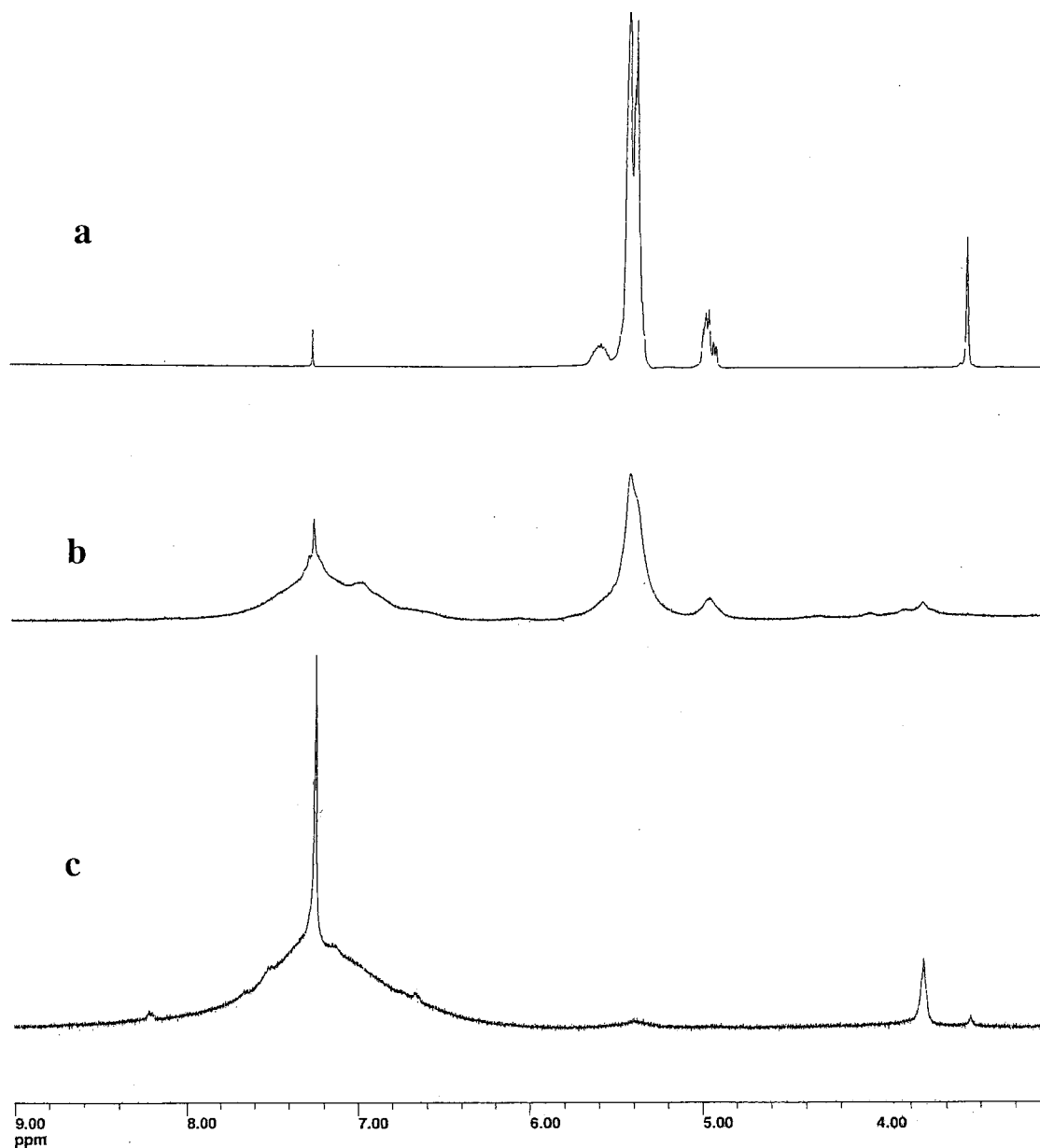
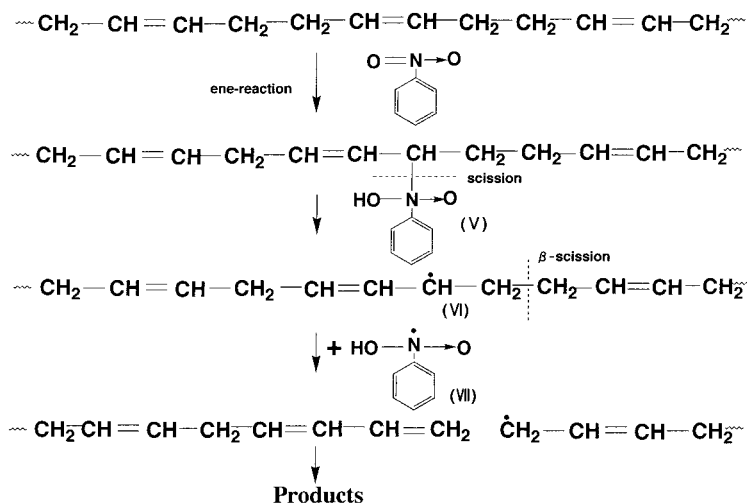


Figure 12 $^1\text{H-NMR}$ spectra of (a) the original polybutadiene and the polybutadienes heated with nitrobenzene at 200°C for (b) 3 and (c) 8 h.

rings derived from nitrobenzene. Furthermore, the molecular weight of the THF-soluble fraction was much lower than that of the parent noncrosslinked AB copolymer. Although the weight loss of the THF-soluble fraction began at the lower temperature than the nonheated original NBR, the residual weight at 700°C tended to be higher for the former. This tendency became more marked with increasing time of heat treatment with nitrobenzene. The DSC-determined T_g of the THF-soluble fraction was higher than that of the original s-NBR. To elucidate the devulcanization mechanism, two types of the model reactions were investigated; one was the reaction of diphenyl disulfide with nitrobenzene, and

the other was the reaction of polybutadiene with nitrobenzene. The former reaction, carried out at 250°C in diphenyl ether, yielded diphenyl sulfide with a loss of diphenyl disulfide and nitrobenzene. The use of a higher molar ratio of nitrobenzene to diphenyl disulfide resulted in a depression of diphenyl sulfide formation. The reaction of *p*-chloronitrobenzene with diphenyl disulfide also gave diphenyl sulfide. The reaction of polybutadiene with nitrobenzene at 200°C caused the main-chain scission of the polymer. The THF-soluble solid product of the model reaction was found by FTIR and $^1\text{H-NMR}$ to contain aromatic rings derived from nitrobenzene. A devulcanization mechanism of s-NBR was pro-



Scheme 2 Main-chain scission of polybutadiene on heating with nitrobenzene.

posed on the basis of a comparison of the results of the model reactions with those of the s-NBR devulcanization.

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