Fourier Transform Near-Infrared and Electron Spin Resonance Studies on the Crosslinking Reaction of Liquid Carboxylated Poly(acrylonitrile-*co*-butadiene) Rubber with Dicumyl Peroxide in Dioxane

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ABSTRACT: The crosslinking reaction of liquid carboxylated poly(acrylonitrile-*co*-butadiene) [or nitrile rubber (NBR); acrylonitrile = 10 wt %] with dicumyl peroxide (DCPO) was studied in dioxane by means of Fourier transform near-infrared spectroscopy (FT-NIR) and electron spin resonance spectroscopy (ESR). Among the three butadiene units (1,2, *cis*-1,4, and *trans*-1,4 units) of NBR, only the pendant vinyl group of the 1,2 unit showed an absorption at 6110 cm^{-1} from the FT-NIR examination of dioxane solutions of NBR, 1-octene, 3,3-dimethyl-1-butene, *trans*-2-octene, *cis*-5-octen-1-ol, poly-*cis*-1,4-butadiene, and poly-1,2-butadiene. The crosslinking reaction was followed *in situ* in dioxane by the monitoring of the disappearance of the pendant vinyl double bond with FT-NIR. The initial disappearance rate (R_0) of the vinyl group was expressed by $R_0 = k[\text{DCPO}]^{0.9}[\text{NBR}]^{-0.2}$ (120°C). The overall activation energy of the reaction was calculated to be 20.7 kcal/mol. This unusual rate equation suggests unimolecular termination due to degradative chain transfer and depressed reactivity of the vinyl group caused by crosslinking. ESR study of the reaction mixture revealed that an allyl-type polymer radical was formed in the reaction, and its concentration increased with time and was then saturated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2095–2101, 2003

Key words: crosslinking; polybutadiene; kinetics (polym.); infrared spectroscopy; ESR/EPR

INTRODUCTION

The crosslinking processes of polybutadiene-based rubbers with peroxides have been studied by many researchers in terms of the physical properties and chemical structures of the crosslinked products.[1–8] However, there are only a few reports on kinetic studies of the crosslinking reactions of these rubbers.[1,9] The radical polymerization of 1,3-butadiene proceeds in two modes, namely, 1,2 polymerization and 1,4 polymerization. As a result, most polybutadiene-based rubbers contain pendant vinyl groups by 1,2 propagation and *cis*-butene and *trans*-butene units by 1,4 propagation.[10] In the crosslinking reactions of such rubbers through radical mechanisms, the reactivity of the pendant vinyl group has been reported to be much higher than those of the butene units, leading to the conclusion that the pendant vinyl group plays the most important role in the crosslinking reactions.[1,9]

We found that the pendant vinyl group in the polybutadiene showed overtone absorption due to the =C—H stretching vibration at 6110 cm^{-1}, whereas the *cis*-butene and *trans*-butene units did not show any absorption near 6110 cm^{-1}. This allowed us to follow *in situ* the reaction of the pendant vinyl group in polybutadiene-based rubbers by Fourier transform near-infrared spectroscopy (FT-NIR).

This article describes the results of a kinetic study of the crosslinking reaction of liquid carboxylated poly-(acrylonitrile-*co*-butadiene) [or nitrile rubber (NBR)] with dicumyl peroxide (DCPO) by means of FT-NIR and electron spin resonance spectroscopy (ESR).

EXPERIMENTAL

Two types of liquid carboxylated NBR (from Aldrich) were used in this study. They differed only in their content of acrylonitrile (AN); that with 10 wt % AN is noted as NBR [number-average molecular weight (M_n) = 3800 (provided by the supplier)], and that with 18 wt % AN is noted as NBR18 [M_n = 3500 (provided by the supplier)]. NBR was mainly used. DCPO was recrystallized from a methanol–water mixture. 1-Octene, *trans*-2-octene, *cis*-5-octen-1-ol, 3,3-dimethyl-1-butene, 1,2-polybutadiene, and poly-*cis*-1,4-butadiene
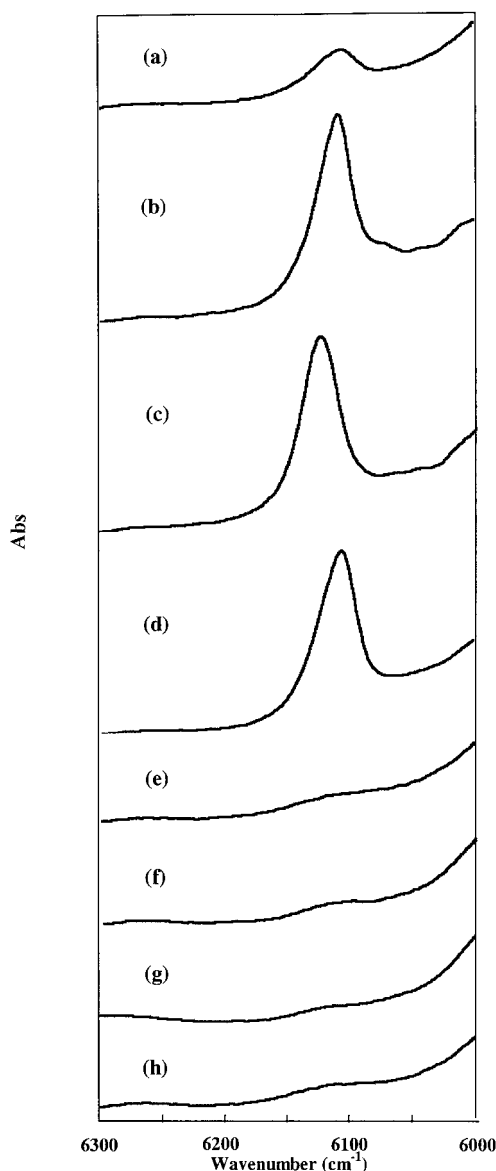
Figure 1 FT-NIR spectra of 1.0*M* solutions of (a) NBR, (b) 1-octene, (c) 3,3-dimethyl-1-butene, (d) poly-1,2-butadiene, (e) *trans*-2-octene, (f) poly-*cis*-1,4-butadiene, (g) *cis*-5-octene-1-ol in dioxane, and (h) dioxane.

were supplied by Tokyo Kasei (Tokyo, Japan) and Aldrich (Milwaukee, WI) and were subjected to FT-NIR measurements. Dioxane was used after distillation. The reaction of NBR with DCPO in dioxane was carried out in a degassed and sealed Pyrex tube (5 mm in diameter) in the custom-made aluminum furnace in which FT-NIR measurements were performed. FT-NIR spectra were obtained with a Jasco INT-400 spectrometer equipped with a MCT detector. Gel permeation chromatography (GPC) was performed at 38°C with a TOSO-HLC 802A chromatograph with tetrahydrofuran as an eluent. M_n and the weight-average molecular weight (M_w) were estimated from the GPC results by calibration with polystyrene standards. [1]H-

NMR and ^{13}C-NMR spectra were obtained with a Jeol EX-400 (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR). ESR spectra of the reaction mixtures in a degassed and sealed ESR quartz tube were recorded on a Jeol-JES-FE 2XG spectrometer operating in the X-band (9.5 GHz) with a transverse-electric-wave-mode cavity. The radical concentration of the reaction mixture was determined by computer double integration of the first derivative ESR spectrum. For this, a solution of 2,2,6,6-tetramethylpiperidin-1-oxyl radical (TEMPO) in dioxane was used as a standard because TEMPO was unstable in the presence of NBR. A MgO marker was used for the calibration of the radical concentration in different media. Dynamic thermogravimetry (TG) of the polymers was performed in a nitrogen atmosphere (20 mL/min flow rate) with a Shimadzu TGA-50 thermogravimeter at a heating rate of 10°C/min. Differential scanning calorimetry (DSC; Shimadzu DSC-50) was used for analysis of the thermal behavior of the polymers (10°C/min heating rate).

RESULTS AND DISCUSSION

FT-NIR spectra of NBR and related compounds

The microstructure of NBR used here was analyzed in CDCl$_3$ by ^{1}H-NMR and ^{13}C-NMR spectroscopy. The NBR consisted of 20.4% 1,2 structure, 21.6% *cis*-1,4 structure, and 58.0% *trans*-1,4 structure as derived from the butadiene unit.

Figure 1 shows the FT-NIR spectra of the 1*M* solutions of NBR, 1-octene, 3,3-dimethyl-1-butene, *trans*-2-octene, *cis*-3-octen-1-ol, poly-*cis*-1,4-butadiene, and poly-1,2-butadiene in dioxane together with that of dioxane as a solvent. The concentrations for the polymers were based on the butadiene monomer unit. Thus, the compounds carrying the vinyl group showed an absorption at 6110 cm^{-1}, whereas the ones with an inner double bond (cis or trans) did not show any absorption there. These results indicate that the
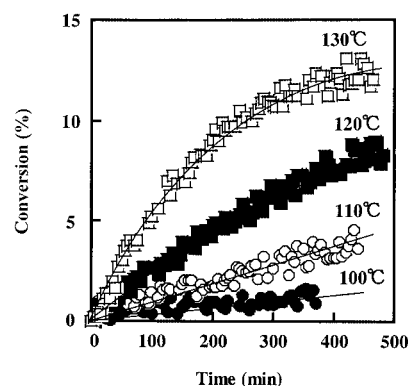

Figure 2 Time–conversion curves in the crosslinking reaction of NBR with DCPO at different temperatures: [DCPO] = 2.00×10^{-2} mol/L and [vinyl group] = 0.408 mol/L.
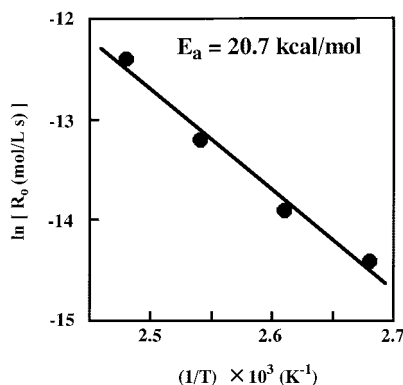
Figure 3 Temperature effect on R_0 of the vinyl group.

Figure 5 Effect of the DCPO concentration on R_0 of the vinyl group at 120°C in dioxane.

absorption of NBR at 6110 cm^{-1} was assignable to the overtone due to the stretching vibration of the =C—H bonds in the pendant vinyl groups.

Kinetic study of the crosslinking reaction of NBR with DCPO in dioxane

The reaction of NBR with DCPO was kinetically studied in dioxane in terms of the consumption of pendant vinyl groups in NBR. The concentration of the pendant vinyl group in NBR was monitored by the absorbance (peak area) at 6110 cm^{-1}.

Figure 2 shows the time–conversion profiles for the reaction at different temperatures, where the concentrations of DCPO and the vinyl group of NBR were 2.00×10^{-2} mol/L and 0.408 mol/L, respectively. The conversion at 130°C showed a tendency to be saturated with time. This resulted from consumption of DCPO in the early stage (half-life period of DCPO at 130°C; = 75 min).[11] The initial disappearance rate (R_0) of the vinyl group at each temperature was determined from the time–conversion curve.

Figure 3 shows the Arrhenius plot of R_0. From the

slope of the plot, the overall activation energy of the reaction of pendant vinyl groups was calculated to be 20.7 kcal/mol.

Figure 4 shows the time–conversion curves observed at different DCPO concentrations at 120°C, with the vinyl group concentration constant at 0.408 mol/L. Figure 5 presents the relationship between R_0 and the DCPO concentration. R_0 increased in proportion to the 0.9th power of the DCPO concentration. This reaction can be regarded as the polymerization of pendant vinyl groups initiated with DCPO. The nearly first-order dependence of the polymerization rate on the initiator concentration suggested a unimolecular termination of the polymer radical.

Figure 6 illustrates the time–conversion curves observed at different vinyl group concentrations at 120°C, with a fixed DCPO concentration at 4.00×10^{-2} mol/L. The conversion of pendant vinyl groups considerably decreased with increasing NBR concentration. However, R_0 (mol/L s) did not show such a significant decrease with increasing NBR concentration because a decrease in conversion was compen-
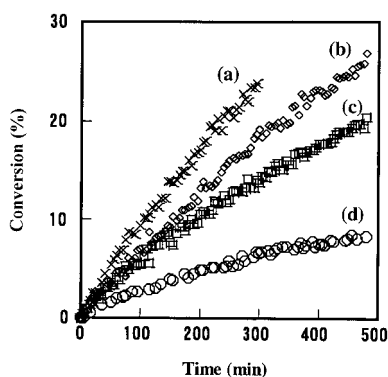

Figure 4 Time–conversion curves in the crosslinking reaction of NBR with DCPO at 120°C in dioxane at different DCPO concentrations. [vinyl group] = 0.408 mol/L and [DCPO] = (a) 8.00×10^{-2}, (b) 6.00×10^{-2}, (c) 4.00×10^{-2}, and (d) 2.00×10^{-2} mol/L.
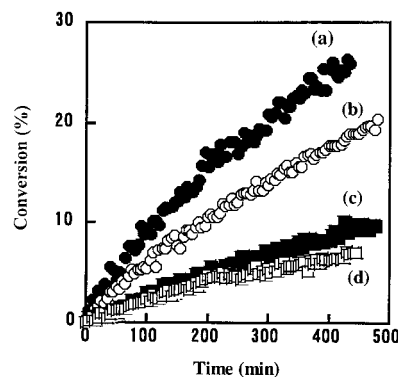

Figure 6 Time–conversion curves in the crosslinking reaction of NBR with DCPO at 120°C in dioxane at different vinyl group concentrations. [DCPO] = 4.00×10^{-2} mol/L and [vinyl group] = (a) 0.204, (b) 0.408, (c) 0.612, and (d) 0.816 mol/L.
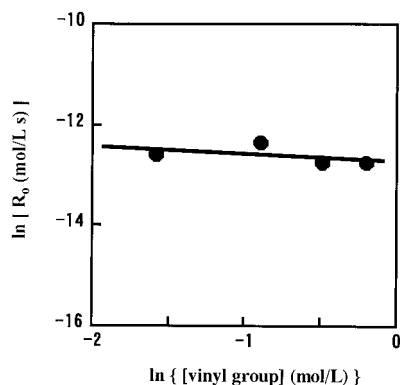
Figure 7 Effect of the vinyl group concentration on R_0 of the vinyl group at 120°C in dioxane.

sated by an increase in the vinyl group concentration used. Figure 7 presents the relation of R_0 to the vinyl group concentration at 120°C. R_0 was proportional to the -0.2nd power of the vinyl group concentration.

From the aforementioned results, R_0 at 120°C was expressed by the following equation:

$$R_0 = k[DCPO]^{0.9} [\text{vinyl group}]^{-0.2} \ (120°C)$$

In the crosslinking reaction of NBR, an intramolecular polymerization process is expected to proceed between the pendant vinyl groups located on the same polymer chain, in addition to the intermolecular reaction. As shown in Scheme 1, the former should lead to the formation of cyclic structures along the polymer chain, whereas the latter should lead to that of crosslinked structures. The formation of crosslinked structures should prevail with increasing NBR concentration. Such crosslinked structures restrict the mobility of unreacted vinyl groups as pendant groups,
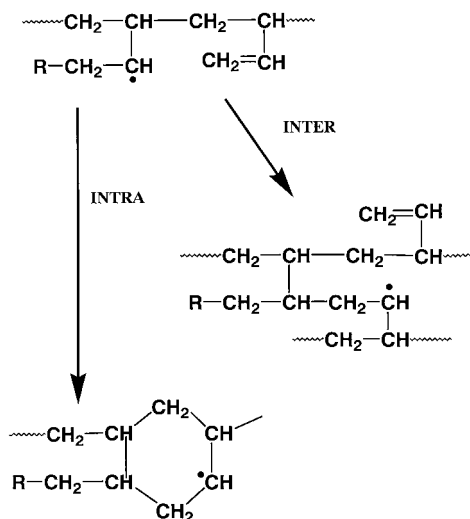
Scheme 1 Intramolecular (INTRA) and intermolecular (INTER) reactions of polymers radicals, where R is polymer chain or fragments from DCPO.
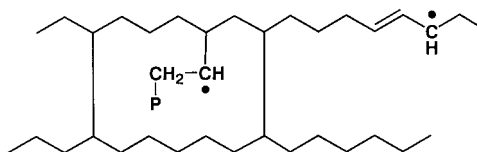
Scheme 2 Unreactive polymer radicals formed during the crosslinking reaction.

leading to a decrease in the reactivity of the vinyl groups. As a result, the reactivity of the vinyl groups decreased with increasing NBR concentration, causing an unusual dependence of R_0 on the vinyl group concentration.

The chain-transfer reactions to polybutadiene were reported to often take place during the crosslinking process, yielding allyl-type polymer radicals (Scheme 2).[1–5] Such allyl radicals are not reactive enough to reinitiate polymerization and lead to unimolecular termination as a result of degradative chain transfer.[12–15] As described later, this reaction system also involved allyl-type radicals. This degradative chain transfer was considered to be responsible for the nearly first-order dependence of R_0 on the DCPO concentration mentioned earlier. The radical polymerization of some allyl monomers involving a degradative chain transfer was reported to show a first-order dependence of the polymerization rate on the initiator concentration.[13]

The polymer radicals formed during the crosslinking reactions may be trapped in the network and be unable to propagate further (Scheme 2); this is also a unimolecular termination. As shown later, however, the accumulation of propagating polymer radicals corresponding to the initiation rate (R_i) was not observed, in the early stage of this reaction system, by ESR.

The reactivity of vinyl groups in NBR was compared with that in NBR18 (17.4% 1,2 structure, 21.7% *cis*-1,4 structure, and 60.9% *trans*-1,4 structure as derived from the butadiene unit) at 120°C, where the DCPO concentration was 4.00×10^{-2} mol/L, as shown in Figure 8. The butadiene monomer unit concentration used here was 2.00 mol/L for both NBR and NBR18. Thus, the vinyl groups of NBR showed a somewhat higher conversion than those of NBR18 with a higher AN content, although the vinyl group concentration (0.408 mol/L) of the NBR reaction system was somewhat higher than that (0.348 mol/L) of the NBR18 system. The presence of AN units might have caused a decrease in the reactivity of the vinyl groups.

ESR study of the crosslinking reaction of NBR with DCPO in dioxane

The reaction of NBR with DCPO was studied in dioxane by ESR. Figure 9 presents the ESR spectral change observed during the reaction of NBR with DCPO at
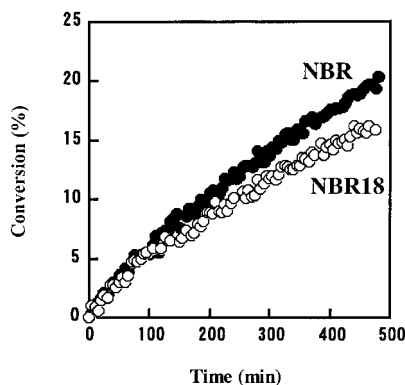
Figure 8 Time–conversion curves in the crosslinking reactions of NBR and NBR18 with DCPO at 120°C in dioxane: [butadiene unit] = 2.00 mol/L and [DCPO] = 4.00×10^{-2} mol/L.

120°C, where the concentrations of DCPO and the vinyl group in NBR were 6.00×10^{-2} and 0.408 mol/L, respectively. Thus, the spectrum intensity increased with time, and the spectrum lines were considerably broadened in the later stage, indicating a restricted motion of the radicals in the crosslinked networks.

Figure 10 shows the time profile of the radical concentration for the same reaction. After an induction period of about 100 min, the radical concentration increased with time and then tended to be saturated. The highest increasing rate of ESR-observable polymer radicals was estimated to be 2.54×10^{-10} mol/L
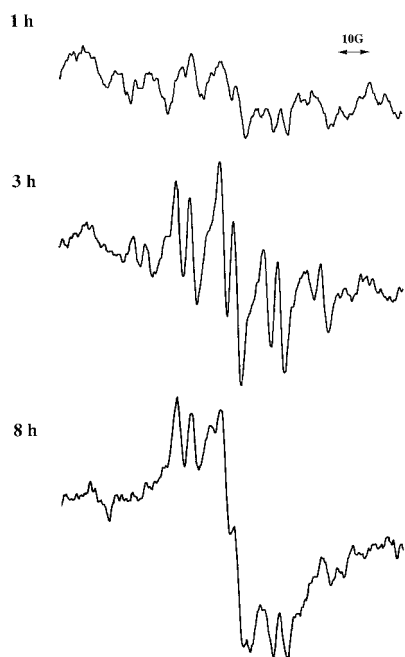

Figure 9 ESR spectral change observed during the crosslinking reaction of NBR with DCPO at 120°C in dioxane: [vinyl group] = 0.408 mol/L and [DCPO] = 6.00×10^{-2} mol/L.
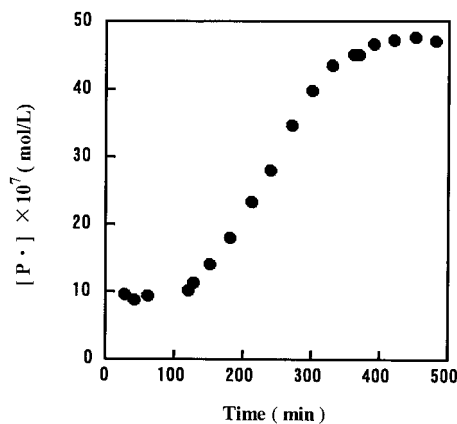

Figure 10 Relationship between time and the polymer radical concentration ([P ·]) observed in the crosslinking reaction of NBR with DCPO at 120°C in dioxane: [vinyl group] = 0.408 mol/L and [DCPO] = 6.00×10^{-2} mol/L.

s from the plot in Figure 10. This was much lower than R_i ($R_i = 2.90 \times 10^{-6}$ mol/L s), which was calculated with the rate constant (k_d; $k_d = 4.83 \times 10^{-5}$ s^{-1})[11] of DCPO decomposition at 120°C and an initiator efficiency (f) of 0.5, where $R_i = 2 k_d f$ [DCPO]. Thus, only about 0.01% of the effective primary radicals were converted into ESR-observable polymer radicals, whereas most of them were deactivated through various reactions.

The observed spectrum was closely similar to the 14-line spectrum of an allyl-type polymer radical (**I**), which was reported to be observed in high-density polyethylene/peroxide systems:[11]

I
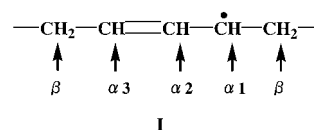
To obtain a well-resolved ESR spectrum, we conducted the reaction of NBR with DCPO of a high concentration (0.50 mol/L) at 120°C in dioxane. The observed spectrum is presented in Figure 11(a). Thus, a 14-line spectrum was clearly observed and showed good agreement with the simulated one [Fig. 11(c)] obtained with the following coupling constants: 6 equivalent hydrogens (β, α_1, and α_2 in polymer radical **I**) of 14.2 G and a hydrogen (α_2 in polymer radical **I**) of 4.3 G. As shown in Figure 11(b), the spectrum of the reaction system disappeared after it was cooled down to room temperature (24°C), indicating that the allyl-type radicals observed at 120°C were fairly short-lived, although they were ESR-observable. Most of them are considered to disappear by coupling reactions, leading to crosslinking.[1,2,5] This conforms with the previous result that the increasing rate of ESR-observable radicals was much lower than R_i.
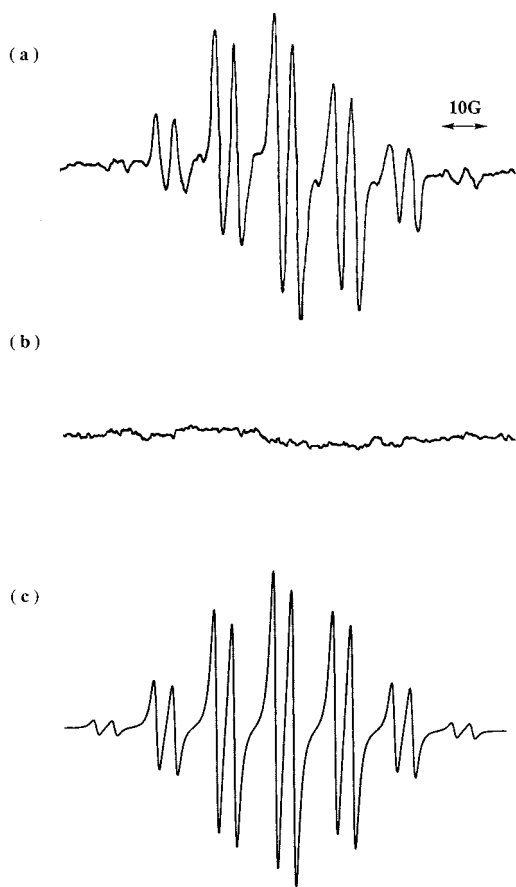
Figure 11 ESR spectra observed for (a) the crosslinking reaction of NBR with DCPO at 120°C in dioxane for 0.8 h, (b) the reaction mixture on being cooled down to 24°C, and (c) the simulated spectrum [vinyl group] = 0.408 mol/L and [DCPO] = 0.50 mol/L.
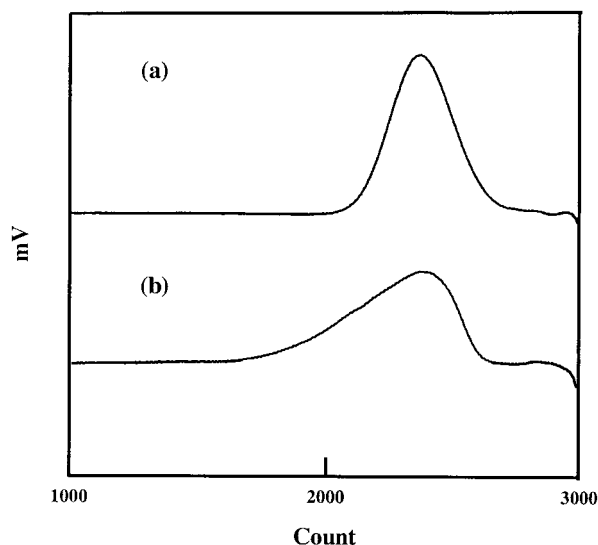

Figure 12 GPC curves of the (a) original NBR and (b) NBR reacted at 110°C for 8 h at a DCPO concentration of 2.00 × 10⁻² mol/L.
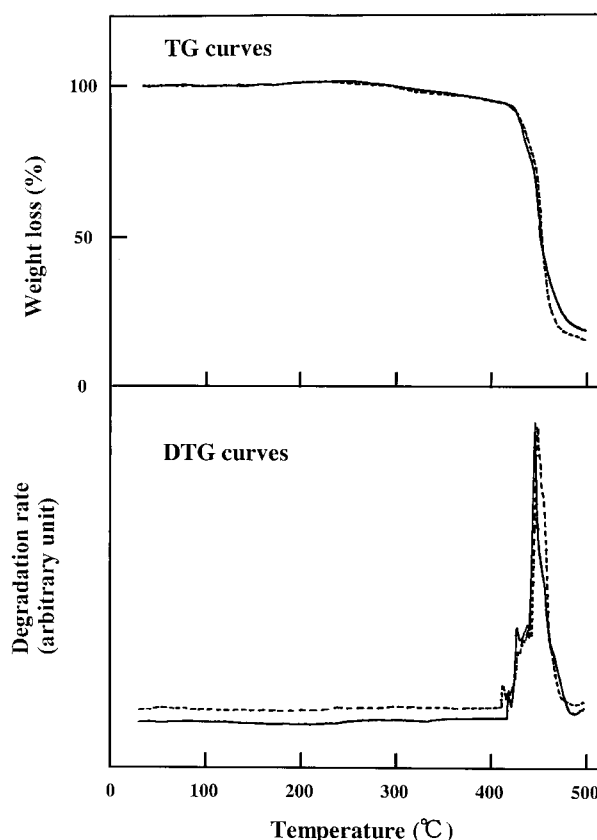

Figure 13 TG and DTG curves of the (—) original NBR and (- - -) NBR reacted 120°C for 8 h at a DCPO concentration of 6.00×10^{-2} mol/L.

Characterization of reacted NBRs

Figure 12 shows the GPC traces of the original NBR [Fig. 12(a)] and NBR reacted at 110°C for 8 h at the DCPO concentration of 2.00×10^{-2} mol/L [conversion of the vinyl group = 4.5%; Fig. 12(b)]. Thus, the reacted NBR ($M_n = 1.2 \times 10^4$ and $M_w/M_n = 5.6$ by GPC) showed a reasonably higher molecular weight and broader molecular-weight distribution than the original ($M_n = 6.0 \times 10^3$ and $M_w/M_n = 2.4$ by GPC). The NBRs reacted at higher temperatures were crosslinked and no longer soluble.

Figure 13 presents the TG and DTG curves of the original NBR and NBR reacted at 120°C for 8 h at a DCPO concentration of 6.00×10^{-2} mol/L (conversion of the vinyl group = 27%). Similar degradation behaviors were observed for both NBRs. The crosslinked NBR showed a maximum degradation rate at a somewhat higher temperature than the original, whereas the residue (22% of the initial polymer weight at 500°C) of the former NBR was rather less than that (25%) of the latter.

Figure 14 shows the DSC curves of the original NBR [Fig. 14(a)] and the NBRs reacted at 120°C for 8 h at DCPO concentrations of 2.00×10^{-2} mol/L [conversion of the vinyl group = 8.3%; Fig. 14(b)] and 6.00
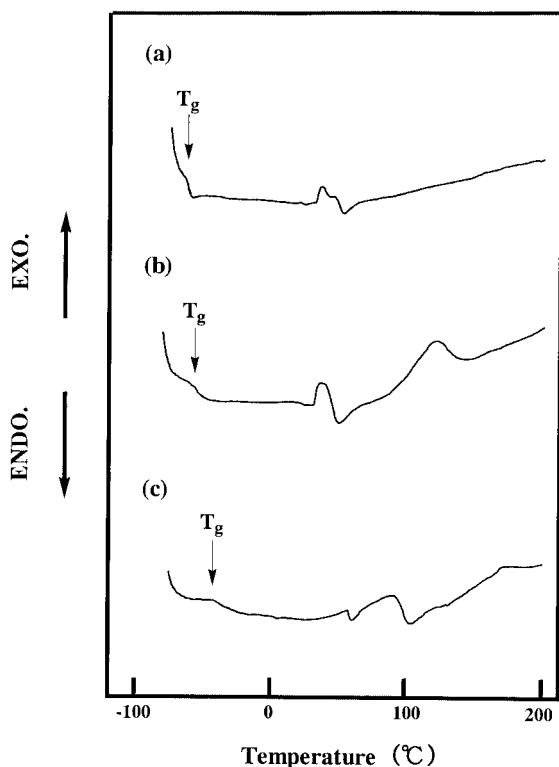
Figure 14 DSC curves of the (a) original NBR and NBRs reacted at 120°C for 8 h at DCPO concentrations of (b) 2.00 $\times 10^{-2}$ mol/L and (c) 6.00 $\times 10^{-2}$ mol/L.

$\times 10^{-2}$ mol/L [conversion of the vinyl group = 27%; Fig. 14(c)]. Thus, the glass-transition temperature (T_g) of NBR gradually increased with the conversion of the vinyl groups (T_g's = -67, -58, and -45°C, respectively).

CONCLUSIONS

The crosslinking reaction of NBR with DCPO was kinetically studied in dioxane. Among the three butadiene units (1,2, cis-1,4, and trans-1,4 units), only the pendant vinyl groups of the 1,2 unit showed an absorption at 6110 cm^{-1} in the FT-NIR spectrum. So, the crosslinking reaction was followed in situ by the mon-

itoring of the disappearance of the pendant vinyl double bond with FT-NIR. R_0 of the vinyl group was expressed by $R_0 = k[\text{DCPO}]^{0.9}[\text{NBR}]^{-0.2}$ (at 120°C). This unusual rate equation resulted from the unimolecular termination due to degradative chain transfer and from the depressed reactivity of the vinyl groups caused by crosslinking. The overall activation energy of the reaction was 20.7 kcal/mol. Allyl-type polymer radicals were observed in the reaction mixture by ESR, the concentration of which increased with time and then was saturated. T_g of the crosslinked NBR was higher than that of the original.

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