# The Study of Polymers by High-Temperature ATR Spectroscopy

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## Synopsis ·

A new high-temperature attenuated total reflectance apparatus (HATR) was constructed and used at different temperatures for making infrared measurements on the same liquid or solid sample. It was found that this method was applicable to the continuous quantitative analysis of changes occurring during chemical reactions such as polymerization, isomerization, and crosslinking. In the bulk polymerization of styrene, the process of monomer consumption could be followed progressively. In the cross-linking reaction of high *cis*-polybutadiene by sulfur-accelerator or peroxide crosslinking systems, the decrease of *cis* content and its partial isomerization to *trans* structure was measured. Furthermore, in the crosslinking reaction of ethylene–propylene terpolymers (EPDM), the consumption of double bonds was observed over the course of the reaction with both sulfur-accelerator and peroxide crosslinking systems. The effect was greatest in the case of methylenenorbornene-type EPDM.

## INTRODUCTION

There have been a number of papers[1-4] on the applications of the attenuated total reflectance (ATR) technique to the quantitative analysis of polymers, but the continuous measurement of ATR spectra at elevated temperatures has not been reported previously. It would be advantageous to make spectral measurements on the same sample either continuously or intermittently. In order to measure the infrared spectra of polymeric materials at elevated temperatures, a high-temperature ATR (HATR) apparatus was constructed and an investigation was made into its practical application to following structural changes during chemical reactions.

With regard to polymerization, Slowinski et al.[5] reported on the measurement up to about 20% conversion in thermal polymerization of styrene using a heated cell, but in the present work the continuous measurement of the bulk polymerization of styrene to higher conversions was examined at various temperatures.

As regards quantitative analysis on changes in microstructure of polybutadiene during crosslinking, results obtained by the ATR method have already been reported,[3] and in this paper continuous measurements using the new HATR apparatus are described.

Moreover, in the crosslinking of ethylene–propylene terpolymer (EPDM) rubbers by either sulfur-accelerator or peroxide system, the consumption of double bonds at vulcanization temperature has been followed progressively. This has been done for EPDM rubbers having low levels of unsaturation of the types provided by the incorporation of different termonomers, namely, dicyclopentadiene, 1,4-hexadiene, and methylenenorbornene.

## EXPERIMENTAL

### Apparatus

A new HATR apparatus for the infrared spectrophotometer JASCO Model IR-G was constructed in cooperation with Japan Spectroscopic Co. Ltd. The apparatus was designed for making measurements on both liquid and solid samples at elevated temperatures in suitable atmospheric conditions. A four-mirror instead of a five-mirror unit was adopted for the optical system, and as a result the reflection efficiency was improved.
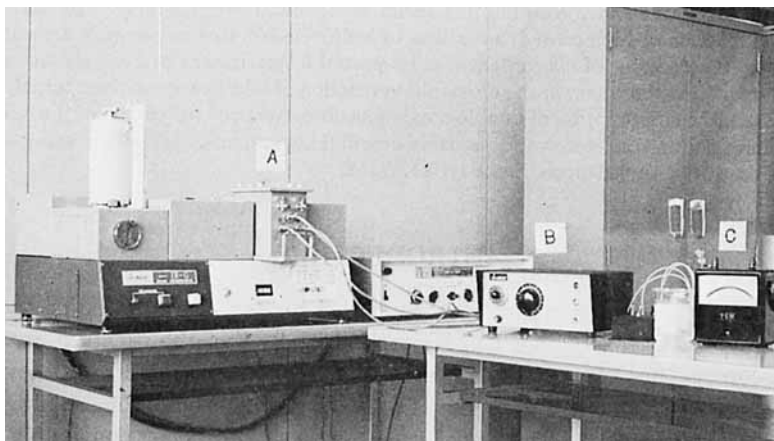


Fig. 1. Infrared spectrometer combined with high-temperature attenuated total reflectance apparatus: (A) HATR apparatus; (B) transformer and thermistor; (C) millivoltmeter.

The HATR apparatus and the infrared spectrometer are shown in Figures 1 and 2; the optical system of the HATR apparatus is shown in Figure 3. Heating of the sample was accomplished by means of four heaters fitted in pairs to each of the two prism holders; the temperature of one prism holder, controlled with a thermistor having an accuracy of about $\pm 1°C$ was recorded by a thermocouple or a thermometer.

The multiple reflection-type prism used as a 5 mm $\times$ 25 mm $\times$ 60 mm solid piece of KRS-5 (mixed crystal of TlBr and TlI) two opposite sides of which were shaped at an angle of 45° as shown in Figure 3.
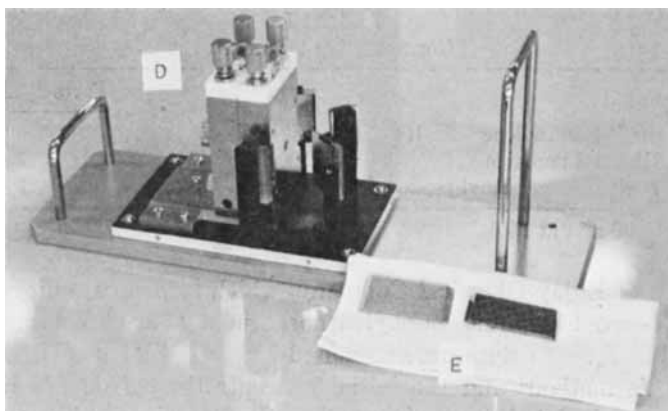
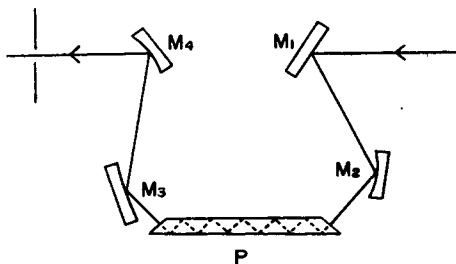Fig. 2. Interior of the HATR apparatus: (D) prism holder; (E) prisms.



Fig. 3. Optical system of the HATR: (M₁) (M₂) (M₃) (M₄) mirrors; (P) prism.

## Sample Preparation

Styrene monomer was distilled under vacuum and mixtures with polystyrene were used to make spectroscopic calibration curves, using *tert*-butylcatechol at a concentration of 10 ppm in order to inhibit polymerization during measurement. Polymerization was carried out using benzoyl peroxide (BPO) as catalyst at a concentration of 1% at 60°, 70°, and 80°C for 4 hr.

BRO1 of Japan Synthetic Rubber Co. Ltd. (97.5% *cis*-1,4; 1.2% *trans*-1,4; 1.3% vinyl) was used as high *cis*-polybutadiene and blended with Diene 35 R of Asahi Chemical Industry Co. Ltd. (35% *cis*-1,4; 57.5% *trans*-1,4; 7.5% vinyl) as low *cis*-polybutadiene for making spectroscopic calibrations in terms of *cis*, *trans*, and vinyl concentrations. For quantitative analyses of microstructure of polybutadiene, extinction coefficients reported by Morero et al.[6,7] were used. The compounding recipe is given in Table I. Curing conditions were 90 min at 150°C. N,N'-Di-β-naphthyl-p-phenylenediamine (Nocrac White) was included as an antioxidant.

The samples of EPDM used in this survey were Royalene 305 of Uniroyal, Inc., Nordel 1070 of E. I. du Pont de Nemours & Co., Inc., and Enjay

TABLE I
Compounding Formula[a]

|  | Parts by weight |
|---|---|
| cis-Polybutadiene (BRO1) | 100 |
| Dicumyl peroxide | 2 |
| N,N'-Di-β-naphthyl-p-phenylenediamine | 1 |

[a] Curing:   90 min at 150°C.

EPT 3509 of Enjay Chemical Company, which incorporate dicyclopenta-
diene, 1,4-hexadiene, and methylenenorbornene as third monomer, re-
spectively.   Iodine values were measured for each EPDM by Rosenmund-
Kuhnhenn's method[8] and the initial concentration of double bonds in-
volved was calculated for each sample.   Spectroscopic calibrations were
made using blends of EPDM and saturated ethylene–propylene copolymer
(EPM) (Dutral N of Montecatini Edison S.p.A.), but in the case of the
1,4-hexadiene-type EPDM, brominated Nordel 1070 was used instead of
EPM.   Compounding recipes and reaction conditions are given in Table II.
Enjay 3509 was cured at 140° and 150°C, and Royalene 305 and Nordel
1070 at 140°C by both sulfur-accelerator and peroxide crosslinking sys-
tems.

TABLE II
Compounding Formulae[a]

|  | Parts by weight | |
|---|---|---|
|  | Sulfur cure | Peroxide cure |
| EPDM | 100 | 100 |
| Zinc oxide | 5 | 5 |
| Stearic acid | 1 | 1 |
| Sulfur | 1.3 | — |
| Tetramethylthiuram disulfide | 1.1 | — |
| 2-Mercaptobenzothiazole | 0.5 | — |
| Dicumyl peroxide | — | 2.7 |
| Total | 108.9 | 108.7 |

[a] Curing:   90 min at 140° and 150°C.

## Measurement

Sometimes absorption positions and the intensities of infrared spectra
change with temperature.   In the present study, absorption positions did
not change, but absorption intensities decreased by from 10% to 50%
at elevated temperatures compared with those measured at room tempera-
ture.   Furthermore, as the refractive indices of both the total reflection
prism and the samples changed with the temperature, calibrations were
carried out at the corresponding reaction temperatures, using suitable
inhibitors so that reaction would be prevented.

With liquid samples, such as styrene monomer, a liquid cell with a bis-
muth or lead amalgam spacer was made on only one side of the multi-

reflectance prism. In the case of rubber samples, compounded rubbers were dissolved or dispersed in suitable solvents and coated evenly to be about 50 $\mu$ in thickness on both sides of the prism after evaporation of the solvents. Satisfactory spectra were obtained by the film-coating technique because the method optimized optical contact with the ATR prism surface.

Measurements were started after samples were set in the HATR apparatus and heated to the reaction temperature. The heating rate used was 24°C/min, and about 5 min were required to attain a temperature of 150°C. Reaction times were calculated from the time the sample reached the chosen reaction temperature.

The HATR apparatus was placed in the sample beam and the reference beam was suitably attenuated. The angle of incidence was fixed at 45°. When the band intensity was weak, 5× ordinate scale expansion was used to increase the observed intensity and thereby minimize calculation errors.

### Correction for Compounding Ingredients

Absorptions due to compounding ingredients were calculated or measured and, where necessary, corrections were made in the measured intensities of the analytical bands used for the polymer analyses.

## RESULTS AND DISCUSSION

### Bulk Polymerization of Styrene

ATR spectra of styrene monomer and polymer are shown in Figure 4. Characteristic absorption bands due to the vinyl group of the monomer were found at 910, 990, and 1630 cm$^{-1}$, and the 990 cm$^{-1}$ band was used for the polymer analyses. Calibration curves were made using various blends of polymer and monomer, from which the concentration of monomer during polymerization was derived. It was confirmed that polymerization did not proceed during the calibration measurements when styrene monomer with inhibitor was subjected to a temperature of 80°C for about 15 min.

The progressive change of conversion with time in bulk polymerization of styrene with 1% BPO at three different temperatures is shown in Figure 5. The temperature dependence of the polymerization rate may be seen distinctly. Polymerization proceeded to more than 40% conversion in 4 hr at 80°C.

### Crosslinking of Polybutadiene

Although it was problematical that extinction coefficients might change with the temperature, Bishop's work[9] indicated that measurements of microstructure obtained at room temperature and at elevated temperature were equal within experimental error. As results given by the ATR
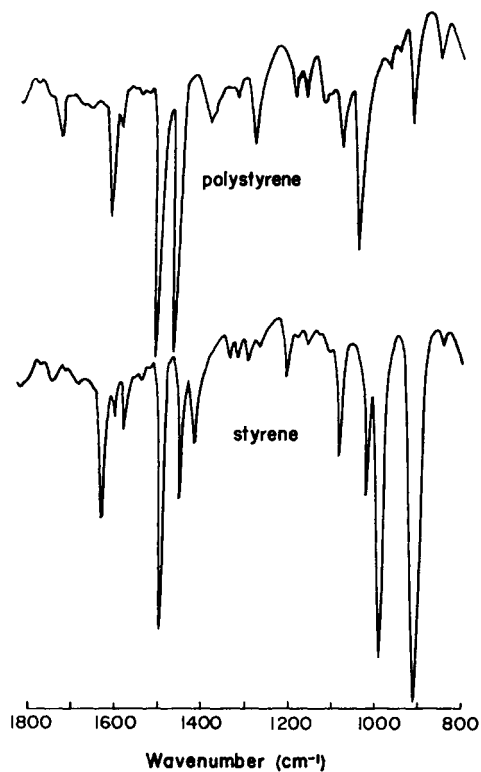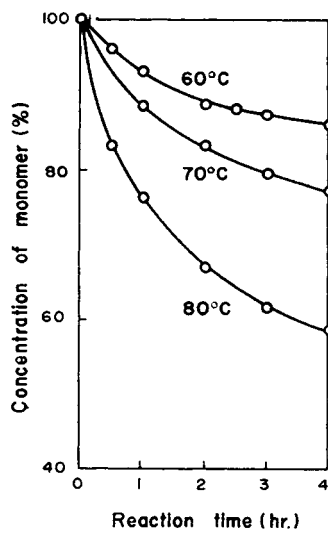
Fig. 4. ATR spectra of polystyrene and styrene.



Fig. 5. Change in concentration of monomer during polymerization of styrene.

method are relative, calibration curves were obtained by comparing the value from the HATR method with that from the well-known solution transmission method.   As a result, linear plots were obtained between HATR values and solution transmission values for *cis*, *trans*, and vinyl structures.

Changes of microstructure during crosslinking by sulfur-accelerator or peroxide crosslinking system are presented in Figure 6.   *Cis-trans* isomerization occurred in both crosslinking systems.   In the peroxide system, the *cis* content decreases more than in the sulfur system, but the increase in *trans* content was smaller.   The vinyl content was constant throughout crosslinking in both systems.

## Crosslinking of EPDM

EPDM has the characteristic absorption bands due to double bonds in termonomer units, as shown in Figures 7 and 8.   The structure of the termonomers in EPDM and the absorption bands used for their quantitative analyses are shown in Table III.   As these bands could not be observed in EPM and as they were removed on bromination, they are considered to be caused by the double bonds of the termonomer units.

With regard to the dicyclopentadiene-type EPDM, quantitative analysis of double bonds has been reported[10] using the absorption band at 3045 cm$^{-1}$; and in the case of the 1,4-hexadiene-type, a study has been made[11] regarding the consumption of double bonds during crosslinking by infrared analysis but the key bands used was not indicated.   Therefore, calibration curves of double bond concentration were made and the suitability of the HATR method for quantiative analysis was investigated.   Calibrations were obtained by making blends of EPDM with EPM.   As the absorption band at
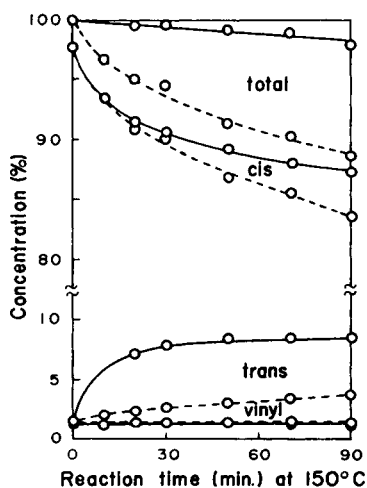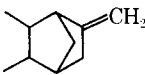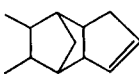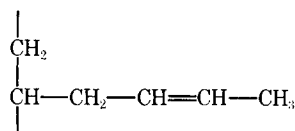


Fig. 6. Change in microstructure during crosslinking of polybutadiene:   (————) sulfur cure;   (– – –) peroxide cure.

TABLE III
Termonomer Structure in EPDM and Key Band

| | EPDM | | |
| --- | --- | --- | --- |
| | Enjay EPT 3509 | Royalene 305 | Nordel 1070 |
| Termonomer | methylene-norbornene | dicyclo-pentadiene | 1,4-hexadiene |
| Structure | | | $CH_2$<br>$CH$—$CH_2$—$CH$=$CH$—$CH_3$ |
| Key band | 870 cm$^{-1}$ | 3045 cm$^{-1}$ | 966 cm$^{-1}$ |

966 cm$^{-1}$ observed in the case of Nordel 1070 overlapped a band due to the propylene units, a brominated sample was used instead of EPM and the calibration curve was obtained from two plots. It was found that each calibration curve was a straight-line plot of double bond concentration with blend ratio, confirming that quantitative analysis for double bond concentration was possible.

As it is important for quantitative measurements that optical contact of the sample with the prism surface should not change during the crosslinking reaction, an investigation into this point was made first of all. Since it was considered that the methyl group (having an absorption band at 1380 cm$^{-1}$) was less sensitive to chemical changes than other groups,[12] EPDM was compounded with ingredients having no methyl group and the absorbance at 1380 cm$^{-1}$ was monitored during the course of the crosslinking reaction. It was found that the absorbance indicated a constant value, confirming that optical content was held constant during the reaction.
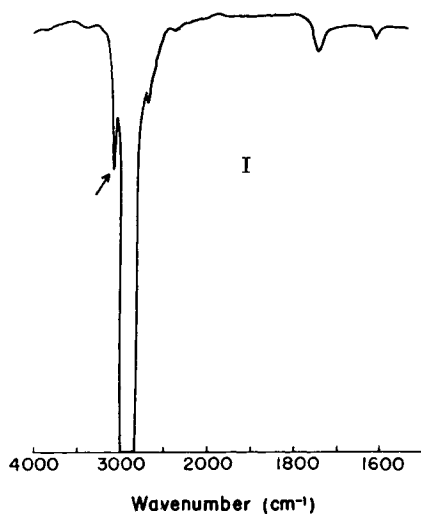
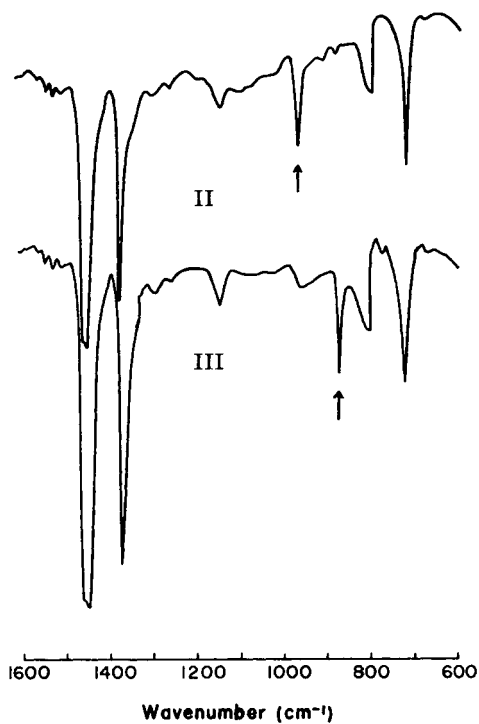Fig. 7. ATR spectrum of Royalene 305.

Fig. 8. ATR spectra of Nordel 1070 (II) and Enjay 3509 (III).

The results of changes of double bond concentration in each EPDM during crosslinking are shown in Figures 9–16.

In the case of Royalene 305, 15% of the double bonds are consumed by sulfur in 100 min, while as much as 40% are consumed by peroxide in the same time, as shown in Figure 9.
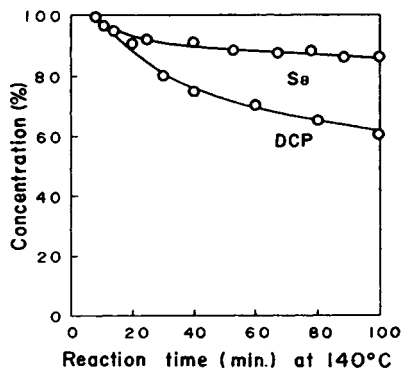


Fig. 9. Change in concentration of double bonds in Royalene 305 during crosslinking at 140°C: $S_8$ = sulfur; DCP = dicumyl peroxide.
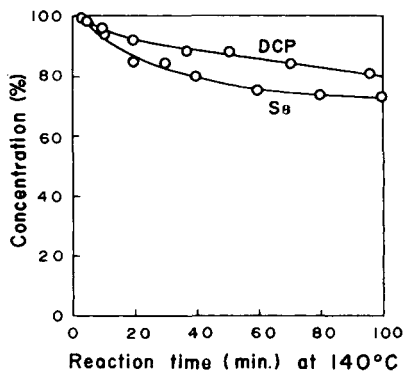
Fig. 10. Change in concentration of double bonds in Nordel 1070 during crosslinking at 140°C:   DCP = dicumyl peroxide;   $S_8$ = sulfur.
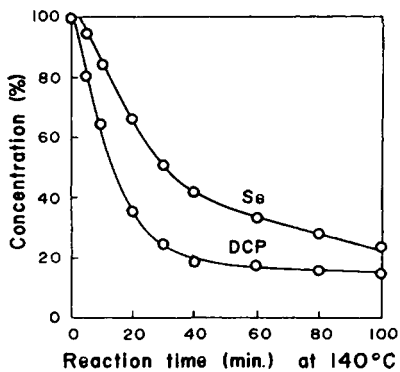


Fig. 11. Change in concentration of double bonds in Enjay 3509 during crosslinking at 140°C:   $S_8$ = sulfur;   DCP = dicumyl peroxide.
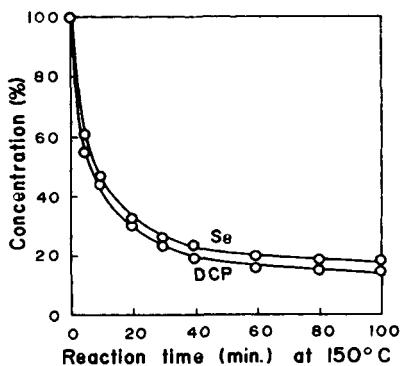


Fig. 12. Change in concentration of double bonds in Enjay 3509 during crosslinking at 150°C:   $S_8$ = sulfur;   DCP-dicumyl peroxide.
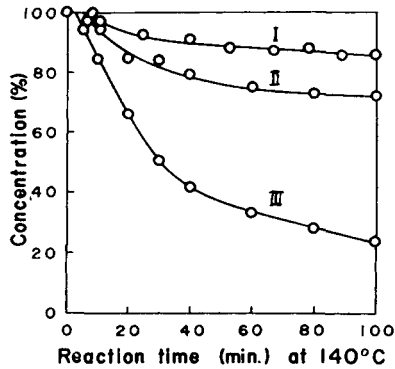
Fig. 13. Change in concentration of double bonds of EPDM in sulfur crosslinking system: (I) Royalene 305; (II) Nordel 1070; (III) Enjay 3509.
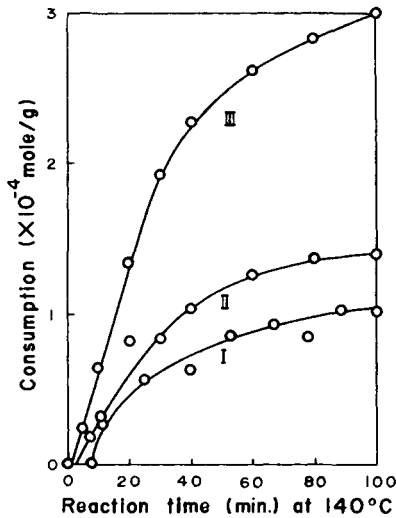


Fig. 14. Change in consumption of double bonds of EPDM in sulfur crosslinking system: (I) Royalene 305; (II) Nordel 1070; (III) Enjay 3509.

In the case of Nordel 1070, double bonds are consumed more in the sulfur system than in the peroxide system, as shown in Figure 10.

In the case of Enjay 3509, the amount of double bonds reacted during crosslinking with peroxide is higher than that with sulfur at 140°C, but in both crosslinking systems double bonds are consumed rapidly in the initial stage of reaction. The rate of decrease at 150°C becomes higher than that at 140°C in both systems and there is little difference between the sulfur and peroxide systems, especially at 150°C.

The rate of decrease of double bonds in the three kinds of EPDM by sulfur curing are given in Figures 13 and 14. The rate of decrease is in the order: Enjay 3509 > Nordel 1070 > Royalene 305, as illustrated in Figure 14. Enjay 3509 exhibits the highest consumption of double bonds.
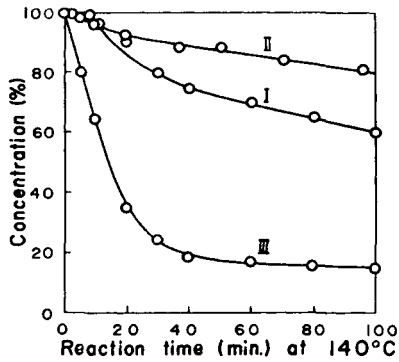
Fig. 15. Change in concentration of double bonds of EPDM in peroxide crosslinking
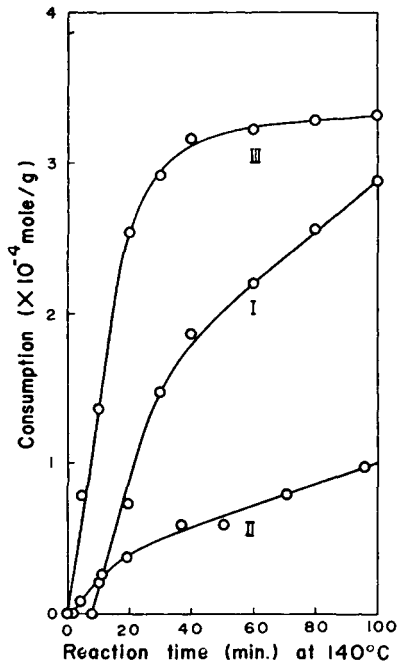system: (I) Royalene 305; (II) Nordel 1070; (III) Enjay 3509.



Fig. 16. Change in consumption of double bonds of EPDM in peroxide crosslinking
system: (I) Royalene 305; (II) Nordel 1070; (III) Enjay 3509.

Consumption of double bonds by peroxide is shown in Figures 15 and 16.
The rate of decrease of double bonds in the three kinds of EPDM using
peroxide crosslinking system is in the order: Enjay 3509 > Royalene 305
> Nordel 1070, as given in Figure 16.

Infrared spectra of all of the samples crosslinked in 100 min were mea-
sured by a transmission method and decreased amounts of double bonds

were found. The results showed that the values calculated from the HATR method and from the transmission method were almost the same. Although it was thought that carbonyl groups might be generated owing to the oxidation in the air during crosslinking, absorption of carbonyl groups at 1720 cm$^{-1}$ was found neither in polybutadiene nor in EPDM.

## DISCUSSION OF HATR APPARATUS

It was found possible to follow the progress of a chemical reaction quantitatively by means of high-temperature multiple reflection-type ATR equipment. The method appears to give results as good as those obtained by the conventional infrared transmission method. With the multireflection-type ATR, it was found that loss of radiation was minimized by fixing the angle of incidence at 45°, and then excellent spectra could be obtained, particularly in measuring a component present at low concentration such as termonomer in EPDM.

With regard to the long-term thermal stability and mechanical properties of the prism, further experience is still needed. As KRS-5 is a rather soft material, it was feared that the prism might be softened and its mechanical stability impaired at higher temperatures. Although there was no problem involved in the use of liquid samples at temperatures below the boiling point or with thin rubber sheets in the experiments, it was noticed that the prism was strained when samples of large volume were used. In fact, deformation of the prism could be observed when rubber samples of 5 mm thickness were heated to about 140°C. It is believed that the application of HATR to infrared analysis could be extended if the prism material were mechanically harder and thermally more stable.

## CONCLUSION

The general usefulness of the high-temperature attenuated total reflectance apparatus in the quantitative analysis of structural changes during chemical reactions has been demonstrated. The main advantage of this technique is to be found in making successive measurements on the same liquid or solid sample at an elevated temperature. In the bulk polymerization of styrene, the temperature dependence of the reaction rate was demonstrated spectroscopically. In the crosslinking reaction of cis-polybutadiene by sulfur-accelerator or peroxide crosslinking systems, the process of cis-trans isomerization was followed quantitatively. In the crosslinking reaction of EPDM by the above systems, the decrease of unsaturation was observed over the course of the reaction. The different reactivities of the three samples of EPDM were demonstrated and the effects of the different crosslinking systems were compared.

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