Simultaneons Measurements of Stress Relaxation and Infrared Dichroic Change of Vulcanized Natural Rubber*

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An instrument for simultaneous measurements of stress and infrared dichroism as the time-dependent behavior of polymer films was constructed by using a double beam infrared spectrometer, and was applied to the study of the stress relaxation of vulcanized natural rubber. The sample film held between clamps of a stretching device was placed just in front of the entrance slit of the spectrometer, where the sample and reference beams came alternately. Two polarizers were used, one in the sample beam and the other in the reference beams, so that the sample and reference beams were polarized to have the electric vectors parallel and perpendicular to the stretching direction of the sample, respectively. This arrangement made possible direct measurements of the difference in the transmittance of the two beams at the same part of the film, and increased the precision of measurements of infrared dichroism. Then, setting the spectrometer at one of the wavenumbers of absorption band maxima, we could record continuously and precisely the change in the dichroism during the stress relaxation. From these records, the orientation functions of transition moments with respect to the stretching direction were calculated. The stress was recorded by means of a couple of strain gages pasted on the cantilever beam of the stretching device. The results of this study suggested that the stress relaxation observed for vulcanized natural rubber was ascribed mainly to the orientation in the amorphous region rather than to that in the crystalline region, the latter being complete almost immediately after elongation.

1. INTRODUCTION

The molecular orientation in polymer films caused by the deformation has been studied by means of various optical techniques, such as the birefringence, light scattering, X-ray diffraction, and infrared dichroism. Among these, the infrared dichroism is one of the most useful methods for this purpose, since it provides valuable informations not only on the orientations of both the crystalline and the amorphous regions but also on the motion of very small and specific parts of molecular chains, instead of the average motion of very large parts. Experimental and theoretical details of this technique have already been discussed by Zbinden[1]. In the ordinary method one usually measures the absorbance by using the polarized infrared beams with the electric vector directed first in parallel and then perpendicularly to the stretching direction of the sample in two separate experiments, and then determines the dichroic ratio and the ori-

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entation function of the transition moment with respect to the stretching direction. This method has been applied almost exclusively to studies in the static state, and papers dealing with the process of the deformation have been very limited in number. Recently, Onogi et al.[2,3] measured the change in dichroic ratios of characteristic absorption bands of polyethylene films while they were being elongated, and discussed the mechanism of the elongation.

Since, however, this method had the disadvantage that the infrared dichroism could not be determined very accurately, especially at low degrees of orientation, Marrinan (quoted by Stein[4]) and Tink (quoted by Zbinden[1]) showed a method of making much more precise measurements of dichroism by using a double beam infrared spectrometer. In this method the sample and reference beams were polarized to have electric vectors parallel and perpendicular to the stretching direction of the sample, respectively, and were thrown alternately on the sample which was placed in front of the entrance slit of the spectrometer. With this arrangement the recorder measures the intensity ratio of the two beams transmitted through the sample, from which one could calculate the difference between the parallel and perpendicular absorbances of the sample.

The method for precise measurements of dichroism was also discussed by Stein[4]. He described a somewhat different optical arrangement using a single beam spectrometer with a rotating polarizer synchronized with the chopper frequency. These two methods have the advantages that the difference between the parallel and perpendicular absorbances at the same part of a film can be obtained directly in one experiment, and that the precision of measurements of dichroism increases by over a hundred-hold. However, very few investigations have been made as yet by using these techniques. Recently, LeGrand[5] presented preliminary data obtained in creep and relaxation experiments for polymer films using a similar technique to that devised by Marrinan and Tink. In this technique, however, a long sample was placed in the sampling area of a double beam spectrometer, and the sample and reference beams (perpendicularly polarized with each other) were thrown on the two parts of the sample. Then transmittances of the two beams were compared at different parts of the sample ; for the purpose of the present experiments this is evidently not an appropriate procedure.

In this study an instrument was constructed to allow simultaneous measurements of stress and infrared dichroism of polymer films by using a double beam infrared spectrmeter, and was applied to the study of the stress relaxation of vulcanized natural rubber. The optical arrangement adopted here was essentially the same as that proposed by Marrinan and Tink. The results give informations on molecular orientations in the crystalline and amorphous regions during the relaxation process of natural rubber.

2. EXPERIMENTAL

Sample and its Ordinary Infrared Spectra

The samples used were commercial films of vulcanized natural rubber having thickness of $50 \pm 5 \mu$ and density of 0.920. Polarized infrared studies of these films showed no evidence of orientation having occurred during the manufacture. When samples were stretched several-hold, there appeared a high infrared dichroism, especially for six absorption bands observed at 1664, 1448, 1380, 1361, 1129, and 844 cm^{-1} by the ordinary method, as shown in Fig. 1. The dichroism of these bands and their tentative assignments determined by referring to the studies by Saunders and Smith⁶⁾, Sutherland and Jones⁷⁾, and Binder⁸⁾ are summerized in Table 1, together with the characteristic behavior of the bands on crystallization which takes place either by cooling to about $-20°C^{9,10)}$ or by stretching. It is apparent from this table that the perpendicular band at 844 cm^{-1} is a crystalline band and the rest come from the amorphous region in the sample.

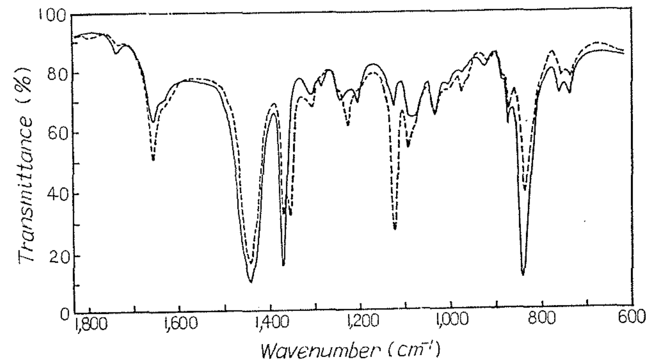

Fig. 1. Polarized infrared spectra of stretched natural rubber.
——, Electric vector perpendicular to elongation.
------, Electric vector parallel to elongation.

Table 1. Infrared absorption bands which give rise to high dichroism on the elongation of vulcanized natural rubber.

Wavenumber (cm^{-1})	Dichroism	Assignment	Effect of crystallization
1664	//	C=C stretching	No change
1448	⊥	CH_3 asym. deformation, CH_2 scissoring	No change
1380	⊥	CH_3 sym. deformation	No change
1361	//	CH_2 wagging	No change
1129	//	CH_3 rocking (in-plane)	Slight increase in intensity
844	⊥	CH deformation (out-of-plane)	Increase in intensity (Crystalline band*)

* In the amorphous state, a band is observed at 835 cm^{-1}. With the increase of crystallinity, it shifts to 844 cm^{-1} and its intensity increases.

Apparatus and Experimental Procedure

The schematic diagram of the apparatus is shown in Fig. 2. The principal part of the apparatus is a Hitachi Model EPI-S2 double beam infrared spectrometer equipped with a rock salt prism. The sample film held between clamps of a stretching device is placed just in front of the entrance slit of the spectrometer,

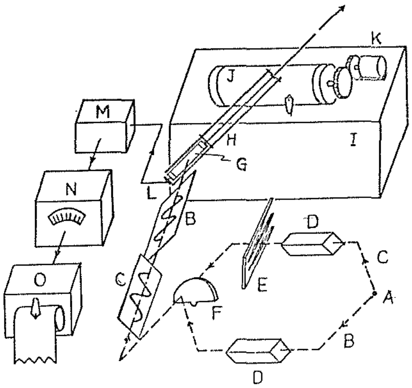

Fig. 2. Schematic diagram of the apparatus.
A, Light source; B, Sample beam; C, Reference beam; D, Polarizer; E, Attenuator; F, Sector mirror; G, Sample; H, Stretching device; I, Monochromator; J, Dichroism recorder; K, Chart drive motor; L, Strain gage; M, Bridge head; N, Strain meter; O, Stress recorder.

where the sample and reference beams* come alternately at a period corresponding to the chopping frequency (10 c.p.s.) of the rotating sector mirror. Two polarizers made of silver chloride plates are used: one is placed in the sample beam and the other in the reference beam, so that the sample and reference beams are polarized to have the electric vectors parallel and perpendicular to the stretching direction of the sample, respectively. If the sample is not dichroic, the two beams transmitted through the sample is of identical intensity and hence no signal is recorded by the spectrometer. However, if the sample is dichroic, there arises the difference in the transmittance between the two beams and hence the spectrometer records the intensity ratio of the two beams transmitted through the sample. As will be shown later, this quantity depends upon the difference between the parallel and perpendicular absorbances of the sample, and therefore is a direct measure of the dichroism of the sample. Then, by setting the spectrometer at one of the wavenumbers of the absorption band maxima, one can record continuously the change in its dichroism during mechanical treatments which give rise to the molecular orientation in the sample. This method has the advantages that the difference between the parallel and perpendicular absorbances at the same part** of the film can directly be obtained, and that, as pointed out by Marrinan[4] and Tink[1], the precision of measurements of dichroism increases by over a hundred-hold as compared with that obtained by the ordinary method.

To eliminate the effect of the polarization characteristics of the monochromator on measurements, the stretching direction of the sample is rotated about the axis of the beam to make an angle of 45° with the entrance slit. Corres-

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* In this technique, the sample and reference beams are not used in their literal meanings, but we still stick to the routine nomenclature.

** The effective area is 12 mm long (the slit height) and between 0.25 and 1.10 mm wide [depending upon the mechanical slit witdth (see Table 2)].

pondingly, each of the two polarizers is also rotated, so that the electric vectors of the sample and reference beams make angles of 45° with the entrance slit in each side, the former being parallel to the stretching direction.

The response of the pen-wedge system of the spectrometer is dependent upon the intensity of the beam incident on the detector. Since in this experiment the beam intensity is reduced by various causes, such as the absorption by the sample and the reflection by the polarizers, this loss in energy must be compensated by properly opening the slits and increasing the amplifier gain.

In this study changes in the infrared dichroism of natural rubber were measured at each constant wavenumber of all the absoption band maxima shown in Table 1, except for the 1448 cm^{-1} band; the absorption of this band was so strong that the energy loss could not be compensated by the above-mentioned method. Table 2 shows the mechanical slit widths adopted for measuring the dichroism of the five absorption bands. The optical slit widths corresponding to these values were about 6 cm^{-1} for all the five absorption bands.

Table 2. Mechanical slit widths used for measuring the change in the infrared dichroism.

Wavenumber (cm^{-1})	Slit width (mm)
1664	0.25
1380	0.32
1361	0.30
1129	0.45
844	1.10

The films were cut into rectangular pieces 28 mm wide and 52 mm long, and were marked with inked lines 10 mm apart. They were held between two clamps with margins of 6 mm, and were rapidly stretched to various elongations less than 600% by manually pulling up a connecting rod attached to the upper clamp. An elongation stop served to fix the degree of elongation of the sample. By tightening a set screw the elongation was held constant during the simultaneous measurements of stress relaxation and infrared dichroic change. The per cent elongation was determined by measuring the final separation of the inked lines.

The stress in the sample was transformed to an electric signal by means of a couple of strain gages pasted on each surface of a cantilever beam which was attached to the lower clamp. The electric signal thus obtained was amplified and fed to a recorder (Toa Electronics Model EPR-2T) to give a trace proportional to stress versus time. The chart speed of this recorder can be changed from 20 mm/hr to 180 mm/min in six steps, and the time required for the pen to travel full scale is less than 0.3 sec.

The experiments were carried out in a room kept at constant temperature (25±0.6°C) and constant humidity (43±1%). By operating in this room, shielding the cantilever beam from air drafts, and keeping the strain meter at an approximately constant temperature by operating its amplifier continuously, the external temperature effects on stress measurements could be reduced to a suitable level.

The thickness of films was measured by using a bench thickness gage. Masurements could be reproduced to $\pm 2\mu$.

3. THEORETICAL CONSIDERATIONS FOR INFRARED DICHROISM AND ORIENTATION FUNCTION

When the sample and the two polarizers are arranged as described above, the intensities I_S and I_R of the sample and reference beams transmitted through the sample are given by

$$\left.\begin{aligned} I_S &= I_P \cdot 10^{-A_{n//}}, \\ I_R &= I_P \cdot 10^{-A_{n\perp}}, \end{aligned}\right\} \tag{1}$$

where I_P is the intensity of the polarized beam emerging from the polarizer, and $A_{n//}$ and $A_{n\perp}$ are the parallel and perpendicular absorbances of the $n\%$ elongated sample, respectively. Then, the quantity T recorded on the spectrometer is given by

$$T = \frac{I_S}{I_R} = 10^{-(A_{n//} - A_{n\perp})}, \tag{2}$$

from which one obtains

$$\log\frac{1}{T} = A_{n//} - A_{n\perp}. \tag{3}$$

This will be called the dichroic difference*.

In the case of uniaxial orientation**, the absorbance A_0 of the unoriented sample is generally expressed as

$$\frac{3A_0}{d_0} = \frac{1}{d_n}(A_{n//} + 2A_{n\perp}), \tag{4}$$

where d_0 and d_n are the thicknesses of unstretched and $n\%$ stretched samples, respectively. From equations (3) and (4) we obtain

$$A_{n//} = A_0\frac{d_n}{d_0} + \frac{2}{3}\log\frac{1}{T}. \tag{5}$$

If θ is the angle between the directions of stretching and the transition moment of the vibrational absorption band, we have

$$A_{n//} = 3A_0\frac{d_n}{d_0}\overline{\cos^2\theta} \tag{6}$$

On the other hand, the orientation function[11~15] F of the transition moment with respect to the stretching direction is defined as

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* Tink[1] called this quantity the dichroic coefficient. However, we prefer the term "dichroic difference", since the quantity $A_{n//}/A_{n\perp}$ is usually called the "dichroic ratio".

** The polarized infrared spectra obtained by the tilting method showed that the molecules of natural rubber were uniaxially oriented in the elongated sample.

$$F=\frac{1}{2}(3\overline{\cos^2\theta}-1). \tag{7}$$

From equations (5), (6), and (7) we finally obtain

$$F=\frac{1}{3A_0}\frac{d_0}{d_n}\log\frac{1}{T}. \tag{8}$$

Therefore, if the values of A_0, d_0, and d_n are given, the changes in the orientation function during mechanical treatments can be obtained by measuring the quantity T as a function of time.

As described above, A_0 is independent of the molecular orientation, but, for the absorption bands which are sensitive to the crystallinity, it depends upon the crystallinitly. Therefore, when the orientation functions are calculated for crystalline bands by using equation (8), it is necessary to correct the values for the change in A_0. On the other hand, measurements of the change in A_0 are very useful in the discussion of the mechanism of the deformation, as they give informations concerning the change in the crystallinity. Since A_0 is given by equation (4), it is proper to determine A_0 by the following manner; one first measures $A_{n\perp}$ by the usual method, and then adds $3A_{n\perp}$ to $\log\frac{1}{T}=A_{n//}-A_{n\perp}$ obtained by the above-mentioned method.

4. RESULTS AND DISCUSSION

Differential Polarized Infrared Spectra

If the elongated sample and the two polarizers are arranged as described above and the quantity T given by equation (2) is recorded against the wavenumber, we obtain a new type of infrared spectrum shown by the solid line in Fig. 3. This will be called the *differential polarized infrared spectrum*. The broken line in this figure represents the same type of spectrum obtained for unstretched sample, giving nearly a straight line. Its small, gradual deviation from the

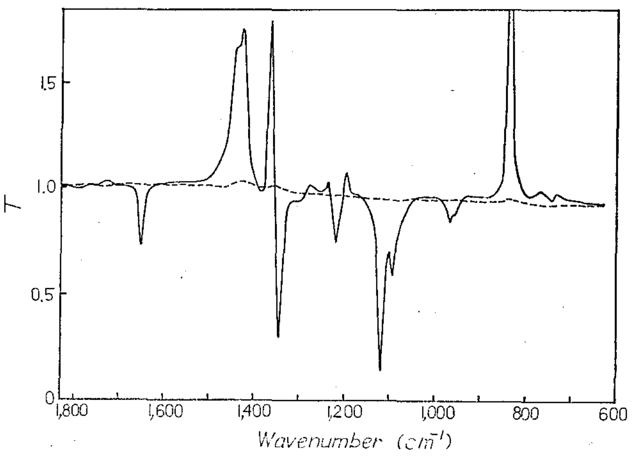

Fig. 3. Differential polarized infrared spectra of stretched. (——) and unstretched (------) natural rubbers.

straight line of $T=1$ may be mainly due to the incompleteness of matching of the two polarizers used. From the comparison between the ordinary (Fig. 1) and the differential polarized infrared spectra (Fig. 3), it is obvious that the parallel bands in the former always appear as the downward peaks in the latter, whereas the perpendicular bands as the upward peaks, as expected from equation (2).

Stress Relaxation and Infrared Dichroic Change

As described above, simultaneous measurements of stress relaxation and infrared dichroic change on natural rubber were made at various elongations less than 600% and at the fixed wavenumbers of the five absorption band maxima at 1664, 1380, 1361, 1129, and 844 cm^{-1}. Fig. 4 is a sketch of the recorder traces

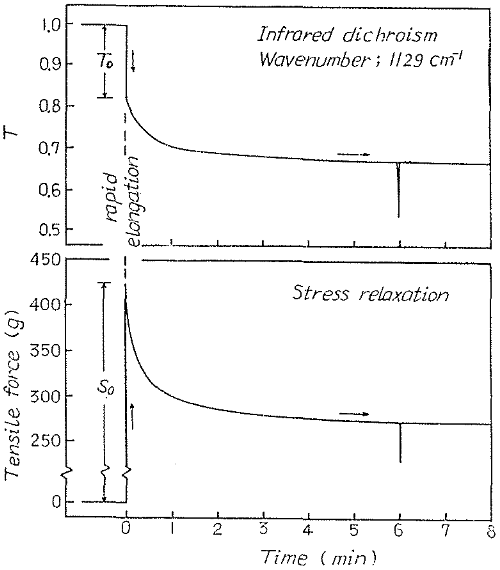

Fig. 4. Sketch of typical traces obtained from simultaneous measurements of stress and infrared dichroism during the stress relaxation at 400% elongation of vulcanized natural rubber. Downward spikes in both traces were recorded in order to confirm the quick response of the two recorders.

obtained from the typical stress relaxation experiment carried out at 400% elongation. When the sample is not stretched, straight lines are obtained by both the dichroism and stress recorders, which serve as bases for subsequent data. When the sample is rapidly stretched and then held at a constant elongation, the pen of the dichroism recorder instantly goes up or down by T_0 from the initial position of the unstretched sample, depending upon the perpendicular or parallel dichroism of the absorption bands, and then gradually moves in the same direction attaining to a constant value. At the same time, the tensile force increases instantly by S_0 and then gradually decreases to an equilibrium value. In Fig. 5, the ratios S/S_0 at six different degrees of elongation are plotted against time. Apparently the stress relaxation is at its maximum at 400% elongation. In order to compare these results with changes in the orientation functions of transition moments, the instantaneous orientation functions F_0 for the five absorption bands

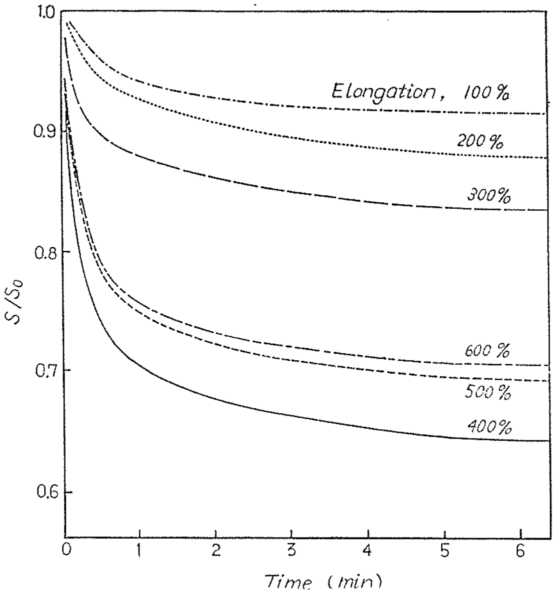

Fig. 5. Stress relaxation of vulcanized natural rubber at 25°C.

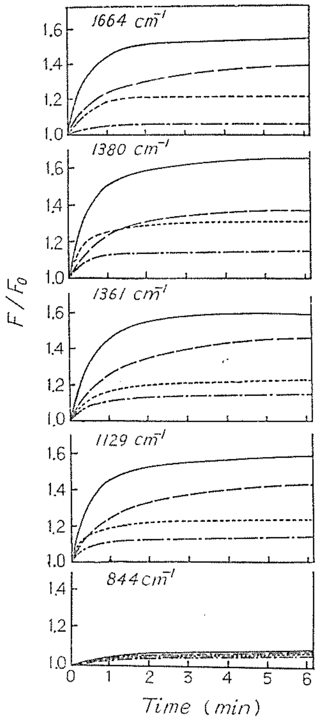

Fig. 6. Time dependence of F/F_0 for the five absorption bands of vulcanized natural rubber.
Elongation ; — —, 300% ; ——, 400% ; ······, 500%; —·—, 600%.

are calculated from T_0 by using equation (8), and the ratios F/F_0 are plotted against time in Fig. 6. In this calculation, d_n is assumed to be constant during the relaxation process of the sample. For the crystalline bands at 844 cm^{-1} the correction for crystallinity change is made by using the results obtained for A_0, which will be shown later. As expected from the recorder traces for infrared dichroism, the ratios F/F_0 increase gradually to constant values, which depend upon the degrees of elongation. Furthermore, it is apparent that for all the absorption bands the ratios F/F_0 also have their maximum values at 400% elongation. There is therefore a close correspondence between the stress relaxation and the molecular orientation. The maxima of 400% elongation observed for both the S/S_0 and F/F_0 ratios are considered to be related to the appearance of crystalline phase due to elongation, if we take into account the fact that the crystallization in natural rubber starts to occur at 400% elongation at room temperature[16].

The comparison of F/F_0 time curves for the five absorption bands shows that the ratios F/F_0 at respective degrees of elongation increase with time in apparoximately the same way for all amorphous bands at 1664, 1380, 1361, and 1129 cm^{-1}, and that for the crystalline band at 844 cm^{-1} the increase of the ratios is much smaller than that for the amorphous bands. These results suggest that in the crystalline region the orientation is complete almost immediately after elongation, while in the amorphous region the molecular chains are oriented gradually during the stress relaxation. The fact that changes in the ratios F/F_0 for the amorphous bands have more or less the same tendency as those in the ratios S/S_0 suggests that the stress relaxation observed here is ascribed mainly to the orientation in the amorphous region rather than to the orientation in the crystalline region.

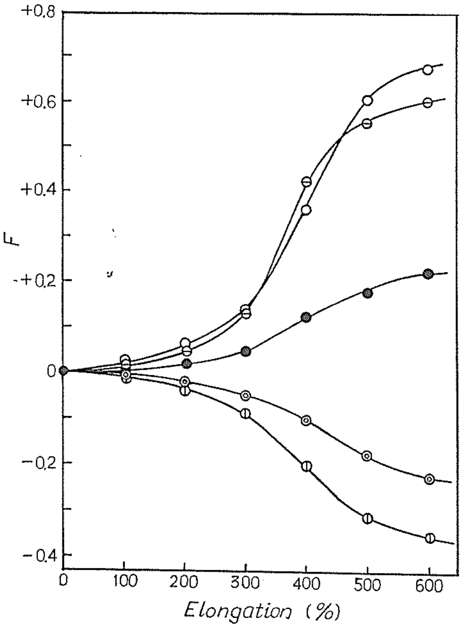

Fig. 7. Variation of the equilibrium orientation functions for the five absorption bands of vulcanized natural rubber with per cent elongation. ●, 1664cm^{-1}; ◎, 1380cm^{-1}; ⊖, 1361cm^{-1}; ○, 1129cm^{-1}; ⦶, 844cm^{-1}.

In Fig. 7 the equilibrium values of orientation functions (obtained at six minutes after elongation) for the five absorption bands are plotted against the degree of elongation. It is apparent that for all the absorption bands the orientation functions change markedly at about 400% elongation, and seem to attain to constant values at about 600% elongation.

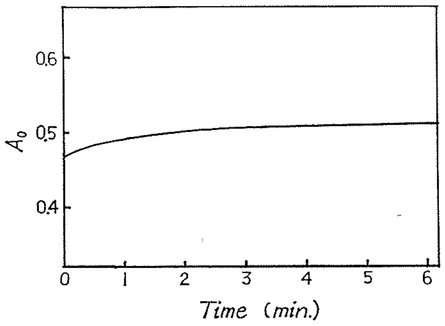

Fig. 8. Variation of A_0 for the 844cm^{-1} band during the relaxation process.

Change in Crystallinity during the Relaxation

Changes in A_0 during the relaxation were measured for the five absorption bands at 1664, 1380, 1361, 1129, and 844 cm^{-1} by using the method described at the last part of chapter 3. A slight increase of A_0 was found only for the 844 cm^{-1} band (crystalline band) as shown in Fig. 8. This suggests that the degree of crystallinity in natural rubber is slightly increased during the relaxation. The correction for this was made on the calculation of the orientation function of this band, as described above.

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