

# Simultaneous Measurements of Stress and Infrared Dichroism of Inflated Polyethylene Films

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*Received August 8, 1966*

The change of stress and infrared dichroism of inflated polyethylene films during elongation and stress relaxation were measured simultaneously. Infrared dichroisms were recorded by means of the differential method reported previously. A remarkable decrease in absorbance at  $730\text{ cm}^{-1}$  and a very small change in specific gravity during elongation were interpreted as the result of degradation of the crystallites into smaller ones by stretching, total crystal content remaining almost constant. It was found that the instantaneously stretched films showed stress relaxation and gradual recrystallization after rapid degradation. Orientations of crystalline polymer during elongation and relaxation were discussed by using orientation functions.

## INTRODUCTION

In the previous paper<sup>1)</sup> Gotoh, Takenaka and Hayama reported the simultaneous measurements of stress relaxation and dichroic change of vulcanized natural rubber obtained by means of differential polarized infrared spectra. This differential method is characterized by the following points: (1) the dichroic difference, instead of the dichroic ratio, can directly be recorded by a single operation with respect to a limited portion of a specimen; (2) the resolving power and sensitivity to the dichroic change are much higher than the ordinary method; and (3) the time dependent behavior of polymer molecules can be recorded with respect to each characteristic absorption frequency.

In this paper, the change of stress and infrared dichroism of inflated polyethylene films, during elongation or stress relaxation, are measured simultaneously by the method mentioned above, and the changes in the orientation and crystalline state of polymers are discussed.

## EXPERIMENTALS

The apparatus for measurements of differential polarized infrared spectra is the same as that shown in the previous paper.<sup>1)</sup> Commercial inflated films of polyethylene (Sumikathene) were used; the density was  $0.920\text{ (g./cc.)}$  and the effective size was  $0.03\text{ mm. thick}$ ,  $28\text{ mm. wide}$  and  $40\text{ mm. long}$ .

Rectangular specimenes were cut so as to make the long sides of them parallel to the mechanical stretching direction in the inflation process. The speci-

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mens were placed in front of the entrance slit, being inclined at the angle of 45° to the slit, and stretched in this direction. Mechanical slit widths used for measuring dichroisms are shown in Table 1.

Table 1. Mechanical slit widths for measuring dichroisms.

Wave length cm. <sup>-1</sup>	Continuous elongation mm.	Stress relaxation mm.
730	0.90	1.13
720	0.96	1.25

### THEORETICAL

In the case of the natural rubber reported previously,<sup>1)</sup> the unstretched specimens exhibited no preferential orientation. Here, we could define the absorbance  $A_0$  of non-oriented specimen by the relation ;

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

where  $d_0$  and  $d_n$  are the thicknesses of the specimens unstretched and  $n\%$  stretched, and  $A_{n//}$  and  $A_{n\perp}$  are the parallel and perpendicular absorbances of  $n\%$  stretched specimens, respectively.

Since the unstretched films of inflated polyethylene have been known to exhibit preferential orientation parallel to the mechanical direction, we can not obtain  $A_0$  directly. Now, we define  $A_n$  as the absorbance of the specimen which is stretched by  $n\%$  but has no orientation, the crystallinity and thickness being the same as that of actual specimens  $n\%$  stretched. Then, we have instead of Eq. (1),

$$3A_n = A_{n//} + 2A_{n\perp} \quad (2)$$

Accordingly, the orientation function  $F$  with respect to the stretching direction is given by

$$F = \frac{1}{3A_n} \log \frac{1}{T}, \quad (2,3) \quad (3)$$

when  $T$  is the quantity recorded on the infrared spectrophotometer and is related to the dichroic difference by the relation,<sup>1)</sup>

$$\log \frac{1}{T} = A_{n//} - A_{n\perp} \quad (4)$$

Thus, from Eqs. (3) and (4) we obtain the orientation function  $F$  if we have  $A_n$ . Since from Eqs. (2) and (4) we have

$$3A_n = A_{n//} + 2A_{n\perp} = \log \frac{1}{T} + 3A_{n\perp}, \quad (5)$$

$A_n$  can be obtained by measuring  $T$  and  $A_{n\perp}$  separately.

### RESULTS AND DISCUSSION

#### 1. Polarized Infrared Spectra of the Inflated Films

Figs. 1 and 2 show the polarized infrared spectra of a commercial inflated

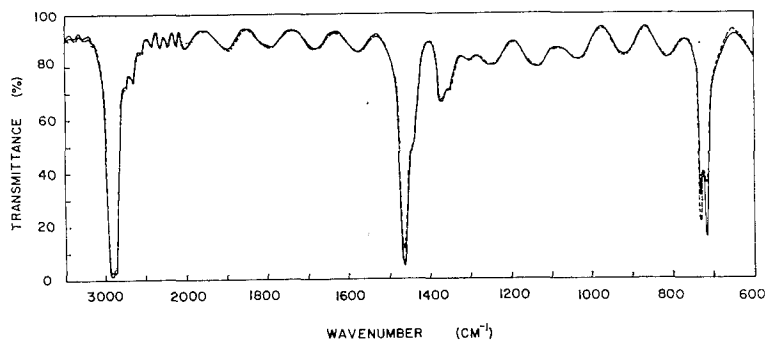


Fig. 1. Ordinary polarized infrared spectra of an inflated polyethylene film (unstretched).

— electric vector perpendicular to elongation  
 .....electric vector parallel to elongation

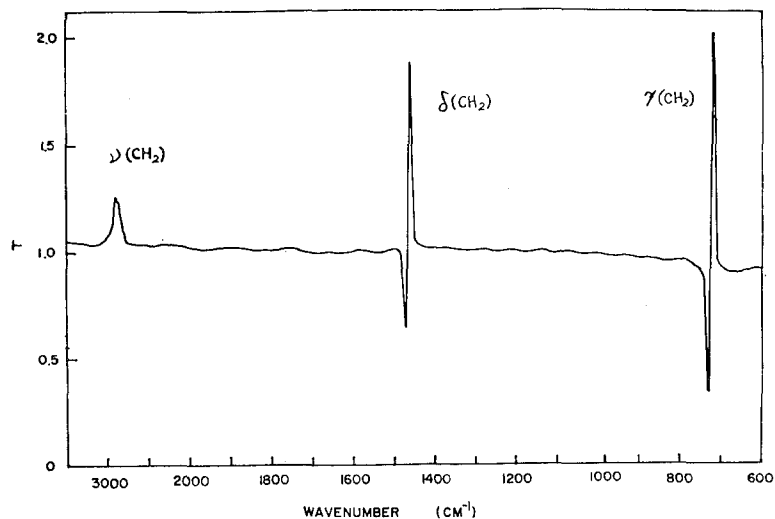


Fig. 2. Differential polarized infrared spectrum of an inflated polyethylene film (unstretched).

Table 2. Polarized infrared spectra of the inflated polyethylen (unstretched).

Wave number cm. <sup>-1</sup>		Dichroism	Assignment
Amorphous	Crystalline		
2900	(2900)	(⊥)	CH stretching
1460	1470 1460	// ⊥	CH <sub>2</sub> scissoring
720	730 720	// ⊥	CH <sub>2</sub> rocking

polyethylene film; the former was obtained by the ordinary method and the latter by the differential one, respectively. Both exhibit the preferential orientation of polymers which took place during the inflation process. The assignments and

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dichroisms of the absorption bands of the unstretched polyethylene films are shown in Table 2. The absorption at *ca.* 2900  $\text{cm}^{-1}$  is very strong, and hence the transmittance through the specimen is too weak to resolve the differential spectrum. A thinner specimen is preferable for more accurate measurements of this band.

While, in the ordinary method,  $\text{CH}_2$  scissoring absorption at *ca.* 1460  $\text{cm}^{-1}$  appears to be a singlet, it splits into a distinct doublet in the differential method; one exhibits the parallel polarization and the other the perpendicular one.

It has been known that the doublet near 725  $\text{cm}^{-1}$  corresponds to the rocking motion of  $\text{CH}_2$  groups and only the lower component at 720  $\text{cm}^{-1}$  exists in the melt, whereas another component at 730  $\text{cm}^{-1}$  appears only after crystallization.<sup>4)</sup> According to the interpretation by Keller and Sandeman<sup>6)</sup> as well as by Stein and Sutherland<sup>5)</sup>, the vibration which occurs at 720  $\text{cm}^{-1}$  in amorphous polymers is splitted into a doublet in crystalline polymer because of the interaction between neighboring groups in crystals. Further, from X-ray diffraction and polarized infrared spectra of the single crystal of hydrocarbon  $\text{C}_{36}\text{H}_{74}$ , Krimm *et al.*<sup>7,8)</sup> concluded that directions of transition moments associated with the bands at 730 and 720  $\text{cm}^{-1}$  are parallel to the a- and b-axes of the crystal, respectively.

In accordance with these interpretations, both results in Figs. 2 and 3 show that the inflated film of polyethylene exhibits a preferential orientation of the crystal, the a-axis being parallel and the b-axis perpendicular to the mechanical direction.

Fig. 3 shows enlarged figures of differential polarized spectra of unstretched and 150 % stretched specimens. It should be noticed that the parallel polarization at 730  $\text{cm}^{-1}$  is inverted to the perpendicular one by a large stretching.

In Fig. 1, interference patterns are exhibited between the regions 800-1300 $\text{cm}^{-1}$  and 1500-2500 $\text{cm}^{-1}$ . From these patterns the thickness of the films stretched by various elongations were calculated, assuming that the specimen has a constant

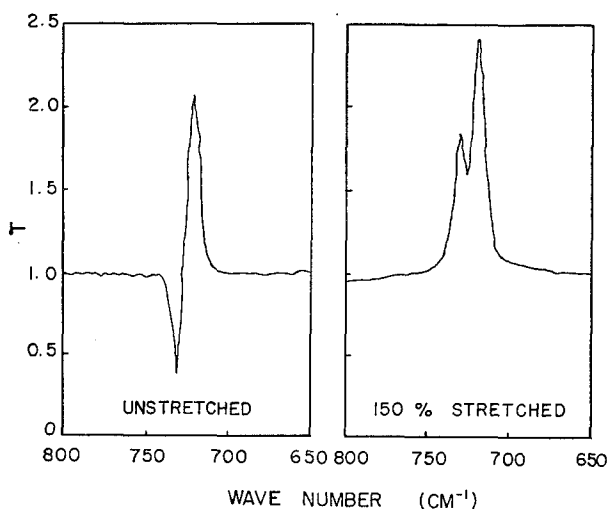


Fig. 3. Differential infrared dichroism of an inflated polyethylene (unstretched and stretched).

refractive index, 1.52, during deformation.

In Fig. 4 the relative thickness of the stretched specimens,  $d_n/d_0$ , are plotted against elongation ratios,  $d_n$  being the thickness of the stretched, and  $d_0$  that of

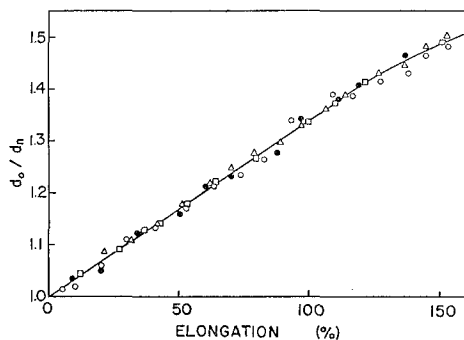


Fig. 4. Relative thickness of stretched films.

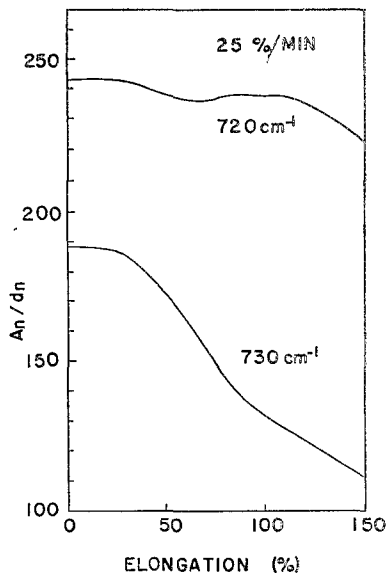


Fig. 5. Change in specific absorbance during elongation.

unstretched specimen. Variations of the film thickness during elongation were obtained by this curve.

## 2. Change in Crystallinity during Stretching

The specimens were stretched continuously at a constant rate, 25 %/min. Fig. 5 shows the change of the specific absorbance\*,  $A_n/d_n$ , during elongation of the specimen with respect to the absorption bands at 720  $\text{cm}^{-1}$  and 730  $\text{cm}^{-1}$ , respectively.

Since, as mentioned in the previous section, the 730  $\text{cm}^{-1}$  band is interpreted to arise from the interaction between rocking modes on neighboring groups in the polyethylene crystals, the large change of  $A_n/d_n$  for the elongation higher than 25% suggests that there occurs some variation in the crystallinity or size of crystallites during elongation. Krimm and Tobolsky<sup>9)</sup> showed a case by means of the X-ray diffraction in which the average crystallite size of polyethylene was reduced by stretching. On the other hand, we could not find any significant change in density until 100% elongation as shown in Fig. 6, using a density gradient tube method; in other words, the total crystal content does not depend significantly on the deformation of the specimen.

Accordingly, it may be reasonable to conclude that the decrease of  $A_n/d_n$  during elongation mainly corresponds to the degradation in size of crystallites of

\* Absorbance per cm.

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polyethylene, total crystal content remaining almost constant as was suggested by Rugg *et al.*<sup>10)</sup> Further, we must take into consideration the possibility of degradation of crystals by unfolding of polymers during deformation as Onogi *et al.* suggested.<sup>11)</sup>

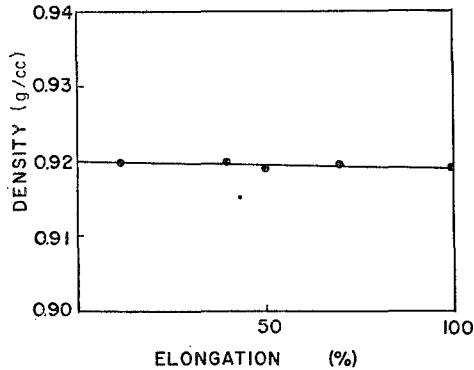


Fig. 6. Change in densities of elongated films.

Figs. 7 and 8 show the stress-strain curve and the change of orientation functions with respect to the 720  $\text{cm}^{-1}$  and 730  $\text{cm}^{-1}$  bands during elongation of the film at a constant rate. These results are almost similar in quality to those reported by Onogi *et al.*,<sup>11)</sup> although some difference can be found quantitatively.

It is seen in Fig. 8 as well as in Figs. 1 and 2 that the a- and b- axes of the crystallites in the unstretched specimen appears to exhibit orientations parallel and perpendicular to the mechanical direction, respectively. From the results shown by Figs. 3, 5, 6, and 8, the decrease in the orientation function of the 730

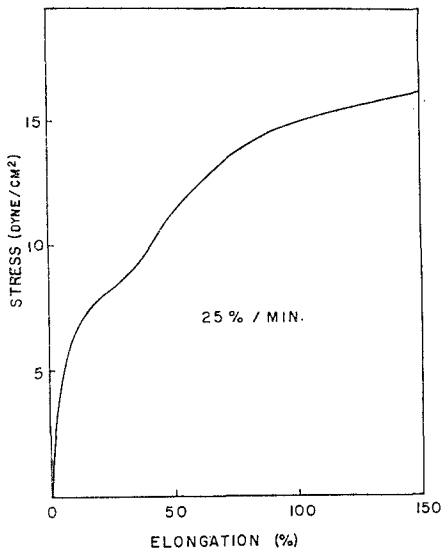


Fig. 7. Stress-strain curve of a polyethylene film.

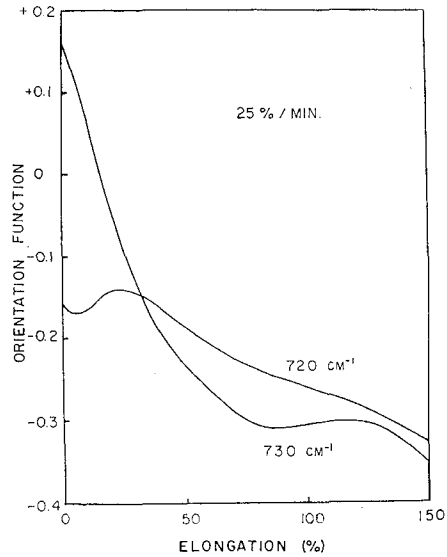


Fig. 8. Change in the orientation function of a polyethylene film during elongation.

$\text{cm}^{-1}$  band and inversion from the positive to the negative side during stretching are interpreted tentatively as that crystallites are degraded into smaller ones and rotated in the direction to which unfolding of the polymer crystallites occurs easily as illustrated by Figs. 9 (a) and (b) so that the *a*- and *b*-axes may have

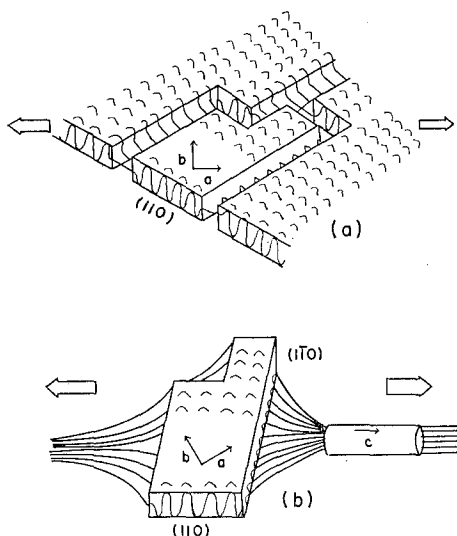


Fig. 9. Models of degradation and orientation of stretched polyethylene crystallites.

components perpendicular to the direction of stretching. Hirai *et al.* suggested this possibility with respect to single crystals of polyethylene by means of electronmicroscopy.<sup>12)</sup>

#### 4. Stress Relaxation

After the specimen was manually stretched instantaneously, the stress relaxation and the dichroic change were recorded simultaneously at two fixed elongations, *i. e.* 50% and 100%. Fig. 10 shows the relative stress relaxation,  $S/S_0$ , plotted against time, where  $S$  and  $S_0$  are the relaxed and instantaneous stress, respectively. The relative relaxations for 50% and 100% elongations show similar trends. In Fig. 11 the change in orientation function during relaxation for two kinds of stretching is plotted against time with respect to the  $720\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$

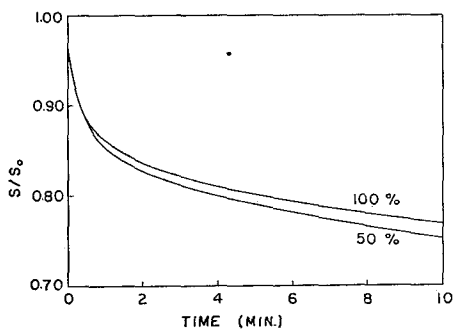


Fig. 10. Stress relaxation of a stretched polyethylene film.

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bands. Although very small, distinct variations are detected. Furthermore, the directions of the variation of orientation functions of  $730\text{ cm}^{-1}$  are opposite to each other for 50% and 100% stretching.

From these results, the orientation of  $730\text{ cm}^{-1}$  band or the a-axis of the

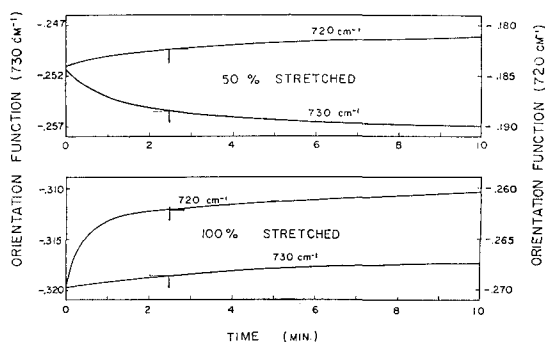


Fig. 11. Change in orientation function during stress relaxation.

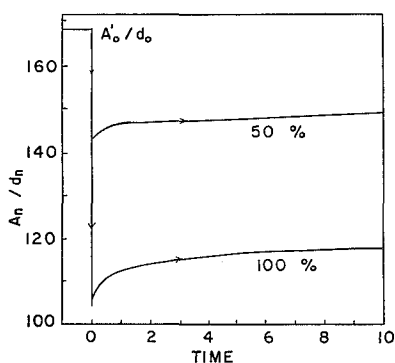


Fig. 12. Change in crystallinity during stress relaxation.

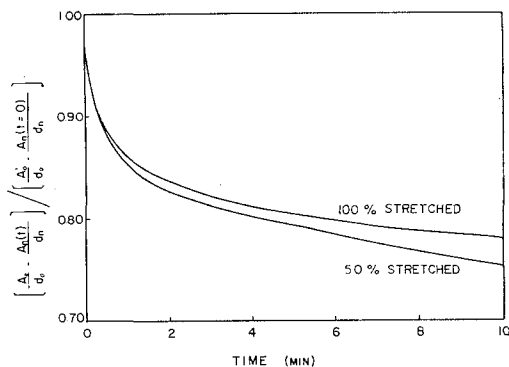


Fig. 13. Recovery of crystallinity during stress relaxation.

crystals may be ascribed to that of degraded crystallites for 50% stretched specimen and to that of unfolded and recrystallized polymers for 100% stretched one as illustrated in Fig. 9 (b).

Fig. 12 shows the change in  $A_n/d_n$  during relaxation, which means degradation of crystals by the instantaneous stretching and the recrystallization during relaxation, both of which are more remarkable for the larger stretching.

In Fig. 13 the recovery of crystallinity,

$$\frac{[A'_0/d_0 - A_n(t)/d_n]}{[A'_0/d_0 - A_n(t=0)/d_n]},$$

is expressed as a function of time, where  $A'_0$  is the absorbance for unstretched specimens. Comparing Fig. 13 with Fig. 10, there seems to be some parallel relations between stress relaxation and recrystallization, although it is difficult to give further discussion since the rheology of large deformation is concerned in this work.



ACKNOWLEDGMENTS

This work has been supported by the Scientific Research Encouragement Grant from the Ministry of Education to which the authors' thanks are due.

REFERENCES

- (1) R. Gotoh, T. Takenaka and N. Hayama, *Kolloid-Z. u. Z. Polymere*, **205**, 18 (1965); *Bull. Inst. Chem. Res., Kyoto Univ.* **43**, 369 (1965).
- (2) R. S. Stein and F. H. Norris, *J. Polymer Sci.*, **21**, 381 (1956).
- (3) R. S. Stein, *ibid.* **31**, 327 (1958).
- (4) G. B. B. M. Sutherland and N. Sheppard, *Nature*, **159**, 793 (1947),
- (5) R. S. Stein and G. B. B. M. Sutherland, *J. Chem. Phys.*, **21**, 370 (1953),
- (6) A. Keller and I. Sandeman, *J. Polymer Sci.*, **15**, 133 (1955).
- (7) S. Krimm, *J. Chem. Phys.*, **22**, 567 (1954).
- (8) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).
- (9) S. Krimm and A. V. Tobolsky, *J. Polymer Sci.*, **7**, 57 (1951).
- (10) F. M. Rugg, J. J. Smith and T. V. Atkinson, *J. Polymer Sci.*, **9**, 579 (1952).
- (11) S. Onogi, T. Asada, M. Hirai and K. Kameyama, *Zairyo*, **14**, 322 (1965).
- (12) N. Hirai, H. Kiso and T. Yasui, *J. Polym. Sci.*, **61**, No. 171 S-1 (1962).