

7. Cragg, L. H., and H. van Oene, *Can. J. Chem.*, **39**, 203 (1961).

8. Schulken, R. M., and M. L. Sparks, *J. Polymer Sci.*, **26**, 227 (1957).

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On the Crystal Transformation of Poly [3,3-(bis-chloromethyl) oxacyclobutane]

The crystalline structure of poly [3,3-(bis-chloromethyl)-oxacyclobutane] was investigated by Sandiford.¹ According to his study, two crystal forms, α and β , are found in the polymer: The α form results when the polymer is annealed through its molten state, whereas the quenched amorphous polymer crystallizes into the β -form when its temperature is raised above the glass transition temperature.

Sandiford gave the unit cell dimensions of the β form (monoclinic) as $a = 6.85$, $b = 11.42$, and $c = 4.75$ Å, and $\beta = 109^\circ 48'$. However, he did not refer to the dimensions of the α form. Recently Hatano and Kambara² investigated the crystal forms of the polymer with x-ray diffractometry and found the crystallizing behavior to be the same as that reported by Sandiford. However, the phenomena of the transformations between the α and β forms have never been examined.

In the present work, the crystallizing behavior and the transformation of crystal forms of this polymer were studied with x-ray diffractometry and infrared spectroscopy. X-ray diffraction curves of the α and β forms are shown in Figure 1 as A and B respectively. Film sample A was prepared by annealing at 160°C . for 3 hr. through its molten state, and then slow cooling to 120°C . during a period of 4 hr. Sample B was heat-treated at 113°C . during a period of $6\frac{1}{2}$ hr., having first been quenched through its molten state in ice water. The patterns of x-ray diffraction of sample A and sample B agree with those of the α and β forms examined by Hatano and Kambara.² The original film samples were obtained from a cyclohexanone solution of the polymer which had been cast into film at 100°C . With respect to the x-ray diffraction curve of sample D, (hot-pressed, 200 kg./cm.² at 190°C .), Figure 1, its crystal is almost the same as the β form. The curve of sample E, which had been crystallized for several hours at room temperature after having first been quenched in ice water, is almost identical with that of sample B. This experimental result shows that (1) the quenched amorphous polymer is

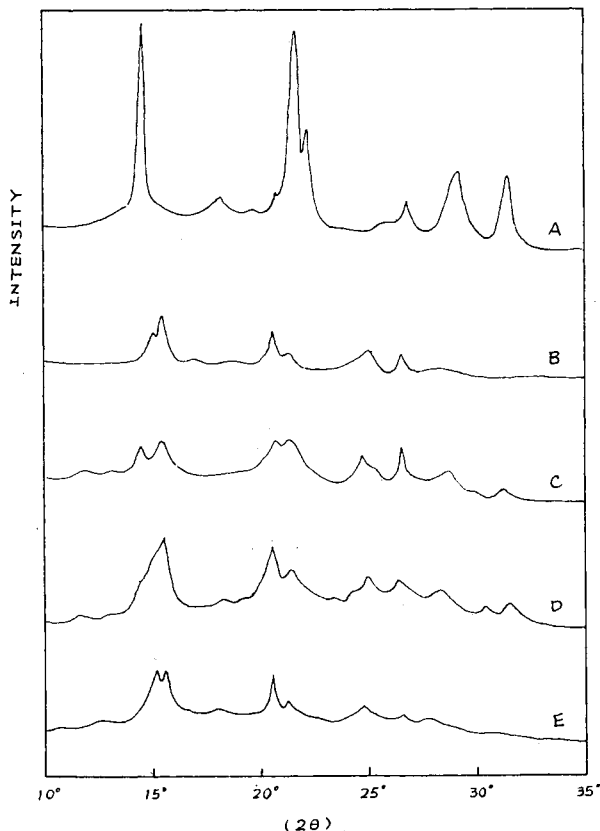


Fig. 1. X-ray diffraction curves under various crystallizing conditions: (A) annealed through molten state; (B) crystallized at 113°C . after quenching; (C) cast from cyclohexanone solution; (D) hot-pressed; (E) crystallized at room temperature after quenching.

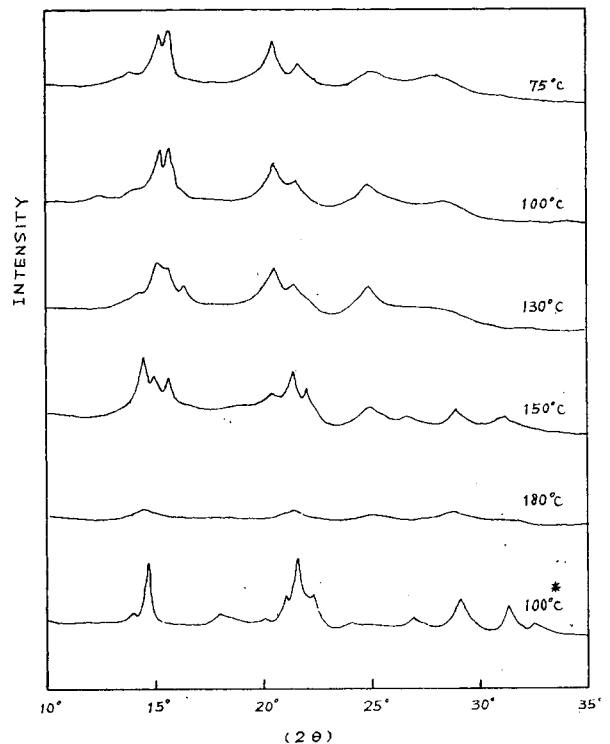


Fig. 2. Effect of temperature on x-ray diffraction curve of the sample E. Temperature of the sample was raised from room temperature up to 180°C .; (*) gradually cooled to 100°C . after having been kept at 180°C .

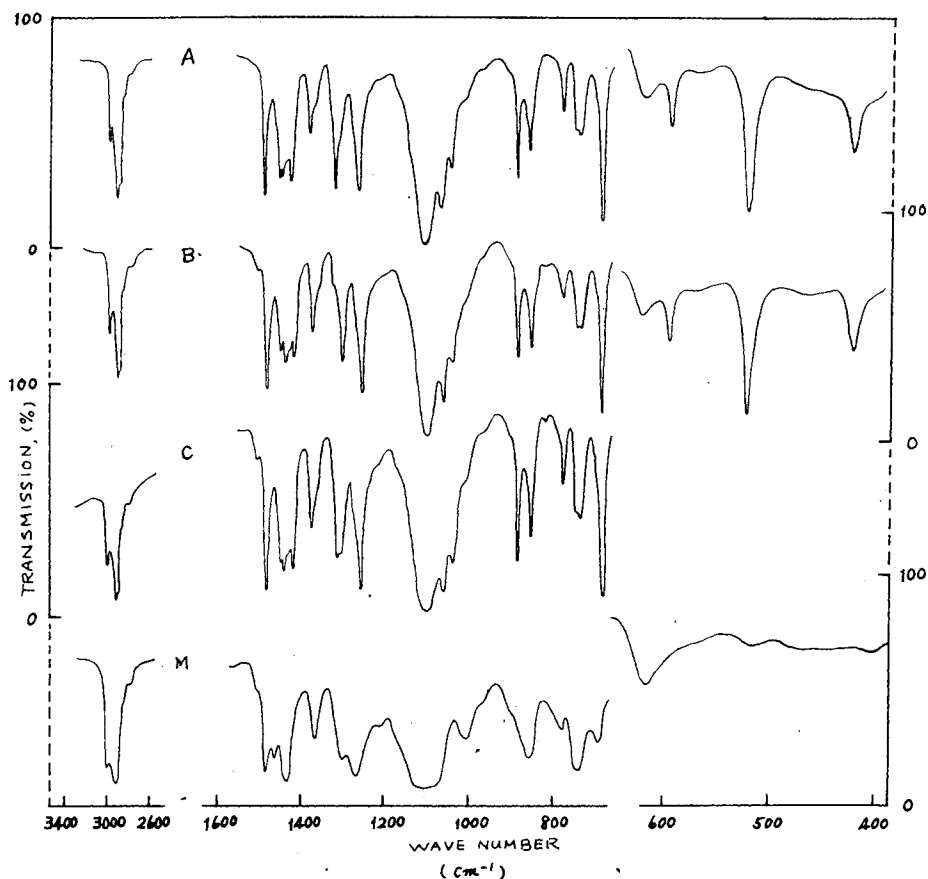


Fig. 3. Infrared spectra under various crystallizing conditions: (A) annealed through molten state; (B) crystallized at 113°C. after having been quenched; (C) cast from cyclohexanone solution; (M) melted at 197°C.

readily crystallized in the structure of the β form when it is allowed to crystallize even at room temperature, and (2) the glass transition temperature of the polymer exists below room temperature.

Transformation of the crystal form of sample E from β to α occurs at a temperature around 130°C., as shown in Figure 2. With a rise in temperature, crystalline peaks of the β form are changed to those of the α form at a temperature around 130°C. At 150°C. more prominent α peaks are observed. The diffraction curve of the sample which had been slowly cooled to 100°C. after having been kept at 180°C. during several minutes have shown only α peaks. However, it is interesting that peaks of both α and β form are recognizable in the diffraction curve of the original film sample C (Fig. 1) which was cast from the cyclohexanone solution and was not heat-treated.

We have confirmed the results mentioned above by the infrared method. The infrared spectra of sample A, α form, and that of B, β form, are shown in Figure 3. A remarkable difference is found in the behavior of the bands at 1325 and at 1315 cm^{-1} . However, no other noticeable spectral differences are observed. Hence we carefully examined the intensity changes of the bands at 1325 cm^{-1} and at 1315 cm^{-1} effected by varying temperatures of sample E. The temperature of the sample was gradually raised from

room temperature up to the melting point of the polymer, and then was slowly lowered to room temperature. Temperature dependence of the optical densities of the bands at 1325 and 1315 cm^{-1} is shown in Figures 4 and 5. With a rise in temperature of sample E, whose crystal structure was supposed to be β , the intensity of the band at 1315 cm^{-1} decreases. However, the band at 1325 cm^{-1} strengthens when the temperature of the sample is raised to a temperature around 130°C. The intensities of both of the bands are decreased when the sample is melted at 185°C. The intensity of the band at 1325 cm^{-1} grows very strong when the sample is gradually cooled through its molten state to room temperature. However, the intensity at 1315 cm^{-1} is not recovered, although it was strong in the spectrum prior to the melting of the sample. It is supposed that the film thickness of the samples are not changed with heating.

Considering the results obtained by the x-ray method, it is interpreted that the bands at 1325 cm^{-1} and at 1315 cm^{-1} are caused by the vibrations in the crystal of the α form and of β form respectively. Thus, we conclude that (1) an amount of α form or of β form in the crystal structure of the polymer can be quantitatively determined by measuring the intensity of the band at 1325 cm^{-1} or of the band at 1315 cm^{-1} respectively, and (2) the crystal transformation from β to α , which occurs at about 130°C., is confirmed by in-

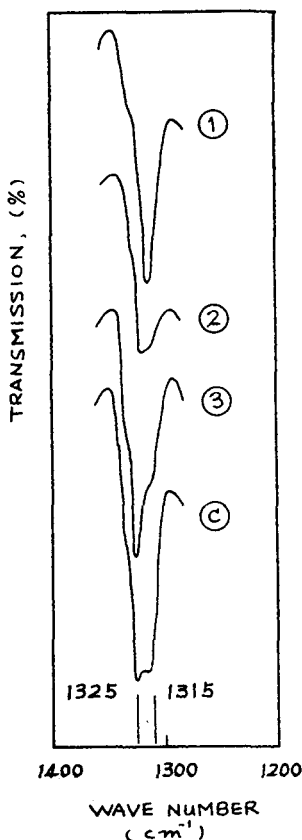


Fig. 4. Effect of temperature on the bands at 1325 cm^{-1} and at 1315 cm^{-1} of the sample E. Temperature of the sample was raised from room temperature up to melting temperature. (1) at 32°C .; (2) at 155°C .; (3) slowly cooled to 35°C . after having been melted; (C) cast from cyclohexanone solution.

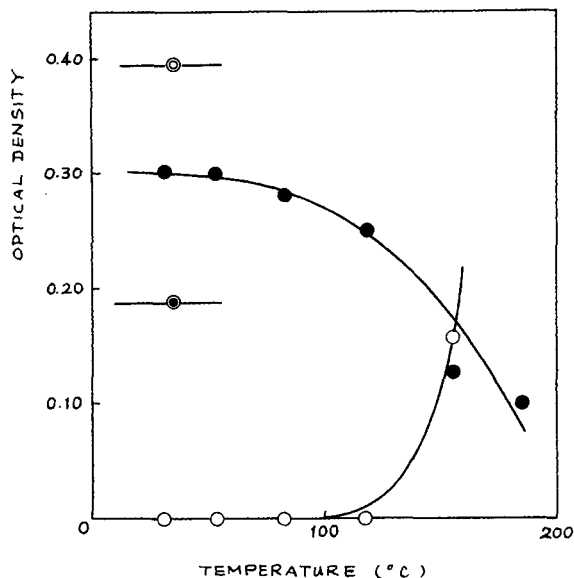


Fig. 5. Temperature dependence of optical densities of the bands at 1325 cm^{-1} (O) and 1315 cm^{-1} (●). Sample E was heated from room temperature up to melting temperature, and ("double circle" for 1325 and "circle with heavy center dot" for 1315) slowly cooled to 35°C . through molten state.

frared spectroscopy as well as x-ray measurements.

The infrared spectra of sample C and its characteristic part of the absorption band are shown in Figures 3 and 4. The doublet of the band at 1325 and 1315 cm^{-1} observed in the spectrum of the sample gives the same result as that obtained by x-ray measurement, so it is supposed that the crystal structure of sample C is composed of both the α and β forms.

In comparing the infrared spectrum of polymer in the molten state (sample M) with spectra of A and B, many crystallization-sensitive bands are recognized. Yet, no

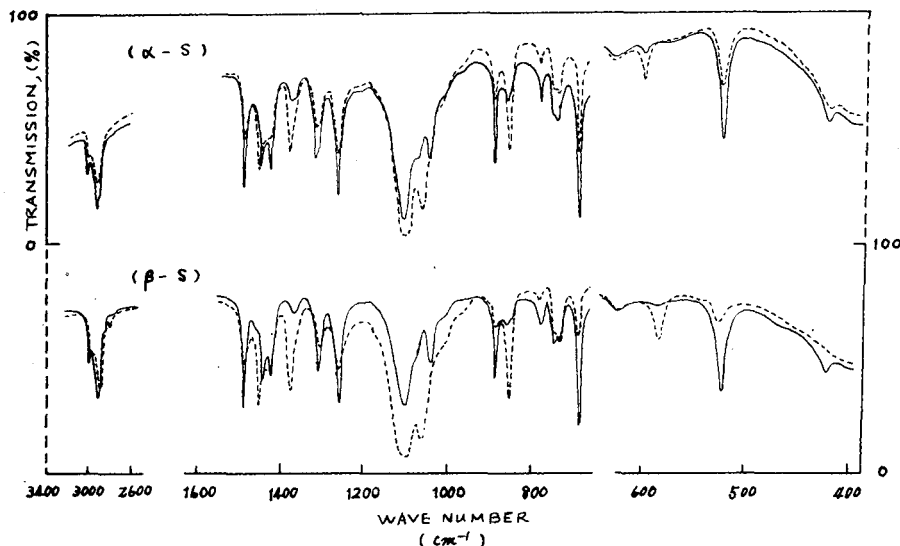


Fig. 6. Infrared dichroism of stretched sample: (α -S) stretched in α -form; (β -S) stretched in β -form; (—) electric vector perpendicular to elongation; (---) electric vector parallel to elongation.

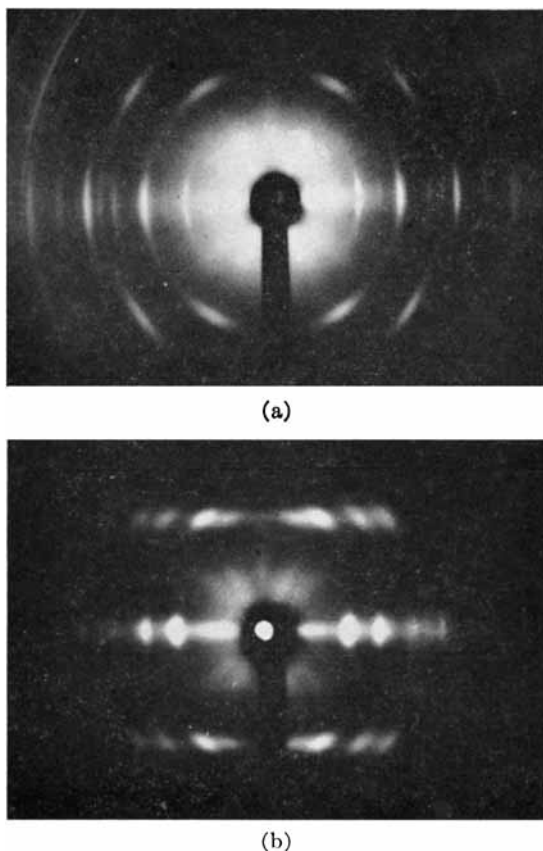


Fig. 7. Fiber photographs of the stretched samples: (a) stretched α form; (b) stretched β form.

other bands characteristic of the α or β form except those at 1325 and 1315 cm^{-1} are observed. The crystallization-sensitive bands common to both forms are observed at 1050, 897, 698, 601, 527, and 428 cm^{-1} . The band at 1017 cm^{-1} becomes strong in its intensity when the sample is melted, and it corresponds to the amorphous band at 1027 cm^{-1} studied by Hatano and Kambara.³

Infrared dichroisms were measured on the stretched sample of α form (α -S) and of the β form (β -S); these are shown in Figure 6. α -S was prepared by stretching the film to a length four times the original length in a glycerine bath at 150°C. and keeping it in the bath for 4 hr. β -S was prepared by stretching the quenched sample to a length five times the original, at room temperature. Remarkable differences in dichroic nature between the α and β forms are not found. The orientation character along the molecular chain of both structures may be considered to be the same. The identity period of the α form is the same as that of the β , or about 4.8 Å; it was determined from the fiber photographs shown in Figure 7. However, no details concerning the molecular structure of either form were found in the present study.

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References

1. Sandiford, D. J. H., *J. Appl. Chem.*, **8**, 188 (1958).

2. Hatano, M., and S. Kambara, *Kogyō Kagaku Zasshi*, **62**, 290 (1959).

3. Hatano, M., and S. Kambara, *Polymer*, **2**, 1 (1961).

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Inhibitor Technique for Chemical Stress Relaxation

For rubber networks undergoing random oxidative scission, the number of moles of cuts $q(t)$ that have been produced up to time t can be measured by stress relaxation at constant extension using the equation:¹

$$q(t) = -N_0 \ln f(t)/f(0) \quad (1)$$

In eq. (1), N_0 is the number of moles of network chains per cc. of the rubber network, $f(t)/f(0)$ is the ratio of stress at time t to stress at time zero. The subject of this note is to show how $q(t)$ is affected by the presence of an antioxidant (inhibitor).

We have measured $q(t)$ by means of eq. (1) in a rubber network produced by photocopolymerizing very thin films (9 mils) of ethyl acrylate with small amounts (2 mole-%) of tetraethylene glycol dimethacrylate. N_0 is obtained from the concentrations of both monomers and polymer density. The value of N_0 for the film studied here is 4.42×10^{-4} moles/cc. This value of N_0 correctly predicted the measured value of the elastic modulus by use of the equation of state for rubber elasticity.

Stress relaxation measurements were carried out at $140 \pm 0.5^\circ\text{C}$. in the absence and in the presence of an antioxidant (inhibitor), namely 2,6-di-*tert*-butyl-*p*-cresol.

The curves for $q(t)$ in the absence of inhibitor and $q_i(t)$, which is the scission in the presence of inhibitor at various levels, are shown in Figure 1. It is clear that the inhibitor affects the curve for $q(t)$ vs. t essentially by producing an induction period t_i which depends on the amount of inhibitor used.

We define $q(t_i)$ as the number of cuts produced in the uninhibited sample after a length of time t_i . In Table I we present data for inhibitor concentration, [Inh], in moles per cc.; t_i produced by [Inh]; $q(t_i)$ corresponding to [Inh]; and finally $q(t_i)/[\text{Inh}]$. This quantity $q(t_i)/[\text{Inh}]$ is a fundamental property of the system which tells how many scissions are suppressed by each inhibitor molecule. It is a quantity that should have wide applicability for the scission of numerous polymer networks.

It is very interesting to note that $q(t_i)/[\text{Inh}]$ is very close to unity in the particular case reported here. This means that one inhibitor molecule suppresses one scission in this system. This is a significant finding which emphasizes the value of our new method.

Each inhibitor molecule is also believed to suppress two radical chains.² If this is true our present finding would mean that there is one effective scission per two kinetic