

## Rheo-Optical Studies of High Polymers. XX. Time and Temperature Dependences of Crystalline and Amorphous Orientation in Low-Density Polyethylene\*

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**ABSTRACT:** The time and temperature dependences of the infrared dichroism for some crystalline and amorphous bands of low-density polyethylene were measured during stress relaxation tests in a temperature range from 25 to 70°C. From the dichroic ratios, the crystalline and amorphous orientation functions were determined. The time and temperature dependences of the strain-optical coefficient are very similar to those of the crystalline orientation functions, but those of the amorphous orientation functions are quite different. It was found that time-temperature superposition could be applied to the time-dependence curves of the crystalline orientation functions, and that the rheo-optical shift factor  $\sigma_T$  determined in the course of the superposition gave the same activation energy as had been reported for the  $\alpha_1$  dispersion process.

The intrinsic birefringence for the crystalline and amorphous phases was evaluated from the experimental results, and the contributions of the crystalline and amorphous phases to the total strain-optical coefficient were separated. The contribution of the amorphous phase is larger than that of the crystalline phase, and the two contributions show quite different dependences on time.

**KEY WORDS** Rheo-Optics / Amorphous Orientation / Crystalline Orientation / Infrared Dichroism / Birefringence / Strain-Optical Coefficient / Orientation Function / Polyethylene /

The crystalline and amorphous orientation in polyethylene have hitherto been investigated by several authors. In many of these investigations the orientation functions have been determined as functions of strain<sup>1-4</sup> or temperature.<sup>5</sup> Yamada and Stein, on the other hand, tried to determine the frequency dependence of crystalline orientation in nylon 6 by a combination of the dynamic birefringence and dichroism techniques.<sup>6</sup> The dynamic X-ray diffraction technique is also useful in determining the frequency dependence of the crystalline orientation.<sup>7</sup>

In our previous paper,<sup>8</sup> the temperature and time dependences of the orientation functions

of crystal axes were measured for high-density polyethylene by employing the infrared dichroism method. The aim of the present investigation was to determine the time and temperature dependences of the crystalline and amorphous orientation for low-density polyethylene, in order to clarify the cause of the time and temperature dependences of the strain-optical coefficient of the same material, reported by us in another paper.<sup>9</sup>

### EXPERIMENTAL

#### *Material*

Annealed films of low-density polyethylene, Dow 900M, were used as samples in this study. To prepare the films, pellets placed between two aluminum plates, 0.3 mm in thickness, were melted for 10 min and then pressed for 10 min at 150°C at a pressure of 50 kg/cm<sup>2</sup> in a laboratory press equipped with heating plates. The samples were cooled to room temperature in the

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press, and then heat-treated in boiling water for 5 min and cooled to room temperature again. The films thus prepared were kept in a desiccator for more than one week before being subjected to measurements. The thickness of some of the films was about  $250 \mu$  while that of others was  $40\text{--}60 \mu$ .

#### Measurements

**Infrared Dichroism.** By means of an infrared spectrometer equipped with a self-recording tensile tester, similar in principle to the Instron Tensile Tester, the variation of the infrared dichroic ratio for some key bands characteristic of polyethylene was measured on the film during stress relaxation measurements at a constant initial strain between 2.5 and 5.0%. The apparatus and measuring techniques have been described elsewhere.<sup>10</sup> The key bands employed were the crystalline bands at  $730$  and  $720 \text{ cm}^{-1}$  and the amorphous bands at  $1303$ ,  $1352$ , and  $1368 \text{ cm}^{-1}$ . Thinner films (thickness =  $40\text{--}60 \mu$ ),  $4 \text{ cm}$  in length and  $2 \text{ cm}$  in width, were used for these measurements.

The orientation functions of crystal axes  $a$  and  $b$ ,  $F_\alpha$ , and  $F_\beta$ , were evaluated from the dichroic ratios for the  $730$  and  $720 \text{ cm}^{-1}$  bands,  $D_{730}$  and  $D_{720}$ , by the following relations:<sup>4</sup>

$$F_\alpha = (D_{730} - 1)/(D_{730} + 2) \quad (1)$$

$$F_\beta = (D_{720} - 1)/(D_{720} + 2) \quad (2)$$

The orientation function  $F_c$  of the crystal  $c$  axis was then determined through the relation,

$$F_\alpha + F_\beta + F_c = 0 \quad (3)$$

The amorphous orientation function  $F_a$  was evaluated from the dichroic ratio  $D$  for the amorphous bands at  $1303$ ,  $1352$ , and  $1368 \text{ cm}^{-1}$  by

$$F_a^{1303} = (D_{1303} - 1)/(D_{1303} + 2) \quad (4)$$

$$F_a^{1352} = (D_{1352} - 1)/(D_{1352} + 2) \quad (5)$$

$$F_a^{1368} = (D_{1368} - 1)/(D_{1368} + 2) \quad (5)$$

**X-ray Diffraction.** The degree of crystallinity  $X_c$  was determined by the method of Wilchinsky<sup>11</sup> from the results of X-ray diffractometry by use of a diffractometer, Model VD-1, manufactured by Shimadzu Manufacturing Co., at temperatures ranging from  $20$  to  $80^\circ\text{C}$ ;  $X_c$  is given by

$$X_c = 1/(1 + 0.869A/C) \quad (7)$$

where  $A$  and  $C$  are respectively the areas corresponding to the amorphous and crystalline phases in the sample. The factor  $0.869$  was regarded as a constant independent of temperature.

## RESULTS AND DISCUSSION

### Crystalline Orientation

The infrared dichroic ratios  $D$  for the two crystalline bands at  $730$  and  $720 \text{ cm}^{-1}$  were measured as functions of time during stress relaxation tests at six temperatures between  $25$  and  $70^\circ\text{C}$ . The initial strain given to the sample film was  $2.5$  to  $3.5\%$ . The orientation functions  $F$  were evaluated from  $D$ , and their ratios to the strain,  $F/\gamma$ , are shown below as functions of time.

Figure 1 shows the variation with time of  $F_\alpha/\gamma$  obtained from  $D_{730}$ . It is evident from this figure that  $F_\alpha/\gamma$  is negative over the entire range of time covered in this experiment, and increases with increasing time until it reaches an equilibrium value at longer times. The time dependency of  $F_\alpha/\gamma$  is greater at lower temperatures, but becomes progressively smaller as temperature rises above  $40^\circ\text{C}$ . The equilibrium value of  $F_\alpha/\gamma$  depends on temperature. The increase in  $-F_\alpha/\gamma$  with time indicates that the crystal  $a$  axis orients more and more perpendicular to the stretching direction as time elapses.

A similar result for  $F_\beta$  is shown in Figure 2.  $F_\beta/\gamma$  is also negative over the entire range of time, and its time dependency is also remarkable only at lower temperatures. The increase of

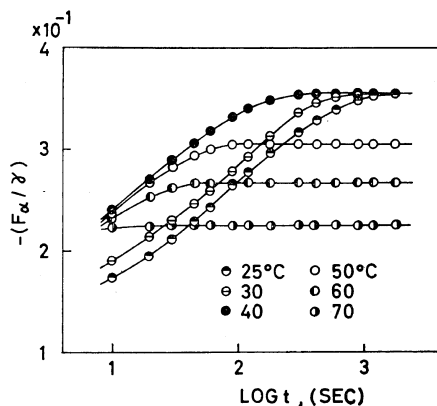


Figure 1. Variation of  $-F_\alpha/\gamma$  with time at various temperatures.

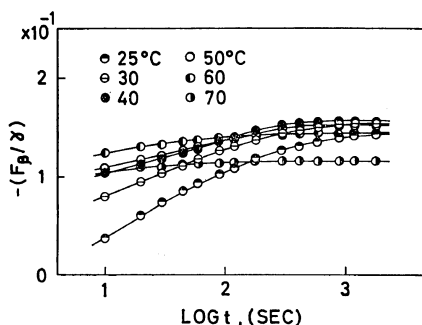


Figure 2. Variation of  $-F_{\beta}/\gamma$  with time at various temperatures.

$-F_{\beta}/\gamma$  with time also shows that the crystal  $b$  axis orients perpendicular to the stretching direction; but the orientation again levels off at longer times.

From the above results it can be seen that the time dependence of  $F_{\alpha}$  and  $F_{\beta}$  is very similar to that of the strain-optical coefficient  $\Delta/\gamma$  for the same material, as reported in a previous paper.<sup>9</sup> It follows, therefore, that the time dependence of the strain-optical coefficient of low-density polyethylene is closely related to and probably determined by the crystalline orientation.

$F_{\alpha}$  and  $F_{\beta}$  at 30 min are plotted against temperature in Figure 3.  $-F_{\alpha}/\gamma$  is almost constant, independent of temperature, below about 40°C; but it decreases with increasing temperature above

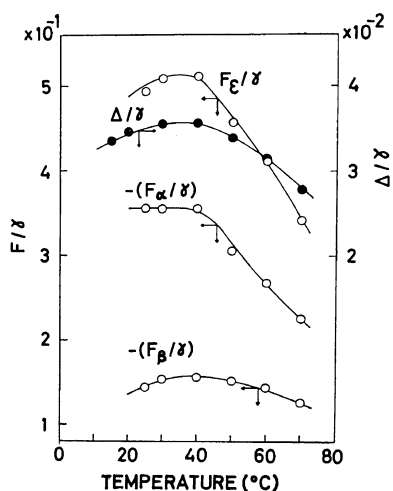


Figure 3. Variation of  $F_{\alpha}/\gamma$ ,  $-F_{\alpha}/\gamma$ ,  $-F_{\beta}/\gamma$ , and  $\Delta/\gamma$  at 30 min with temperature.

40°C.  $-F_{\alpha}/\gamma$  is more than two times larger than  $-F_{\beta}/\gamma$ .

$F_{\epsilon}$  evaluated from eq 4 is also plotted against temperature in Figure 3.  $F_{\epsilon}/\gamma$  is positive and increases with temperature until it reaches a maximum at about 40°C. After passing through the maximum, it decreases rather rapidly with rising temperature. The shape of the temperature-dependence curve of  $F_{\epsilon}/\gamma$  is very similar to that of  $-F_{\beta}/\gamma$ . The strain-optical coefficient  $\Delta/\gamma$  is also plotted in the same figure. It is clear from this figure that the temperature dependence of the strain-optical coefficient is very similar to that of  $-F_{\beta}/\gamma$  and  $F_{\epsilon}/\gamma$ .

Such a similarity between  $\Delta/\gamma$ ,  $F_{\epsilon}/\gamma$ , and  $-F_{\beta}/\gamma$  was also found for high-density polyethylene, as reported in a previous paper,<sup>8</sup> and this indicates that the temperature dependence of the strain-optical coefficient of both low- and high-density polyethylene can be attributed to that of the crystalline orientation.

#### Amorphous Orientation

Since the degree of crystallinity of the sample films employed in this study was as low as about 50% at 30°C, it was expected that the contribution of the amorphous orientation to the birefringence might be comparatively large. Therefore, the dichroic ratios for the amorphous bands at 1303, 1352, and 1368  $\text{cm}^{-1}$  were determined during stress relaxation tests under a constant initial strain of 3.5 to 5.0%, at five temperatures

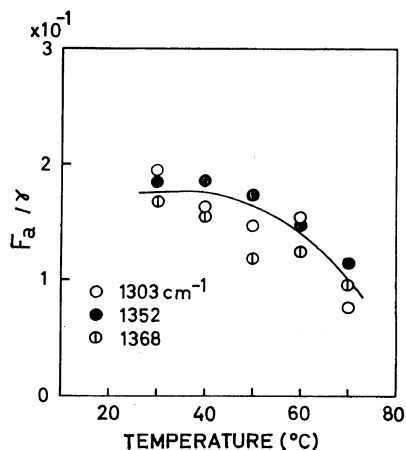


Figure 4. Variation of  $F_{\alpha}/\gamma$  at 30 min with temperature.

between 30 and 70°C. From the dichroic ratio at 30 min the amorphous orientation function  $F_a$  was evaluated; its ratio to the strain is plotted against temperature in Figure 4. As is evident from this figure, values obtained for  $F_a/\gamma$  from each of the three amorphous bands show fairly good agreement.  $F_a/\gamma$  is almost constant at temperatures lower than 40°C, but decreases with increasing temperature above 40°C, indicating a decrease in the amorphous orientation at higher temperatures.

In Figure 5,  $F_a/\gamma$  from  $D_{1352}$  at 30°C is plotted as a function of time.  $F_a/\gamma$  is almost independent of time, but decreases rather slightly with increasing time. This tendency of  $F_a/\gamma$  is quite different from that of the strain-optical coefficient and of the crystalline orientation, which increase with increasing time as mentioned above. This result, therefore, also supports the above conclusion that the variation of the strain-optical coefficient with time is determined by that of the crystalline orientation.

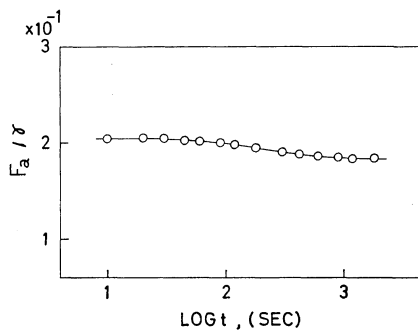


Figure 5. Variation of  $F_a/\gamma$  from  $D_{1352}$  at 30°C with time.

#### Time-Temperature Superposition of the Crystalline Orientation Functions

As mentioned in previous papers,<sup>9,12</sup> time-dependence curves of the strain-optical coefficient measured for low- and high-density polyethylene at various temperatures can be superposed into master curves at arbitrary reference temperatures. Furthermore, as mentioned above, the time dependence of the strain-optical coefficient is very similar to that of the crystalline orientation functions  $F_c/\gamma$ ,  $-F_a/\gamma$ , and  $-F_\beta/\gamma$ , and the former can be considered to be determined by

the latter. If this is true, time-temperature superposition should also be applicable to the time-dependence curves of  $F_c/\gamma$ ,  $-F_a/\gamma$ , and  $-F_\beta/\gamma$ , and the shift factor determined in the course of the superposition should give the same activation energy as that for the strain-optical coefficient.

To confirm this, superposition was applied to the three sets of time-dependence curves for  $-F_a/\gamma$ ,  $-F_\beta/\gamma$ , and  $F_c/\gamma$  in such a way as to give the best superposition for all three sets by horizontal shifts with the same shift factor. The reference temperature was 30°C. The superposition was satisfactory at temperatures below 40°C, while the curves above 50°C could not be superposed well. The respective master curves for  $-F_a/\gamma$ ,  $-F_\beta/\gamma$ , and  $F_c/\gamma$  are shown in Figures 6, 7, and 8. The abscissa of each of these figures is the reduced time  $t/o_T$ , where  $o_T$  is the rheo-

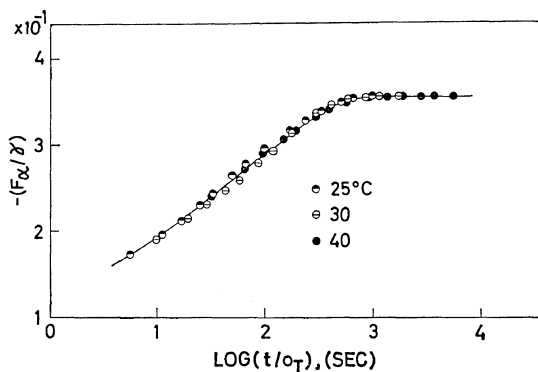


Figure 6. Master curve of  $-F_a/\gamma$  plotted against reduced time at 30°C.

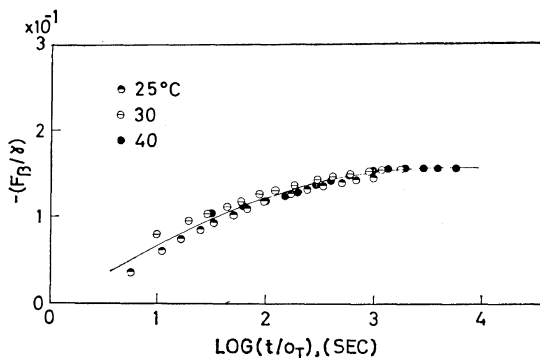


Figure 7. Master curve of  $-F_\beta/\gamma$  plotted against reduced time at 30°C.

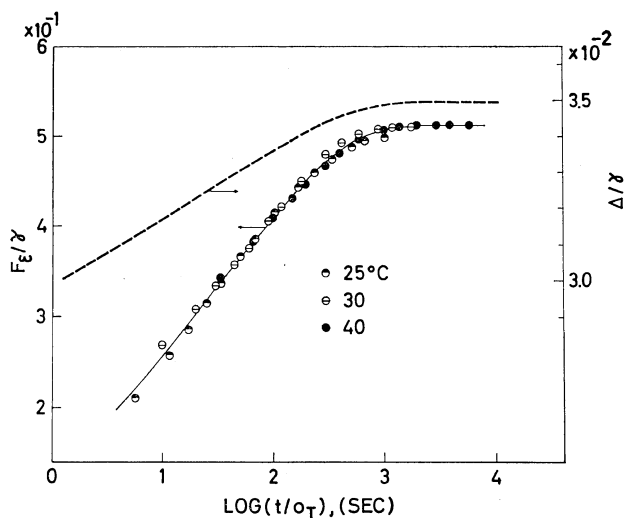


Figure 8. Master curves of  $F_e/\gamma$  and strain-optical coefficients  $\Delta/\gamma$  plotted against reduced time at 30°C.

optical shift factor. As is evident from these figures, the master curves are fairly smooth, but that for  $-F_\beta/\gamma$  is rather poor. This is due to the fact that  $-F_\beta/\gamma$  has very much lower values over the entire range of time as compared with the other orientation functions, and its accurate determination is thus very difficult.

In Figure 8 is also shown the master curve for the strain-optical coefficient. This curve manifests quite the same tendency as that for  $F_e/\gamma$ , suggesting that the time dependence of the birefringence is ascribable to that of the crystalline orientation.

On the basis of these master curves, the relaxation process in the lamellae of low-density polyethylene may now be discussed. Since  $-F_a/\gamma$ ,  $-F_\beta/\gamma$ , and  $F_e/\gamma$  increase with increasing time, it is apparent that the  $a$  and  $b$  axes orient perpendicular to, and the  $c$  axis parallel to, the stretching direction as time elapses. The fact that  $-F_a/\gamma$  and  $F_e/\gamma$  are larger than  $-F_\beta/\gamma$  indicates that rotation about the  $b$  axis or twisting of the lamellae is predominant, as compared with rotation about the  $a$  axis or bending of lamellae. On instantaneous stretching of the sample film, amorphous chains also orient parallel to the stretching direction, but the orientation changes only little with time. This indicates that the amorphous orientation is accomplished in a very

short time, as was indicated in a previous paper,<sup>13</sup> and relaxes only slightly even after a long period.

The rheo-optical shift factor  $o_T$  determined in the course of the time-temperature superposition of the time-dependence curves of the crystalline orientation functions gives a straight line when plotted against the reciprocal absolute temperature  $1/T$ , as is shown in Figure 9. This straight line gives an activation energy of 22.0 kcal/mol, which shows good agreement with the values obtained for various types of polyethylene by various rheo-optical methods.<sup>12</sup>

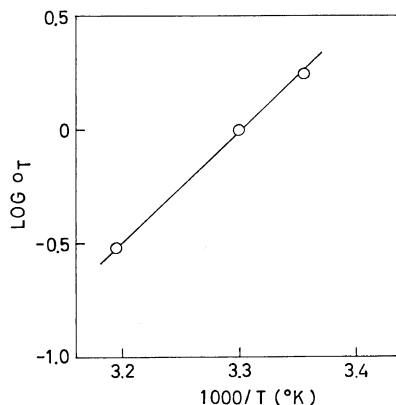


Figure 9. Variation of the rheo-optical shift factor  $o_T$  with reciprocal absolute temperature.

Experimental results on the dynamic mechanical loss for polyethylene, particularly for high-density types, indicate the existence of the so-called  $\alpha_c$  absorption peak at temperatures between 40 and 80°C, depending upon the type. This absorption peak is generally believed to split into two different dispersions,  $\alpha_1$  and  $\alpha_2$ . In a previous paper,<sup>12</sup> we ascribed the rheo-optical dispersion observed for high-density polyethylene at about 80°C to the  $\alpha_1$  dispersion and considered it to be associated with the bending and twisting of lamellae, because the temperature at which the dispersion appears and the activation energy correspond to those for the  $\alpha_1$  dispersion. In the case of the low-density polyethylene treated in this study, the  $\alpha_c$  absorption peak was not clearly observed in the dynamic viscoelastic data. However the rheo-optical dispersion, that is the increase in the strain-optical coefficient and crystalline orientation functions with time and temperature, is also considered to correspond to the  $\alpha_1$  dispersion; and it is clear from the above master curves of the orientation functions that this dispersion is due to the crystalline orientation. This conclusion is consistent with the earlier one drawn from dynamic birefringence<sup>13,14</sup> and dynamic X-ray diffraction<sup>7</sup> studies.

#### Contributions of the Crystalline and Amorphous Orientation to the Strain-Optical Coefficient

When we assume a simple 2-phase model for crystalline polymers, the strain-optical coefficient  $K = \Delta/\gamma$  can be given by

$$K = K_c + K_a + K_f \quad (8)$$

where  $K_c$ ,  $K_a$ , and  $K_f$  represent respectively the contributions of the crystalline and amorphous phases and the form birefringence.  $K_c$  and  $K_a$  in this equation can be written as

$$K_c = X_c \{ (n_a - n_c)(F_a/\gamma) + (n_b - n_c)(F_b/\gamma) \} \quad (9)$$

$$\text{and } K_a = (1 - X_c) \Delta_a^0 (F_a/\gamma) \quad (10)$$

where  $n_a$ ,  $n_b$ , and  $n_c$  are respectively the refractive indices in the directions of the  $a$ ,  $b$ , and  $c$  axes and  $\Delta_a^0$  is the intrinsic birefringence for the amorphous phase.

Assuming that

$$n_c \gg n_a \text{ and } n_b$$

$$\text{and } n_a \simeq n_b \simeq (n_a + n_b)/2 \simeq \bar{n}$$

eq 9 can be rewritten as

$$K_c = -X_c \{ (n_c - \bar{n})(F_a/\gamma + F_b/\gamma) \} = X_c \Delta_c^0 (F_c/\gamma) \quad (11)$$

where  $\Delta_c^0$  is the intrinsic birefringence for the crystalline phase.

When the form birefringence can be neglected, eq 8 thus reduces to

$$K = X_c \Delta_c^0 (F_c/\gamma) + (1 - X_c) \Delta_a^0 (F_a/\gamma) \quad (12)$$

Now, to separate the contributions to  $K$  of the crystalline and amorphous phases, we must determine  $\Delta_c^0$  and  $\Delta_a^0$ . There have been several attempts to evaluate these quantities,<sup>15</sup> but reliable values have not been definitely established. We therefore tried to evaluate these quantities from our experimental results.

Equation 12 gives

$$K/(X_c F_c/\gamma) = \Delta_c^0 + (1 - X_c) F_a \Delta_a^0 / X_c F_c \quad (13)$$

This indicates that when we plot  $K/(X_c F_c/\gamma)$  against  $(1 - X_c) F_a / X_c F_c$ , a straight line should be obtained, and its slope and intercept should give  $\Delta_a^0$  and  $\Delta_c^0$ . Since  $K$ ,  $F_c$ , and  $F_a$  at different temperatures can be obtained from Figures 3 and 4, the above plot can be drawn so long as  $X_c$  is known.

The temperature dependence of  $X_c$  determined from X-ray diffraction data is shown in Figure 10. It is evident from this figure that  $X_c$  is about 50% at 30°C and decreases continuously with increasing temperature. Employing these values of  $X_c$  along with those of  $K$ ,  $F_c$ , and  $F_a$  at different temperatures,  $K/(X_c F_c/\gamma)$  was plotted against  $(1 - X_c) F_a / X_c F_c$  to give Figure 11, where  $F_a$  from  $D_{1352}$  is employed. Although the number

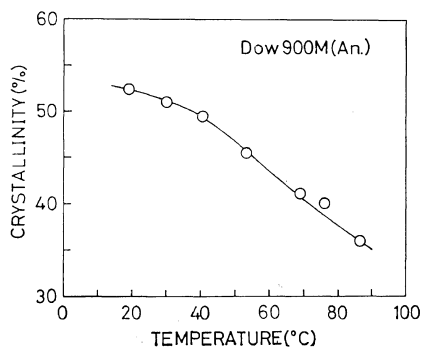
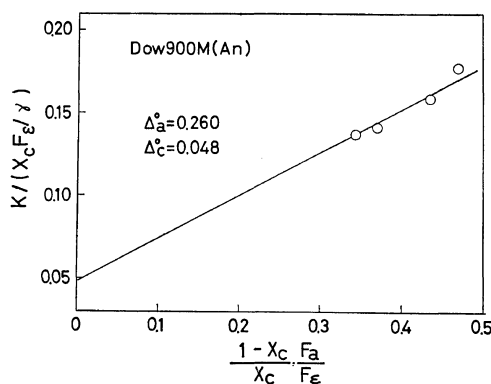


Figure 10. Variation of the degree of crystallinity with temperature.

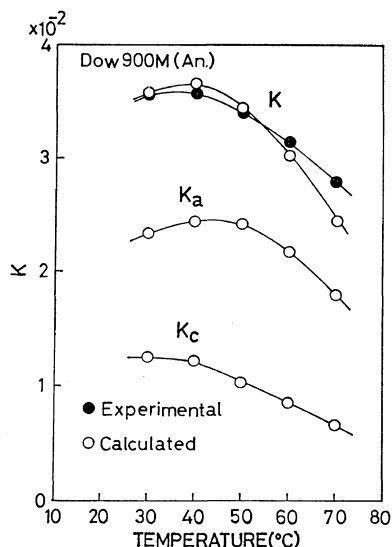


**Figure 11.**  $(\Delta/\gamma)/(X_c F_e/\gamma)$  plotted against  $(1-X_c)F_a/X_c F_e$  for low-density polyethylene at 30°C.

of experimental points is rather small, these points satisfy well, giving

$$\Delta_a^0 = 0.260 \text{ and } \Delta_c^0 = 0.048$$

The value of  $\Delta_a^0$ , 0.260, is very close to the 0.261 which is obtained by use of the bond polarizability as determined by Denbigh.<sup>16</sup> On the other hand, the value of  $\Delta_c^0$ , 0.048, is somewhat smaller than the 0.0585 calculated from the refractive indices given by Bunn and Daubeny<sup>17</sup> and the crystalline orientation functions from X-ray diffraction data.<sup>15</sup>

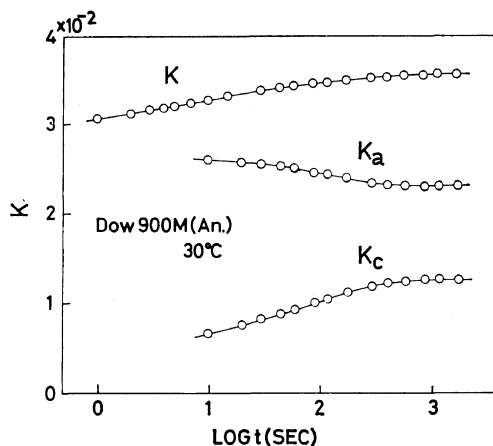


**Figure 12.** Variation of the strain-optical coefficient and its components with temperature.

Next, from eq 9 and 10,  $K_a$  and  $K_c$  at different temperatures were calculated; the results are shown in Figure 12. In this figure,  $K$  determined as  $(K_a + K_c)$  is also compared with the experimental values. As is evident from this figure, the calculated values (open circles) of  $K$  coincide well with the experimental ones (closed circles).  $K_c$  is almost constant with respect to temperature at lower temperatures, but decreases with increasing temperature at higher temperatures. On the other hand,  $K_a$  shows a peak at about 45°C and is about two times greater than  $K_c$ . In other words, the contribution of the amorphous phase to the total birefringence is much greater than that of the crystalline phase.

Finally,  $K_c$  as a function of time was calculated from  $F_c/\gamma$  at 30°C, and  $K_a$  at the corresponding times was then obtained as  $(K - K_c)$ .  $K_c$  and  $K_a$  thus calculated, as well as  $K$ , are shown in Figure 13 as functions of time.  $K_a$  determined directly from  $F_a/\gamma$  in Figure 5 gives almost the same curve as that in Figure 13, indicating that the above-determined value of  $\Delta_a$  is very appropriate. It is clear from this figure that  $K_c$  increases rapidly while  $K_a$  decreases slightly with increasing time; this is consistent with the slight decrease in  $F_a/\gamma$  with increasing time which has already been noted in Figure 5. Here again,  $K_a$  is much greater than  $K_c$  over the entire range of time covered in this study.

It can be concluded from these results that the amorphous orientation plays a more important



**Figure 13.** Variation of the strain-optical coefficient and its components with time.

role than the crystalline in determining the magnitude of the strain-optical coefficient and the birefringence. The time dependence of the strain-optical coefficient and birefringence, however, is determined by the crystalline rather than the amorphous orientation.

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