

Orientation and Crystal Transformation in Polybutene-1 under Stress Relaxation

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(Received January 21, 1974)

ABSTRACT: The stress relaxation and birefringence relaxation of polybutene-1 were simultaneously measured at different temperatures ranging from 14 to 80°C. The relaxation curves obtained could be well superposed by vertical and horizontal shifts at short relaxation times, during which little crystal transformation takes place. However, at long relaxation times, various nonsuperposed curves branched out from the master curve. Such branching out cannot be observed for polyethylene and polypropylene. The superposed part represents the orientation of crystallites of mod. II, whereas the nonsuperposed part must result from a crystal transformation. Thus, the relaxation processes in polybutene-1 involve the crystallite orientation and crystal transformation from mod. II to mod. I.

The intrinsic birefringences for the mod. I and mod. II crystals could be evaluated from the strain-optical coefficients for the superposed and nonsuperposed parts along with orientation functions of mod. I and mod. II crystallites, as determined by X-ray methods.

KEY WORDS Rheo-Optics / Crystal Transformation / Orientation /
Stress Relaxation / Polybutene-1 / Intrinsic Birefringence /

As mentioned in a previous paper,¹ it is well known that the tetragonal crystal modification (mod. II) in polybutene-1 transforms into the hexagonal crystal modification (mod. I) when a fresh sample of this material is allowed to stand after preparation.²⁻⁹ The crystal transformation is also accelerated by stretching.^{1,8} Therefore, the variation of the mechanical properties of this material with time can be fully understood only when this transformation is taken into consideration.

In a previous paper,¹ therefore, the infrared dichroism technique which had been developed by us was employed to elucidate the crystal transformation and orientation during stress-strain measurements; this technique was found to be very powerful for separating the contribution of the crystal transformation to the stress-strain behavior from that of the crystal orientation. It was anticipated from the results obtained in this study that the crystal transformation in polybutene-1 must also affect the stress relaxation and rheo-optical relaxation phenomena

observed under a constant strain. However, such an effect has not hitherto been studied at all.

In this paper, therefore, the stress relaxation and birefringence relaxation were simultaneously measured by means of the time-dependent birefringence method for a fresh polybutene-1 film in the course of aging at different temperatures. Combining results obtained by such viscoelastic and rheo-optical measurements with those from X-ray diffraction measurements, the effect of crystal transformation on the relaxation phenomena, which cannot be observed for polyethylene and polypropylene,¹⁰⁻¹² was separated from that of crystallite orientation. The intrinsic birefringences for the modifications I and II crystals were also evaluated and discussed.

EXPERIMENTAL

Material and Characterization

Commercial pellets (Hostalen from Hüls Co.) of polybutene-1 were placed between two aluminum plates and were heated at 170°C for 10 min in a laboratory press equipped with heating

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plates. The sample was pressed at 170°C and at a pressure of 100 kg/cm² for 5 min. The sample was then removed from the press and quenched by plunging it into an ice-water bath. The films thus prepared were designated as fresh samples. The films used for the relaxation and X-ray diffraction studies were about 270 μ thick, while those for the infrared studies were about 100 μ thick.

The degree of crystallinity, expressed in weight fraction units, was measured at several temperatures by an X-ray technique proposed by Turner-Jones;⁷ these results were then converted into volume fraction units by assuming that the densities of the crystalline and amorphous phases are 0.90^{7,13} and 0.87¹⁴ g/cm³, respectively. The results are shown in Figure 1.

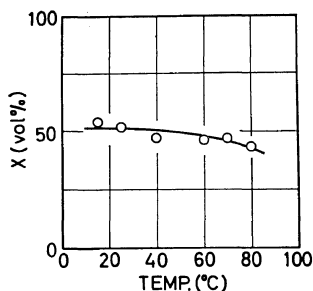


Figure 1. The variation of the degree of crystallinity (vol%) X with temperature for fresh sample of polybutene-1.

H_v light-scattering patterns for the fresh film showed the so-called "four-leaf clover" pattern, which has been shown to arise from spherulitic structures. By the method¹⁵ proposed by Stein and Rhodes, the radius of the spherulite was determined to be 1–4 μ .

Measurements

The crystal transformation from mod. II to mod. I in polybutene-1 was detected by an infrared absorption method. From the ratio of the absorbance A_{846} of the 846-cm⁻¹ band to the absorbance A_{1150} of the 1150-cm⁻¹ band, A_{846}/A_{1150} , the degree of crystal transformation, Φ , was determined by the use of a previously prepared calibration curve of A_{846}/A_{1150} vs. Φ , which was determined for laminated films of fresh and completely aged samples of different thicknesses.

The details are described in a previous paper.¹ In order to determine accurately the low degrees of crystal transformation, a laminate made up of the film to be tested together with a completely aged film was employed.

The birefringence and the stress relaxation of the sample films were simultaneously measured by means of a combined optical/rheometer instrument. This consisted of an Instron type tensile tester (the Tensilon UTM-III of the Toyo Measuring Instrument Co.) and an optical system designed to measure the birefringence continuously by an intensity method. The details of the instrument were described elsewhere.¹⁶ A quarter-wave plate was inserted into the optical system in order to measure the very low birefringence of polybutene-1 as accurately as possible. The stress relaxation measurements were carried out with film specimens 5 cm in length and 1.5 cm in width under a strain of about 2.0% resulting from rapid stretching at a rate of 400%/min in the temperature range from 14 to 80°C.

X-ray diffraction measurements were carried out with a conventional diffractometer, manufactured by the Shimadzu Manufacturing Co. (Model VD-1). The specimens were pulled with a hand stretcher in an oven regulated at the desired temperatures.

RESULTS AND DISCUSSION

Time Dependent Birefringence and Relaxation Modulus

Film specimens having different degrees of crystal transformation were obtained by holding fresh samples in air at room temperature for varying periods of time. The results for the strain-optical coefficient Δ/γ (birefringence/strain) are shown in Figure 2.

As is evident from this figure, the strain-optical coefficient increases with time in all cases, that is, for the various films having different initial degrees of crystal transformation, Φ_0 . The strain-optical coefficient, however, decreases with increasing Φ_0 ; the coefficient for films having a value of Φ_0 larger than 0.69 becomes negative over the entire range of time scale covered by this study. The lower the initial degree of crystal transformation, the larger variation of strain-optical coefficient with time becomes.

Orientation and Crystal Transformation in Polybutene-1

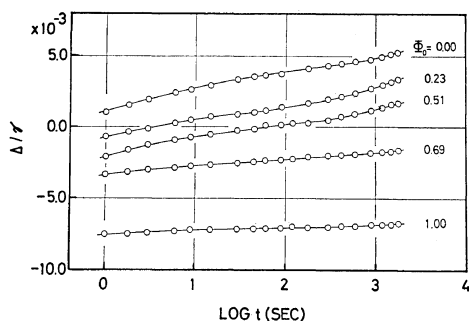


Figure 2. The variation of strain-optical coefficient Δ/γ with time t for films of polybutene-1 having different degrees of initial crystal transformation Φ_0 at room temperature.

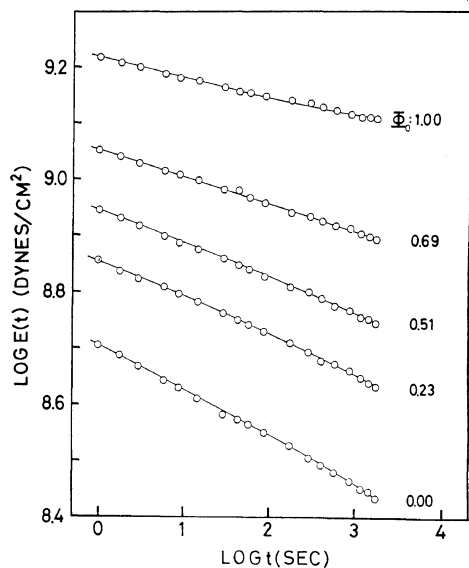


Figure 3. The variation of relaxation modulus $E(t)$ with time t for films of polybutene-1 having different degrees of initial crystal transformation at room temperature.

Figure 3 shows the variation of relaxation modulus with time for films having different initial degrees of crystal transformation. The higher the initial degree of crystal transformation, the higher the relaxation modulus becomes. The relaxation modulus for the completely aged film was about three times higher than that for the fresh film. But the change in the relaxation modulus with time is larger for films having lower initial degrees of crystal transformation.

Negative birefringence can be attributed to

the deformation of spherulites as a whole;¹⁷ this can take place in a very short time and is essentially independent of time.¹⁷ For fresh films, positive birefringence is observed. This is due to the fact that the positive contribution from the orientation of crystallites overrides the negative contribution from the deformation of spherulites. For an aged film, negative birefringence was observed and the variation in birefringence with time was much smaller than that for a fresh film. These results may suggest that the contribution of deformation of spherulites to the birefringence for an aged film becomes larger by aging, and that the crystallites of mod. I can orient only a little because of their low mobility.

The increase in Δ/γ and decrease in $E(t)$ at larger times may be due to the crystal transformation. This is expected from the fact that the crystal transformation is a much slower process than the crystallite orientation.

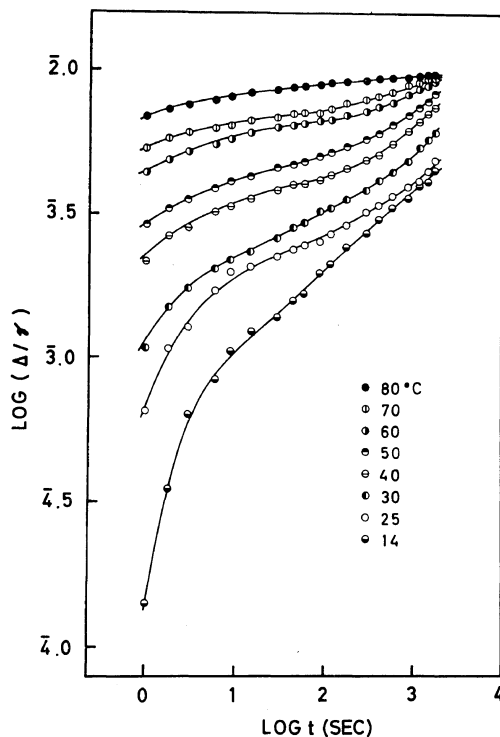


Figure 4. The variation of strain-optical coefficient Δ/γ with time t for fresh samples of polybutene-1 at different temperatures.

Figure 4 shows the time dependence of the strain-optical coefficients for the fresh film at temperatures between 14 and 80°C. It can be seen that the strain-optical coefficient increases with temperature. At temperatures below 70°C, the strain-optical coefficient does not reach an equilibrium value, but rather increases more and more after passing through an inflection point. Such behavior was not observed for other crystalline polymers. However, the strain-optical coefficient at 80°C showed an equilibrium value.

A time-temperature superposition was applied to the strain-optical coefficient curves; the resulting master curve is shown in Figure 5. Not only a horizontal shift but also a vertical shift were necessary to obtain the smooth master curve. As is evident from Figure 5, the master curve has nonsuperposed branches, indicating that the long-time ends of the curves could not be well superposed. The superposed part for the strain-optical coefficient increases with increasing time and reaches an equilibrium value. Such behavior is very similar to other crystalline polymers, but the nonsuperposed branches have not been observed for other polymers. The superposed part represents the orientation process of mod. II crystallites during a relaxation experiment. On the other hand, the branches might result from a crystal transformation, which

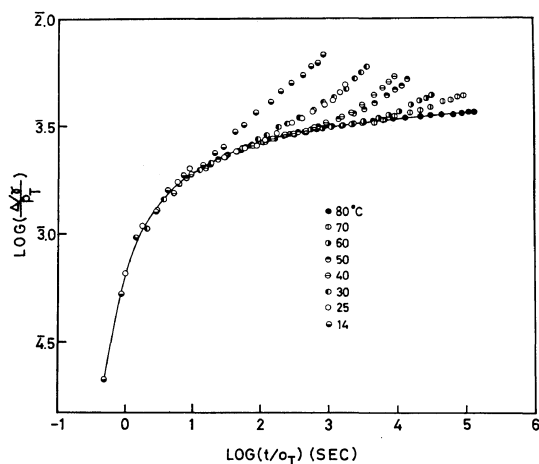


Figure 5. The variation of strain-optical coefficient (Δ/γ) with reduced time (t/a_T) for fresh samples of polybutene-1. The reference temperature is 25°C. p_T is a vertical shift factor.

is a much slower process than the crystallite orientation process.

To make this point clearer, the strain-optical coefficient corresponding to a branch, $(\Delta/\gamma)_s$, was separated from that for the superposed part. Such a separation was carried out within 10 to 30 min after the stretching; at such times the values of $(\Delta/\gamma)_s$ were so large that experimental errors in the strain-optical coefficients and in the superposition procedures could be ignored. The variation of $(\Delta/\gamma)_s$ with time at various temperatures is shown in Figure 6. As is evident from Figure 6, $(\Delta/\gamma)_s$ increases almost linearly with time in the temperature range between 14 and 70°C. The rate of increase in $(\Delta/\gamma)_s$ becomes highest at 40 and 50°C.

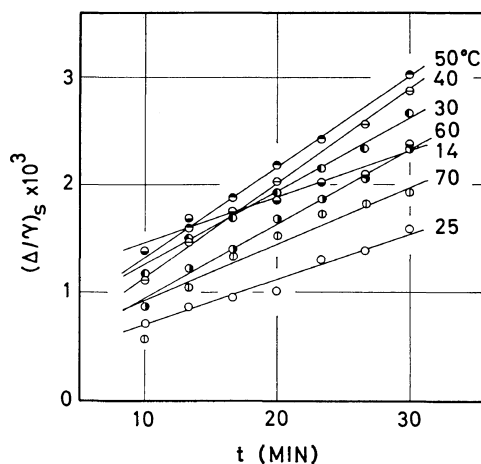


Figure 6. The variation of the separated strain-optical coefficient, $(\Delta/\gamma)_s$, with the time at different temperatures.

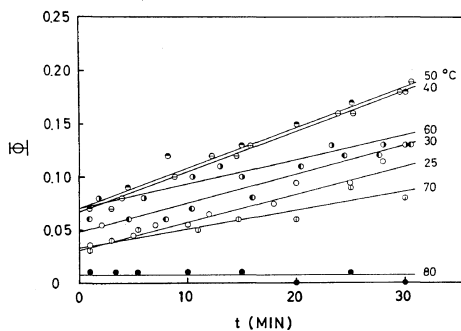


Figure 7. The variation of the degree of crystal transformation with time at different temperatures at an applied strain of 2–3% for polybutene-1.

The time dependence of the degree of crystal transformation was measured at different temperatures by an infrared technique, as described above. The same strain as in the relaxation measurements was applied to the specimens. The results are shown in Figure 7. As is evident from the figure, the degree of crystal transformation at different temperatures (except 80°C) increases almost linearly with time, and the rate of increase shows a maximum at 40 and 50°C. This is very similar to the time dependence of $(\Delta/\gamma)_s$ shown in Figure 6. The degree of crystal transformation at 80°C is negligibly small. This explains why the strain-optical coefficient as a function of time and temperature could be superposed satisfactorily at 80°C (see Figure 5). These facts suggest that the nonsuperposed branches of the strain-optical coefficient must be attributed to crystal transformation.

The orientation functions F_I and F_{II} for the mod. I and mod. II crystallites at a strain of 10% were evaluated at different temperatures from the intensity distribution of X-ray diffraction. Such a high strain makes the intensity distribution quite clear and thus a reliable orienta-

tion function can be obtained. The (200) plane was used for the evaluation of the orientation function of mod. II crystallites, and the (110) plane for that of mod. I crystallites. The mean-square cosine of ϕ_{200} can be calculated by the following equation, where ϕ_{200} is the angle between the stretching axis and the reciprocal lattice vector of the (200) plane, and $I_{200}(\phi)$ the diffracted intensity from the (200) plane at an angle ϕ :

$$\langle \cos^2 \phi_{200} \rangle = \frac{\int_0^{\pi/2} I_{200}(\phi) \cos^2 \phi \sin \phi \, d\phi}{\int_0^{\pi/2} I_{200}(\phi) \sin \phi \, d\phi} \quad (1)$$

If one assumes the axial orientation, $\langle \cos^2 \phi_c^{II} \rangle$ can be expressed by eq 2, since the mod. II crystal form is tetragonal. That is,

$$\langle \cos^2 \phi_c^{II} \rangle = 1 - 2 \langle \cos^2 \phi_{200} \rangle \quad (2)$$

where ϕ_c^{II} is the angle between the stretching axis and the c -axis of mod. II crystal. F_{II} is given by the following equation:

$$F_{II} = \frac{3 \langle \cos^2 \phi_c^{II} \rangle - 1}{2} \quad (3)$$

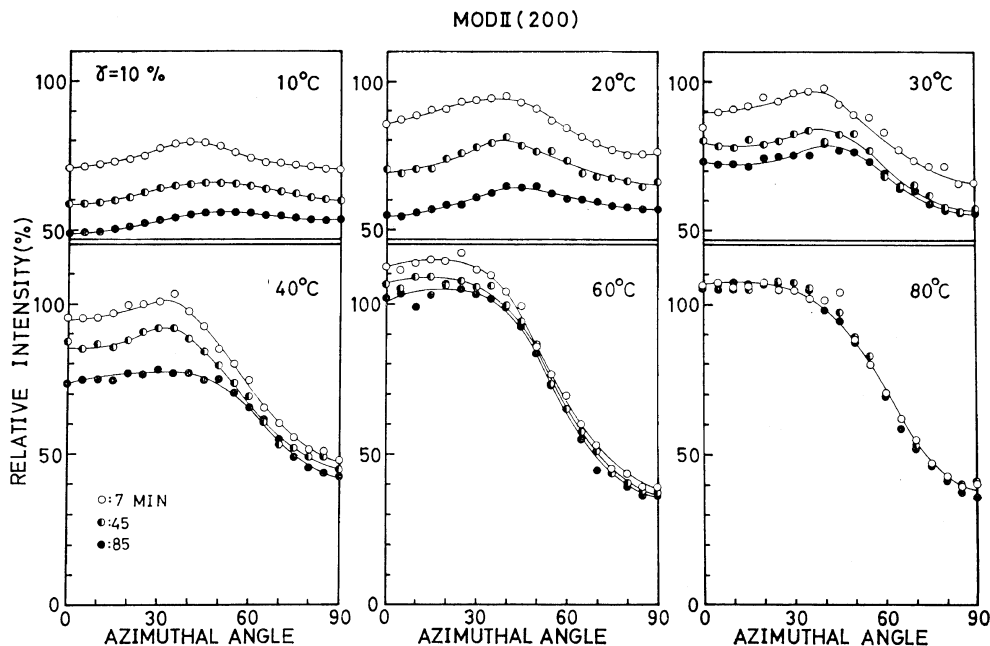


Figure 8. The variation of the diffracted intensity of the (200) plane for the mod. II crystallites with the azimuthal angle at different times and temperatures.

For mod. I crystallites, which have a hexagonal form, F_I can be determined using the (110) reflection in a similar fashion.

Figure 8 shows the azimuthal angle ($90 - \phi_{200}$) dependencies of the (200) plane intensity for mod. II crystals at different times and temperatures. As is evident from the figure, the intensity in the equatorial regions decreases more than does the intensity in the polar regions. This suggests that the crystal transformation takes place more in the equatorial regions than in the polar regions, as was observed also by Yee and Stein.⁹ At 80°C, the diffraction intensity vs. azimuthal angle curves do not change with time, showing that the crystallite orientation does not change at least after 7 min. These curves show that a crystal transformation does not take place.

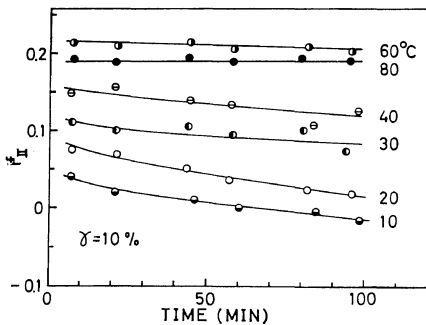


Figure 9. The orientation function of mod. II crystallites F_{II} with time at different temperatures.

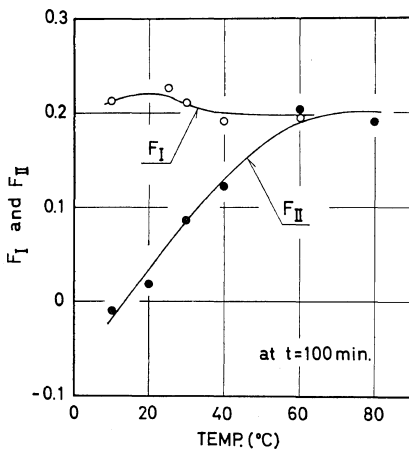


Figure 10. The variation of F_I and F_{II} determined by X-ray techniques with temperature at 100 min after stretching.

The orientation functions of the mod. II crystallites were calculated by eq 1—3 and plotted against time in Figure 9. As is evident from the figure, F_{II} decreases with increasing time, suggesting that the orientation of the mod. II crystallites decreases as a result of the crystal transformation—that is, the more the c -axis of mod. II crystallites oriented to the stretching direction, the more mod. II crystallites transform into mod. I crystallites.

At different temperatures, the orientation function F_I (at 100 min after stretching) was evaluated. At this time, the diffracted intensity for the (110) plane of mod. I crystal was large enough to allow an accurate evaluation of F_I . In Figure 10, both F_I and F_{II} at 100 min are plotted against temperature. As is evident from Figure 10, F_I is almost constant at 0.2 independent of temperature, although F_{II} is dependent on temperature. This suggests that F_I is almost independent of time, too.

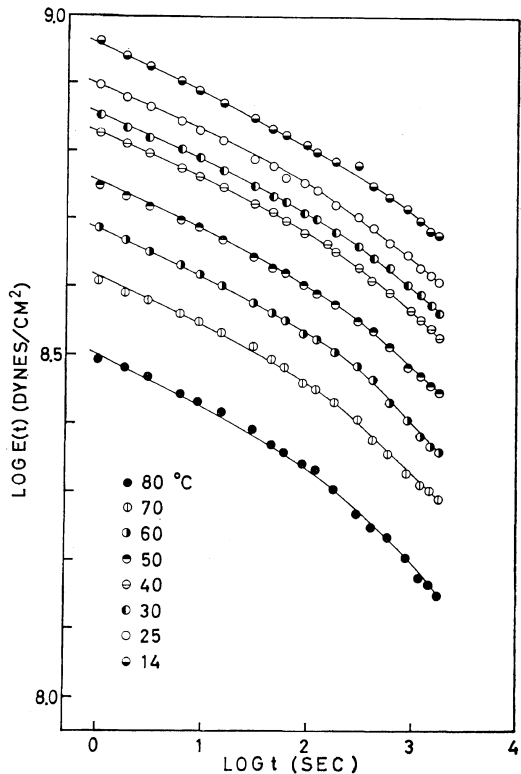


Figure 11. The variation of relaxation modulus $E(t)$ with the time t at different temperatures between 14 and 80°C for fresh samples.

In Figure 11 are shown the time dependence curves of the relaxation modulus measured simultaneously with the birefringence at various temperatures. As is evident from this figure, the relaxation modulus decreases with increasing time. The higher the temperature, the lower the relaxation modulus.

The time-temperature superposition was applied also to the relaxation modulus curves. Here again, not only horizontal but also vertical shifts were necessary to obtain a smooth master curve. In the master curve shown Figure 12, nonsuperposed branches are seen at the long-time end, just as in the case of the strain-optical coefficient. The arrows in the figure represent the relaxation times at which branches come out from the superposed portion in the master curve of the strain-optical coefficient. As is evident from Figure 12, the branching points of both curves are very close to each other. The branches must be due to a crystal transformation, which allows the stress to relax to a greater extent.

The logarithms of rheo-optical and mechanical horizontal shift factors, σ_T and a_T , are plotted against reciprocal absolute temperature in Figure 13. Both plots give straight lines, whose slopes are related to the activation energies ΔH_a . Values of 14.3 kcal/mol and 12.7 kcal/mol were obtained for the rheo-optical and mechanical relaxation processes respectively. These activation energies

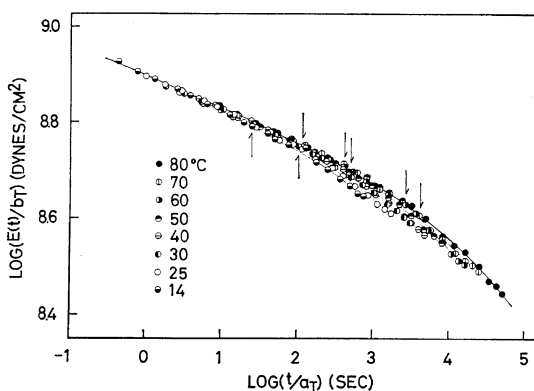


Figure 12. The variation of relaxation modulus $E(t)$ with reduced time (t/a_T) for fresh samples. The reference temperature is 25°C. b_T is a vertical shift factor. Arrows show branching points in the master curve of the strain-optical coefficient.

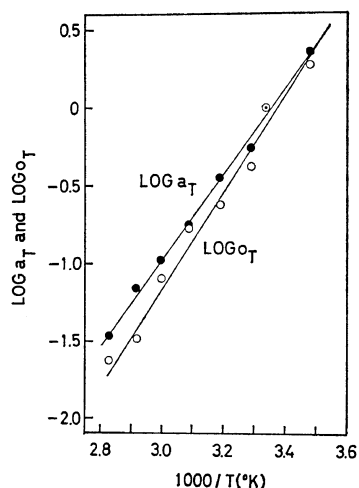


Figure 13. The variation of $\log a_T$ and $\log \sigma_T$ with $1/T$. The reference temperature is 25°C.

are for the orientation process of mod. II crystallites, and they appear to be a little smaller than those for polyolefins; typical values for such materials are 25 kcal/mol for the α_1 relaxation mechanism of polyethylene^{11,18,19} and 18–20 kcal/mol for the α relaxation mechanism of isotactic polypropylene.¹²

The Evaluation of Intrinsic Birefringence of Modification I and Modification II

In general, the total strain-optical coefficient for crystalline polymers can be expressed by the following equation:

$$\Delta/\gamma = (\Delta/\gamma)_c + (\Delta/\gamma)_a + (\Delta/\gamma)_f \quad (4)$$

where $(\Delta/\gamma)_c$, $(\Delta/\gamma)_a$, and $(\Delta/\gamma)_f$ are the contributions to the total birefringence from the crystalline region, the amorphous region, and form birefringence, respectively. In the case of polybutene-1, $(\Delta/\gamma)_c$ must be expressed by the following equation:

$$(\Delta/\gamma)_c = X[\Delta_{II}^0(F_{II}/\gamma)(1-\Phi) + \Delta_I^0(F_I/\gamma)\Phi] \quad (5)$$

where Δ_I^0 and Δ_{II}^0 are the intrinsic birefringence of mod. I and mod. II crystals, respectively. Here X is the crystallinity of the sample. Equation 5 can be rewritten as follows:

$$(\Delta/\gamma)_c = X\{(\Delta_I^0 - \Delta_{II}^0)(F_I/\gamma)\Phi + [(F_{II}/\gamma)(1-\Phi) + (F_I/\gamma)\Phi]\Delta_{II}^0\} \quad (6)$$

The first term of eq 6 corresponds to the increase in Δ/γ due to the crystal transformation.

Table I. $d(\Delta/\gamma)_s/dt$, $d\Phi/dt$, and their ratio at different temperatures

Temp, °C	$d(\Delta/\gamma)_s/dt$, min ⁻¹	$d\Phi/dt$, min ⁻¹	$(d(\Delta/\gamma)_s/dt)/(d\Phi/dt)$
30	6.8×10^{-5}	3.20×10^{-3}	2.12×10^{-2}
40	8.8	4.00	2.20
50	8.4	3.90	2.15
60	6.9	3.05	2.26
Average:			2.18×10^{-2}

Therefore it represents the nonsuperposed branch $(\Delta/\gamma)_s$ mentioned above. This can be obtained by subtracting the experimental value of the superposed portion $(\Delta/\gamma)_m$ from that of the total strain-optical coefficient Δ/γ . That is,

$$(\Delta/\gamma)_s = X(\Delta_{I1}^0 - \Delta_{II1}^0)(F_{I1}/\gamma)\Phi \quad (7)$$

Therefore,

$$\Delta_{I1}^0 - \Delta_{II1}^0 = \frac{(\Delta/\gamma)_s}{X(F_{I1}/\gamma)\Phi} \quad (8)$$

And $(\Delta/\gamma)_m$ is expressed by the following equation:

$$\begin{aligned} (\Delta/\gamma)_m &= \Delta/\gamma - (\Delta/\gamma)_s \\ &= (\Delta/\gamma)_a + (\Delta/\gamma)_r + (F_{II1}^*/\gamma)X\Delta_{II1}^0 \quad (9) \end{aligned}$$

where F_{II1}^* is the orientation function obtained by assuming that crystal transformation does not take place. It is well known that $(\Delta/\gamma)_a$ and $(\Delta/\gamma)_r$ are independent of time in the range covered by this study. Also, the summation of $(\Delta/\gamma)_a$ and $(\Delta/\gamma)_r$ is negligibly small compared with $(F_{II1}^*/\gamma)X\Delta_{II1}^0$ at the temperature range covered by this study, as expected from Figure 5. Therefore, the last term in eq 9 corresponds to the second term in eq 4. Therefore,

$$F_{II1}^* = F_{II1}(1 - \Phi) + F_{I1}\Phi \quad (10)$$

Both $(\Delta/\gamma)_s$ and Φ increase almost linearly with increasing time, as shown in Figures 6 and 7. The slopes of those lines, $d(\Delta/\gamma)_s/dt$, $d\Phi/dt$, and their ratio were calculated at different temperatures between 30 and 60 °C. These results are summarized in Table I. This temperature range appears to be suitable for the calculations, because the rate of crystal transformation is large. As shown in Table I, the ratio of $d(\Delta/\gamma)_s/dt$ to $d\Phi/dt$ is almost constant and independent of temperature. The value may give the value of $(\Delta/\gamma)_s/\Phi$ in eq 8. Between 30 and 60°C, F_{I1} at 100 min after stretching is almost constant at

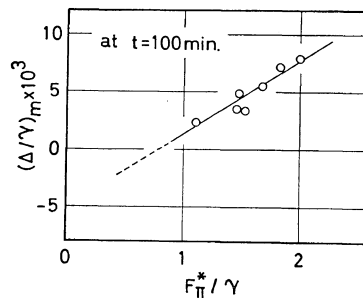


Figure 14. The variation of $(\Delta/\gamma)_m$ with F_{II1}^*/γ at 100 min after stretching at various temperatures between 14 and 70°C.

0.2, as shown in Figure 10. The degree of crystallinity in volume fraction is also almost constant, 0.50, between 30 and 60°C, as shown in Figure 1. Therefore, $\Delta_{I1}^0 - \Delta_{II1}^0$ can be found from eq 8 to be 2.18×10^{-2} . On the other hand, $(\Delta/\gamma)_m$ at 100 min after stretching was estimated from the master curve at various temperatures. F_{II1}^* at 100 min after stretching was calculated from eq 10 by using the values of F_{I1} and F_{II1} shown in Figure 10. $(\Delta/\gamma)_m$ is plotted against F_{II1}^*/γ at 100 min after stretching in Figure 14. This plot can be approximated by a straight line, whose slope is 6.3×10^{-3} . As is evident from eq 9, the slope gives $X\Delta_{II1}^0$. Therefore Δ_{II1}^0 can be evaluated. Its value is 0.013, and consequently Δ_{I1}^0 has the value of 0.034.

The intrinsic birefringence for the crystalline phase of polyethylene is 0.058, which may be estimated from the refractive indices of *n*-paraffins.²⁰ That for polypropylene is estimated from a knowledge of the carbon-carbon bond polarizability values and the unit cell structure.²¹ The values were found to be 0.067 and 0.015, using the Denbigh bond polarizability²² and Bunn-Daubeny bond polarizability²³ values, respectively. The values of 0.013 for the mod. II crystal and 0.034 for mod. I crystal are com-

parable with values for polyethylene and polypropylene.

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