

The Effect of Radiation-Induced Cross-Linking on the Relaxation of Taut Tie Molecules During Annealing of Drawn LDPE

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SYNOPSIS

Shrinkage, retractive stress, and infrared dichroism of the drawn low-density polyethylene (LDPE) as-drawn and irradiated by ^{60}Co -ray have been measured under different annealing conditions. The shrinkage and the disorientation of the irradiated sample was undergone more rapidly than that of unirradiated one as the temperature was continuously increased, surpassing a certain value, and a higher degree of shrinkage and disorientation was achieved finally for the irradiated sample when the samples were annealed with free ends. For the samples heated isothermally with fixed ends, the retractive stress went through a maximum and then attenuated to a limited value, and the degree of such a stress attenuation for the unirradiated sample was much more than that for the irradiated sample. These results show that the taut tie molecules (TTMs) in drawn PE can relax by the pulling of chain segments out of crystal blocks that they anchored in at elevated temperatures higher than the α transition and also by the displacing of microfibrils if the samples were annealed with free ends. The cross-links produced by irradiation prohibit the former process. It was further observed that the dependence of the average extinction coefficient of the band at 2016 cm^{-1} on that of the band at 1894 cm^{-1} is related to irradiation and annealing conditions, which has also been explained by the relaxation of TTMs and the function of irradiation-induced cross-linking on the relaxation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Peterlin¹ developed a satisfactory model of oriented crystalline polymers more than a decade ago. According to this model, the polymers oriented by drawing are composed of some microfibrils in which there are highly oriented folded chain crystals separated by amorphous layers and connected by many taut tie molecules (TTMs). Some of the TTMs adjoin the neighbor microfibrils (interfibrillar TTMs) and some locate within the amorphous layers (intrafibrillar TTMs). These TTMs result from the tie molecules in the original, undrawn polymers and remain in the amorphous state after drawing.² They play a major role on the mechanical properties of the oriented polymers.³ Dijkstra and Pennings⁴ explained the dependence of the modulus of ultrahigh

molecule weight polyethylene fibers on the fraction of the TTMs by a simple model. However, the real structure of oriented crystalline polymers, especially oriented by cold drawing, is more complicated. In their studies of annealing of drawn LDPE and isotactic polypropylene by measuring retractive stress, Decandia et al.^{5,6} observed the drop of retractive stress from a maximum to a limited value as the samples were detected isothermally. This has been explained by the structural change: The chain segments are rapidly pulled out of the crystal lattice in which the interfibrillar tie molecules are anchored and so the contour length of the tie molecules is increased. In a more recent study, Prasad and Grubb⁷ found that the 1063 cm^{-1} band in the Raman spectra of deformed PE develops a broad low intensity tail extending to 1000 cm^{-1} , which is attributed to result from the TTMs. Up to now, this Raman spectrum technique was the only one available for direct observation of TTMs.

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The purpose of this study was to investigate the effect of irradiation on structural change of drawn LDPE, especially on the relaxation of TTMs during annealing using the measurements of shrinkage, infrared absorption, and retractive stress.

EXPERIMENTAL

Preparation of Samples

Low-density polyethylene (LDPE) pellets with MFR = 2.0 were produced by the Qian Jin Chemical Plant, Beijing, China. The pellets were heated above the melting point for 7 min and then were press-molded into a 1 mm-thick sheet at 150°C for 5 min. The sheet was then taken into another hydraulic press and cooled to room temperature.

High-density polyethylene (HDPE) sheets were prepared with the same procedure as were the LDPE sheets, except that the compression-molding temperature was 160°C. The HDPE pellets, called Marlex 6001, with MFR = 0.5 were produced by the Phillips Petroleum Company.

Oriented specimens were prepared by cold-drawing 60 × 20 mm² sheets with a tensile testing machine at ca. 20°C. A crosshead speed of 10 mm/min was used. Draw ratios obtained by measuring the distances between pen marks were equal to 3.4 and 9.0 for the LDPE and HDPE samples, respectively.

Irradiated samples were obtained by the following procedure: Drawn LDPE and HDPE sheets sealed in a glass tube *in vacuo* were irradiated by ⁶⁰Co-ray with a dose rate of 1.2 × 10⁴ Gy/h and then the samples were taken out after being stored in the tube for 2 days.

Annealing

The oriented samples with fixed ends were directly immersed into silicon oil and annealed for 100 min at given temperatures (±0.4°C).

Shrinkage

The strips of oriented sample were vertically hanged while their temperatures were continuously raised at a rate of 10°C/min. The length of the strips was recorded and the shrinkage rate of the samples obtained.

Infrared Spectra

IR spectra were recorded by a Digilab FTS-20E Fourier transformation photometer incorporating a

wire grid polarizer. The absorption of polarizer was subtracted from the spectra. The axial directions of the oriented samples and the polarizer were at +45° and -45° to the spectrometer slit, respectively. The typical spectra of drawn LDPE in the range of 1800–2100 cm⁻¹ are shown in Figure 1. The base lines applied for the evaluation of the absorbance are also indicated in the figure.

The orientation function (f) characterizing the orientation of uniaxially deformed samples was calculated from the dichroic ratio $D = A_{\parallel}/A_{\perp}$, where A_{\parallel} and A_{\perp} are the absorbance of polarized radiation parallel and perpendicular to the draw direction, respectively. The relation between dichroic ratio (D) and the orientation function is as follows⁸:

$$f = \frac{D - 1}{D + 2} \frac{D_0 + 2}{D_0 - 1} \quad (1)$$

with $D_0 = 2 \cot^2 \beta$, where β is the angle between transition moment and the chain axis. The orientation function of the sample annealed at 40°C was taken as a reference. Then, a relative orientation function of F_{rel} is defined as

$$\begin{aligned} F_{\text{rel}}(T) &= \frac{f(T)}{f(T = 40)} \\ &= \frac{(D(T) - 1)(D(40) + 2)}{(D(T) + 2)(D(40) - 1)} \quad (2) \end{aligned}$$

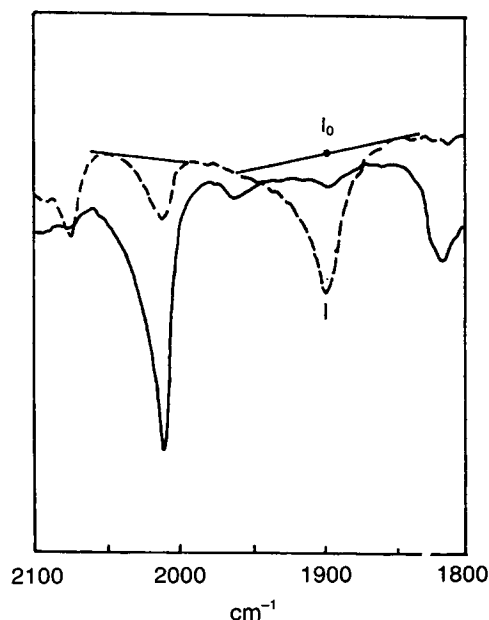


Figure 1 Infrared spectra of drawn LDPE with polarized radiation parallel (—) and perpendicular (----) to the draw direction. The base lines are indicated.

At the same time, the average extinction coefficient, which is irrelevant to the orientation of sample, was calculated from the parallel and perpendicular extinction coefficients by the relation

$$A = \frac{A_{\parallel} + 2A_{\perp}}{3} \quad (3)$$

Retractive Stress

The retractive stress of the samples was determined with an Instron model 1121 mechanical tester. When the oven reached to a given temperature, the sample was rapidly clamped between the two crossheads and the change of retractive stress with time recorded. When the temperature dependence of retractive stress was detected, the samples were prestressed to ca. 0.5 MPa and then the temperature was gradually increased. Because of a lack of a programmable temperature controller, the rates of heating and cooling were not controlled.

RESULTS AND DISCUSSION

Shrinkage

Dependence of shrinkage of the irradiated and unirradiated drawn samples on temperature is shown in Figure 2. It is seen that irradiation affects the drawn LDPE and HDPE in a similar way. The shrinkage increases of irradiated samples are slower than those

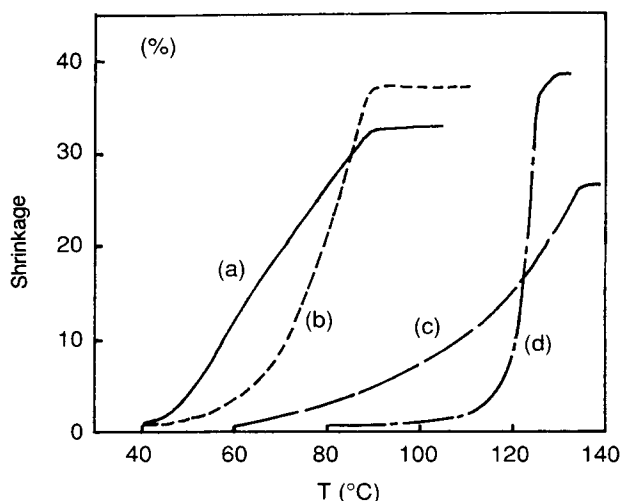


Figure 2 Temperature dependence of shrinkage of the samples: (a) LDPE as-drawn; (b) LDPE drawn and irradiated with doses of 2.44×10^6 Gy; (c) HDPE as-drawn; (d) HDPE drawn and irradiated with doses of 3.84×10^6 Gy.

of unirradiated samples in the low-temperature region ($< 70^\circ\text{C}$ for LDPE and 115°C for HDPE), but much faster in the high-temperature region, and the shrinkage of the irradiated samples exceeds that of the unirradiated as the temperature surpasses certain values.

According to Peterlin's structural model,² annealing drawn crystalline polymer mobilizes the almost fully extended amorphous tie molecules that try to assume the thermodynamically required random conformations and the oriented crystalline sample shrinks if annealed with free ends, which permits the crystal blocks in different microfibrils and connected by almost extended TTMs to move toward the position that they had before plastic deformation. Hence, the end-to-end distance or the fraction of the TTMs in the amorphous region is reduced. The shrinkage rate of the sample is determined by competition of the retractive forces of TTMs with the frictional forces or the Van der Waals forces among neighbor fibers and/or microfibrils. With increasing temperature, the retractive forces increase and the cohesive (or frictional) forces decrease. When the retractive forces increase to a certain value surpassing the frictional forces, the sample begins to shrink. As temperature reaches into the α transition temperature range, the entropic retractive forces of TTMs may be lower than the frictional forces but higher than what is needed to pull some chain segments out of the crystalline blocks and disentangle them in the amorphous region; the pulling of the chain segments and the disentanglement would permit the relaxation of TTMs as well as the displacement of the microfibrils.

The irradiation of drawn polyethylene was carried out in a vacuum environment: The main results were chain cross-links formed within the amorphous region and the paracrystallite.⁹ Thus, it is impossible for some chains in the amorphous region to disentangle and some chain segments attached by the TTMs to be pulled out of crystal lattice even at temperatures higher than the α transition because of these cross-links. In such a case, more TTMs could be maintained and could exerted retractive forces on the blocks that they are anchored in. Therefore, the irradiated sample shrinks more rapidly in the high-temperature region (Fig. 2). On the other hand, it can be predicted that irradiation-induced cross-linking at the molecules belonging to different microfibrils seldom takes place because of the serious separation of the microfibrils. However, the existence of a few of such cross-links would inhabit some microfibrils to displace, resulting in lower shrinkage at low temperatures for the irradiated samples in

Figure 2. As soon as this resistance is overcome, the irradiated samples in which there are more mobilized TTMs shrink more rapidly.

It seems surprising that the irradiated samples have higher shrinkage than that of the unirradiated ones at a high enough temperature, such as at 90°C for the drawn LDPE and 130°C for the drawn HDPE (Fig. 2). This can also be interpreted by the effect of irradiation on the relaxation of TTMs. The TTMs, with the equal contour length and end-to-end distance, in irradiated and unirradiated samples, would reach to the same relaxed state while the temperature was increased to one certain value. Some TTMs with the cross-linked ends in crystalline blocks should have originally been able to relax by both pulling chain segments out of crystal lattice and displacing the microfibrils if the sample were not irradiated, but now they can relax only by displacing the microfibrils in a greater magnitude to reach the same relaxed state. Therefore, the irradiated samples have a higher level of shrinkage at high temperatures. The effect of irradiation on the shrinkage of oriented HDPE has been simply explained in the literature¹⁰ by that irradiation induces the melting point of sample to decrease.

Disorientation

Infrared (IR) spectroscopy has been used to investigate the orientation of drawn HDPE⁸ and disorientation of annealed, hot-drawn LDPE.¹¹ It is known that the band at 1894 cm⁻¹ arises from the crystalline phase entirely and is polarized perpendicular to the *c* crystallographic axis, although it is unclear whether the net transition moment lies along the *a* axis or the *b* axis or along some intermediate directions. Using the relative orientation function F_{rel} [eq. (2)] to describe the change in orientation, it is unnecessary to consider the direction of transition moment. Figure 3 shows variation of the dichroism of the band at 1894 cm⁻¹ and the corresponding orientation function with annealing temperature for the irradiated and unirradiated samples. Below 76°C, the irradiated sample has a higher orientation than that of the unirradiated one, but the difference in the F_{rel} between the two samples is small. Above 76°C, the irradiated sample disorients more than does the unirradiated one.

Plots of the dichroism of the band at 2016 cm⁻¹ vs. annealing temperature are presented in Figure 4. Qualitatively, the effect of irradiation on the dichroism of the band at 2016 cm⁻¹ is similar to that on the shrinkage (Fig. 2) and on the relative orientation function of crystallites (Fig. 3). It is noted that, in the low-temperature region, the D_{2016} shows

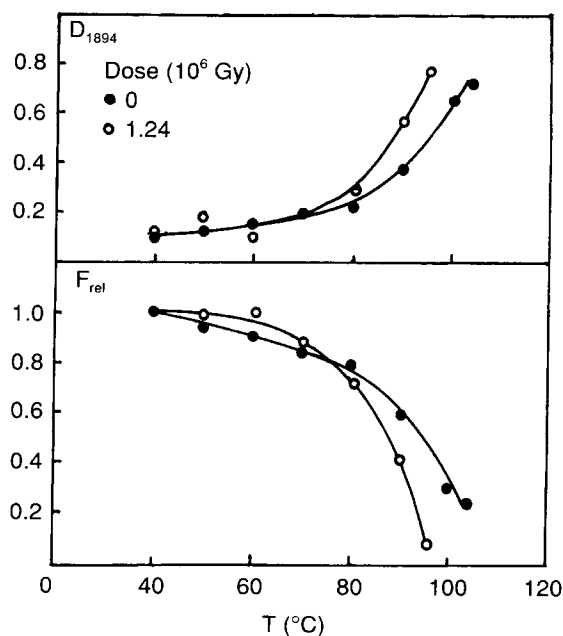


Figure 3 Dichroic ratio and relative orientation function of the band at 1894 cm⁻¹ as a function of annealing temperature for the LDPE samples as-drawn (●) and irradiated with doses of 1.24 × 10⁶ Gy (○).

a great difference but the D_{1894} a small difference (Fig. 3) between the irradiated and unirradiated samples.

The 2016 cm⁻¹ band has been attributed to both crystalline and amorphous phases.⁸ The nature of the amorphous component has not been clearly established. Read and Stain⁸ thought that the amorphous component was due to extended *trans* sequences because the band is a combination involving both the 1295 and 720 cm⁻¹ fundamentals. Through analyzing the results obtained on this band, appearing at 2033 cm⁻¹, of cross-linked amorphous polyethylene at 170°C, Read and Hughes¹² suggested that the orienting units comprise, on average, *trans* sequences of about seven chain bonds. Krimm¹³ suggested that the infrared band also involves some combination between the infrared bands at 1303 and 720 cm⁻¹, indicating that some *gauche* units may be partially involved in the amorphous component. In any case, this band should be partially devoted by the almost fully extended TTMs except for the crystalline molecule chains and perhaps some *gauche* units. In the low-temperature region, the great difference in D_{2016} (Fig. 4) arises mainly from the TTMs and perhaps some *gauche* units because of the small difference in D_{1894} (Fig. 3). This is identical with the result that the irradiated sample has small shrinkage (Fig. 2), resulting in a lesser degree of disorientation of the TTMs and some *gauche* units.

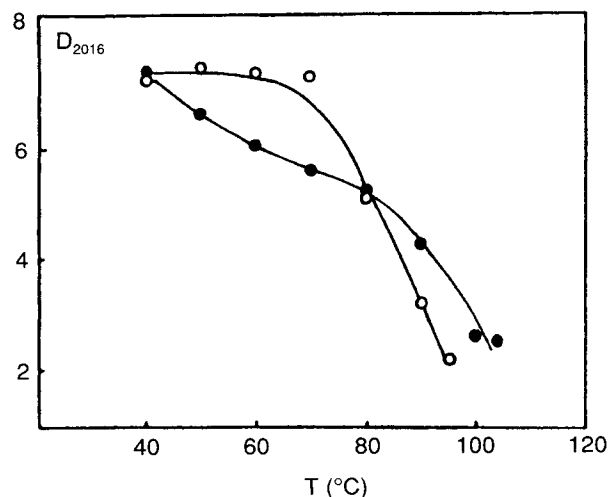


Figure 4 Dichroic ratio of the band at 2016 cm^{-1} as a function of annealing temperature for the LDPE samples as drawn (●) and irradiated with doses of $1.24 \times 10^6\text{ Gy}$ (○).

In the high-temperature region, where the α transition locates, the higher degree of disorientation of crystals (Fig. 3) and TTMs (Fig. 4) as well as the shrinkage of the samples is interpreted by that irradiation-induced cross-links prevent some chain segments from pulling microfibrils out of crystalline blocks.

Retractive Stress

When drawn polymer is annealed with fixed ends, TTMs in it tend to return from their extended state to the initial relaxed state before being drawn, which exerts entropic retractive forces to the microfibrils. Consequently, the sample has a bulk retractive force. Only the TTMs with T_g below the annealing temperature contribute to the retractive stress.⁵ The T_g of amorphous materials, including the TTMs, in a semicrystalline polymer is related to their chain mobility. The restraint of crystals on the amorphous chains tends to reduce the chain mobility and so promote the T_g . The retractive force contributed by each mobilized TTM at temperature T depends on the ratio of the end-to-end distance h and the contour length L of the mobilized section between the blocks it is anchored in. According to Kuhn and Grün,¹⁴ one has

$$f = \frac{3kTh}{h_0^2} \left(1 + \frac{3h}{5L} + \dots \right) \quad (h \rightarrow 0)$$

$$= \frac{kT}{h_0^2} \frac{L^2}{L - h} \quad (h \rightarrow L) \quad (4)$$

where k is the Boltzmann constant, and h_0 , the root-mean-square end-to-end distance of the chains with contour length L . It means that a high retractive force at the mobilization of the almost fully extended TTM decays rapidly, as by increasing L (pulling of some chain elements out of the crystalline blocks) or decreasing h (pulling the crystalline blocks closer together) the ratio h/L becomes smaller. The initial TTM is gradually transformed in a lax tie molecule (TM).

The time dependence of the retractive stress of the samples with fixed ends under the given temperatures is shown in Figure 5. The influence of irradiation on the retractive stress of drawn LDPE is similar to that on the retractive stress of drawn HDPE. The retractive stress first increases rapidly to a maximum as a consequence of the gradual heating of the sample and subsequently drops to a limiting value. That of the irradiated samples drops much less and approaches a higher limiting value than that of the irradiated ones. Because of the fixation of the ends of sample, it is impossible for fibrils and/or microfibrils to mutually displace. The TTMs can relax only by pulling some chain segments out of crystalline blocks through the α transition and

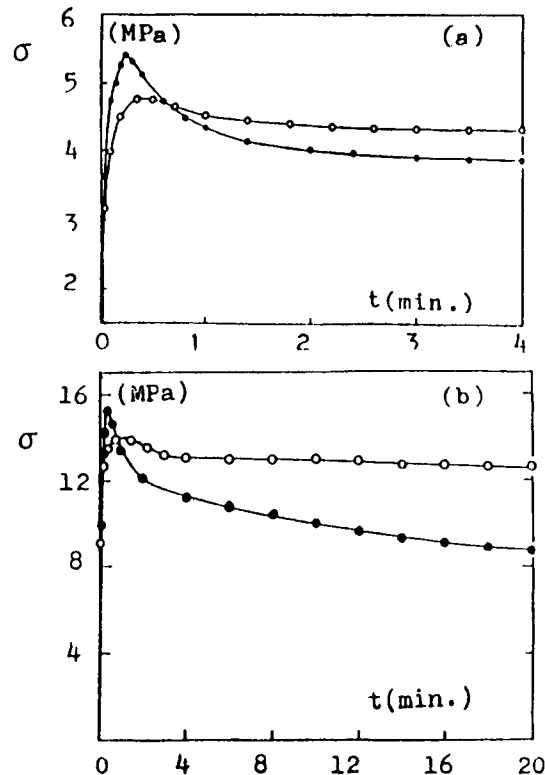


Figure 5 Time dependence of retractive stress for (a) LDPE and (b) HDPE samples measured at 85 and 110°C, respectively. Irradiation doses: (●) 0; (○) $1.24 \times 10^6\text{ Gy}$.

the disentanglement in the amorphous region.⁵ Figure 5 illustrates clearly that the cross-links produced by irradiation inhibit such a process. In addition, the maximums of retractive stress of irradiated samples are lower than those of unirradiated ones, reflecting the role of irradiation on the fraction of the TTMs.

Figure 6 presents retractive stress of the irradiated and unirradiated samples as a function of temperature in the heating and cooling cycle, 30–99–30°C. The retractive stress of both irradiated and unirradiated samples increases with increasing temperature up to 85°C, and that of the irradiated sample is higher at temperatures below ca. 57°C and lower between 57°C and 85°C, indicating that the effect of irradiation on the T_g arrangement of the TTMs or the fraction of the TTMs mobilized under a certain temperature is rather complicated. It is possible that irradiation makes the total TTMs decrease more or less but the TTMs with low T_g increase. On the other hand in the high-temperature region (> ca. 65°C), retractive stress depends on the competition of two contrary effects according to eq. (4). It increases with increasing temperature T and decreases with increasing L due to relaxation of TTMs by pulling some chain segments out of crystalline blocks through the α transition of the crystalline region. In Figure 6, we see also that the retractive stress of the unirradiated sample increases to a maximum and starts to decrease at 84°C, but

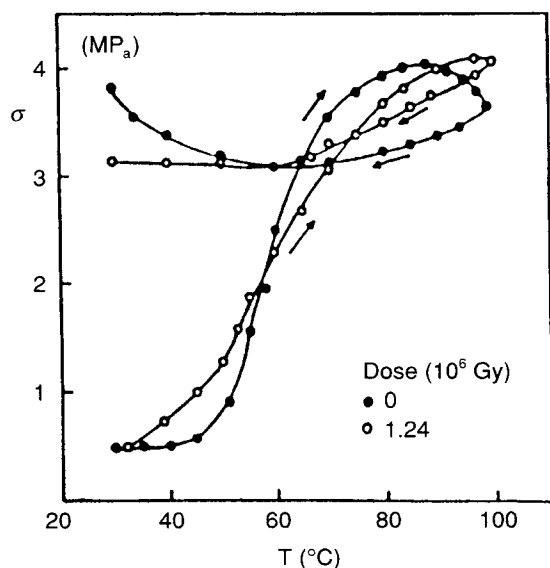


Figure 6 Variation of retractive stress with temperature during heating from 30 to 99°C and cooling to 30°C for the LDPE samples as-drawn (●) and irradiated with doses of 1.24×10^6 Gy (○).

that of the irradiated sample increases up to 99°C. No drop of retractive stress was observed for the irradiated sample until it broke if temperature was continuously increased. This may also be understood if one takes into account the function of irradiation-induced cross-links: The cross-links in amorphous and crystalline regions had made the relaxation of some TTMs impossible.

When the samples were cooled from high to low temperature, retractive stress did not return along the original path because of the irreversibility of the TTMs' relaxation. Based on eq. (4), retractive stress should have been linearly decreased with decreasing temperature if the states of TTMs did not change. However, as shown in Figure 6, with decreasing temperature, the slope of retractive stress curves decreases, the retractive stress of unirradiated sample goes upward below 60°C, and that of the irradiated one is almost constant. A similar phenomenon has also been observed for several drawn amorphous polymers, including bisphenol-A polycarbonate, PMMA, etc.¹⁵ As an explanation, the energy storage mechanism has been proposed by Adams and Farris.¹⁵

Average IR Absorbance

As discussed above, the 2016 cm^{-1} band is partly devoted by the intra- and interfibrillar TTMs in the *trans-trans* conformation. To confirm the relaxation of the TTMs, the average extinction coefficients of the bands at 2016 and 1894 cm^{-1} were calculated for the drawn samples. Figure 7(a) presents the temperature dependence of the two extinction coefficients for the drawn LDPE annealed with free ends. The extinction coefficient of the band at 1894 cm^{-1} (E_{1894}) increases but that (E_{2016}) of the band at 2016 cm^{-1} decreases with increasing temperature for both the irradiated and unirradiated samples. The smaller extinction coefficient of the irradiated sample annealed at 40°C is due to the damage of irradiation to the crystalline phase because the annealing effect is very little at so low a temperature. To demonstrate variation of the amorphous chains attributed mainly to the band at 2016 cm^{-1} , the extinction coefficient of this band has been plotted against that of the band at 1894 cm^{-1} in Figure 7(b). The E_{2016} decreases more rapidly with increasing the E_{1894} for the irradiated sample than for the unirradiated one. For the latter, the E_{2016} decreases linearly with increasing the E_{1894} .

The extinction coefficients of the samples annealed with fixed ends are presented in Figure 8. With increasing the E_{1894} , the E_{2016} decreases linearly

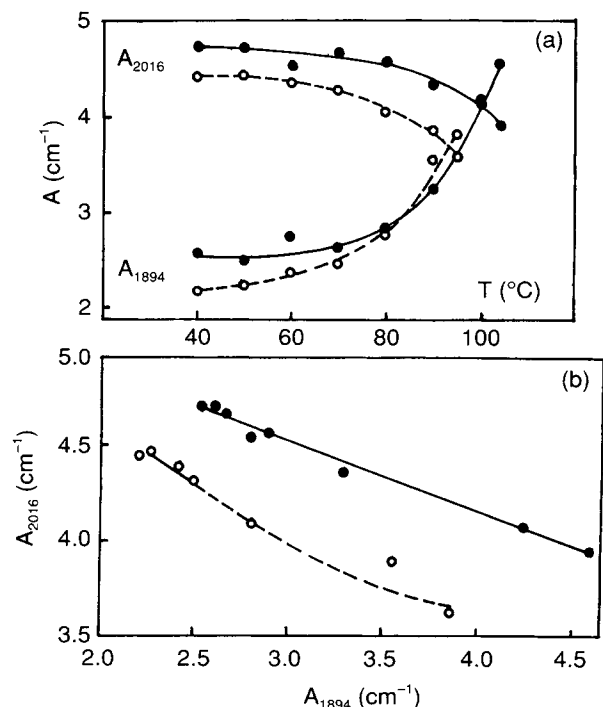


Figure 7 (a) Average extinction coefficients of the bands at 2016 and 1894 cm^{-1} as a function of annealing temperature; (b) plots of the average extinction coefficient of the band at 2016 cm^{-1} vs. that of the band at 1894 cm^{-1} for the LDPE samples, (●) as-drawn and (○) irradiated by doses of 5.27×10^5 Gy, annealed with free ends.

for the irradiated sample [Fig. 8(b)], being similar to the results of the samples annealed with free ends [Fig. 7(b)]. However, the E_{2016} shows no remarkable reduction but a small increase at high annealing temperature for the irradiated sample [Fig. 8(b)]. In addition, comparing the two straight lines in Figures 7(b) and 8(b), we can see that they have approximately the same rate of inclination, but all the values of D_{2016} in Figure 8(b) are higher than that in Figure 7(b).

The observed increase in the E_{1894} , e.g., from 2.6 to 4.5 in Figure 7, with increasing annealing temperature, is attributed to the increase in crystallinity. This results possibly from the cure of many defects in the crystalline region and the thickening of crystals. According to our knowledge, no one has observed the change in crystallinity of annealed drawn LDPE using IR spectra, but the relative change in the amount of crystalline species, when PE was drawn from a drawn ratio 5 to 20, has been observed to from 0.1 to 5.2 by measuring the E_{1894} .¹⁶ In contrast, the increase more than 70% in the E_{1894} detected in our experiment is acceptable.

All the results in Figures 7 and 8 are consistent

with the preceding discussion. The band at 2016 cm^{-1} is associated with crystalline phase, so any increase in crystallinity will result in an increase in the E_{2016} . The observed reduction in the E_{2016} (Figs. 7 and 8) results from the strong decreases, which may surpass the increase in the crystalline species, of the amorphous chains with *trans-trans* conformation (or the TTMs) and maybe of some *gauch* units. If the samples are annealed with fixed ends, TTMs relax only by pulling some chain segments out of the crystalline region through the α transition and the disentanglement in the amorphous region. The cross-links induced by irradiation prohibit this process; therefore, the contribution of the increased crystallinity to the band at 2016 cm^{-1} can complement the decreases of the TTMs and some *gauch* units for the sample irradiated by 5.27×10^5 Gy [Fig. 8(b)]. Consequently, the absorption of the sample does not decrease with increasing the E_{1894} . If samples are annealed with free ends, the TTMs are depleted chiefly by the relative sliding of the microfibrils besides the pulling of some chain segment out of the crystalline blocks. Therefore, all the E_{2016} have smaller values in Figure 8 than in Figure 7 for the unirradiated samples, and with increasing E_{1894} , a more substantial drop of the absorbance of the band at 2016 cm^{-1} is detected for the irradiated sample (Fig. 7) than for the unirradiated samples

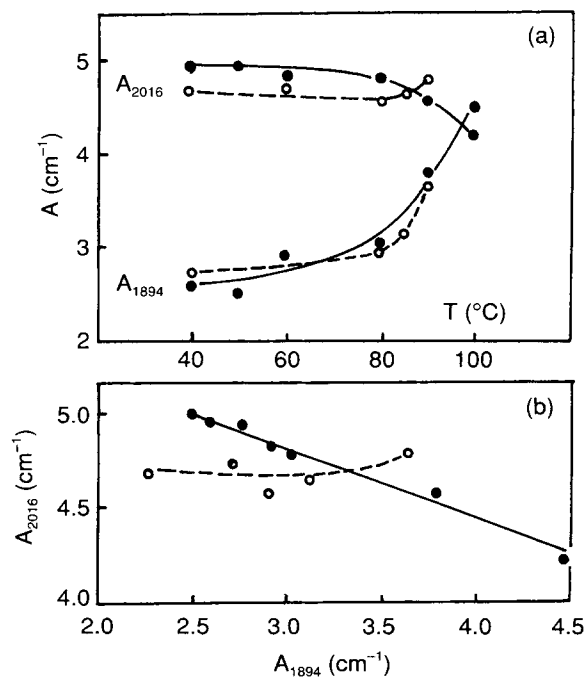


Figure 8 The same plots as Figure 7 for the LDPE samples, (●) as-drawn and (○) irradiated with doses of 5.27×10^5 , annealed with fixed ends.

because the irradiated sample achieves more shrinkage above a certain temperature (Fig. 2).

CONCLUSION

The shrinkage and the IR disorientation of cold-drawn LDPE annealed with free ends, the retractive stress of the samples heated with fixed ends, and the average extinction coefficients of the IR bands at 1894 and 2016 cm^{-1} are dependent on irradiation and annealing conditions. The dependence can be explained with the microfibrillar structure model of oriented crystalline polymers. All the results are associated with the TTMs in drawn LDPE. The TTMs in the samples with fixed ends can relax by pulling some chain segments out of crystalline lattice via the α transition process during annealing. In addition to such relaxation, the TTMs in the sample annealed with free ends are still depleted by the relative displacement of microfibrils. The cross-links, in the crystalline blocks, induced by irradiation hinder the former process.

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