

Shrinkage and Retractive Force of Drawn Isotactic Polypropylene during Heating

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Synopsis

The semi-crystalline isotactic polypropylene was drawn to $\lambda = 6,7,8,9,11$ and the drawn samples heated to temperatures between 40 and 160°C. The shrinkage of the sample with $\lambda = 7$ and 11 was measured as function of time and temperature. The effect of shrinkage is higher with the smaller draw ratio as if the drawing increased the thermal stability of the sample. With fixed ends the drawn samples were heated at a constant rate and the retractive stress observed. It increases with λ and the heating rate. At the same drawing ratio λ , the curves of the retractive stress show a maximum and subsequently drop to a substantially smaller value that increases with the draw ratio and the distance of the highest temperature of the heating from the melting point of the sample. The cooling curve of the first run almost coincides with the heating and cooling curve of the next runs if one does not surpass the maximum temperature of heating of the first run. The time dependence of the retractive stress after an initial maximum decays more rapidly to the limiting value $\sigma_{\infty}(T)$ the higher the temperature of the experiment. The limiting value $\sigma_{\infty}(T)$ rapidly decreases with T and increases with λ .

INTRODUCTION

The asymptotic values of the changes of the sorption and diffusion coefficients in drawn, and drawn and annealed isotactic polypropylene (iPP) were just reported.¹ The present paper describes the shrinkage at free ends and the retractive stress at fixed ends of a drawn sample heated after drawing to temperatures between room temperature and a few degrees below the melting temperature.

EXPERIMENTAL

The iPP of $M_n = 15,600$ and $M_w = 307,000$ was drawn at room temperature to $\lambda = 7$ and at 80°C to $\lambda = 6, 8, 9, \text{ and } 11$. The initial dog-bone specimen had a drawable length of 1 cm and a cross section $5 \times 0.4 \text{ mm}^2$. The constant velocity of the clamps was 0.6 cm/min. The apparent draw ratio $\lambda = l/l_0$ of the material was determined from the displacement to l of the marks that in the stretched but undrawn sample were at a distance $l_0 = 0.6 \text{ cm}$. Both values were measured under applied stress in the stretching instrument. The elastic deformation makes the apparent l/l_0 a little higher than the actual draw ratio that is achieved by purely plastic deformation. The difference, however, is so small that it may be neglected.²

The drawn sample was permitted to shrink in an oil bath at a temperature between 40 and 160°C. For measuring the retractive stress, one has clamped

the sample between the claws of a dynamometer cell and heated in the bath. In order to begin with a completely straight sample, one has applied an initial stretching force corresponding to a tensile stress of a little more than 1 MPa. One finds all the details of the treatment of the measurements in connection with the retractive force in Ref. 3.

RESULTS

The amount of *shrinkage* of free samples drawn to $\lambda = 7$ and 11, respectively, is shown in Figures 1 and 2. The former figure shows the time dependence of the shrinkage $1 - l/l_\lambda$ for both samples at room temperature after annealing for t_A at $T_A = 130^\circ\text{C}$, the latter figure the limiting values $1 - l_\infty/l_\lambda$ obtained after a long annealing time when the length did not change observably. The temperature interval was 10 K. At the highest temperature of the experiment, 155°C for $\lambda = 7$ and 160°C for $\lambda = 11$, the asymptotic length $l_\infty = 0.155 \times l_7$ and $0.265 \times l_{11}$ of the shrunk sample is still slightly above l_0 , that is, roughly $l_7/7 = 0.14 \times l_7$ and $l_{11}/11 = 0.09 \times l_{11}$, respectively. Note that the shrinkage is much more conspicuous for the sample with the smaller λ than for that with the higher draw ratio, although in the former case the maximum shrinkage temperature was farther away from the melting at 165°C than in the latter case.

According to the measurement of drawn linear polyethylene (PE)^{4,5} and nylon fibers⁶ even at the melting point, the sample free to shrink never returned to the length before the drawing. During the drawing some chains slipped irreversibly and hence do not show any tendency to return to the length of the initial sample. The explanation for the incomplete shrinkage given in Ref. 5 is very likely in disagreement with other experiences. At sufficiently high heating all the crystalline bridges of TTM melt and hence do not prevent a full recovery. But the pulling out of the ends of TTM from the crystal blocks they are anchored in is an irretrievable process. Such an explanation is in full agreement with the observations on drawn nylon.⁶

The behavior found in PE and in nylon fibers immediately applies to any drawn polymer. Hence, one expects that the measured maximum shrinkage will always yield a longer length than that of the sample before the drawing.

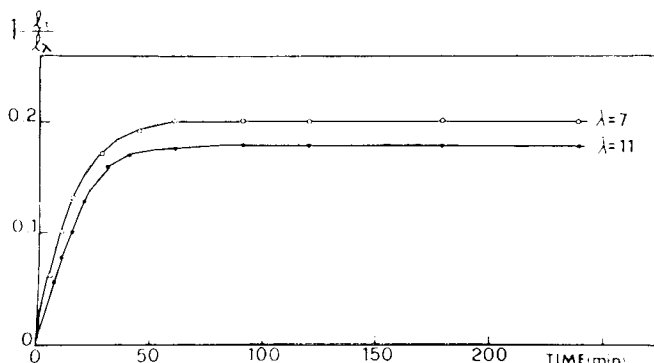


Fig. 1. The time (t_A) dependence of the shrinkage $1 - l/l_\lambda$ for the samples drawn to a draw ratio $\lambda = 7$ and 11, respectively, heated to $T_A = 130^\circ\text{C}$.

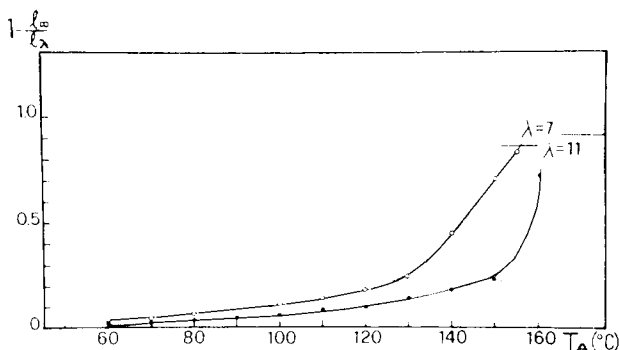


Fig. 2. The temperature (T) dependence of the maximum relative shrinkage $1 - l_{\infty}/l_{\lambda}$ for the sample drawn at room temperature to $\lambda = 7$ and at 80°C to the draw ratio $\lambda = 11$, respectively. The maximum theoretically achievable value $1 - l_{\infty}/l_{\lambda} = 0.86$ in the former and 0.91 in the latter case is indicated by short horizontal lines.

This fact was used for the determination of the so-called *molecular draw ratio*⁷ that in PE seems to be proportional to the axial elastic modulus of the specimen⁴ and hence to the fraction of taut tie molecules (TTM) in the amorphous section.⁸ The general fact that the asymptotic length of the shrunk sample is higher than that before the drawing is supported by our observation of the sample drawn to $\lambda = 11$. The data of the sample with $\lambda = 7$ are on the limit of this effect. The shrunken sample has almost the same length as the material before the drawing.

The shrinkage below 100°C is usually considered as a sign of the intrinsic instability of the drawn material.^{9,10} It shows up in drawn iPP as it does in drawn linear² and branched^{3,11} PE. At room temperature it is part of the aging process that continues over months and years.¹² In the present paper we shall not be involved with that.

But one must not forget that after the drawing, annealing, and standing at room temperature the slow crystallization of almost fully extended TTM in the bridges crossing the amorphous layers between the crystalline blocks of each microfibril increases as the sample length.¹³ Hence the observed shrinkage or expansion is the difference of both effects, the true shrinkage, and the partial recovery of the amorphous deformation on one side and the slow crystallization on the other side.

The sample drawn at room temperature to $\lambda = 7$ definitely shows a small length reduction even below 60°C that is not shown in Figure 2. It is uncertain whether a similar but smaller reduction also occurs with the sample drawn at 80°C to $\lambda = 11$. In both cases reported the extrapolation to room temperature seems to be extended over so wide a temperature range, from 60 to 20°C , that one may hardly assume the results to have any convincing validity, although they are pointing in the expected direction.

The *retractive stress* of the sample with fixed ends was investigated in repeated heating and cooling cycles. Figures 3 and 4 show the retractive force of the samples drawn to $\lambda = 7$ and 11 at heating rates $\Delta T/\text{min}$ equal to 0.5 , 1.0 , and 2 K/min. The sample was heated from 20 to 160°C (Fig. 3)

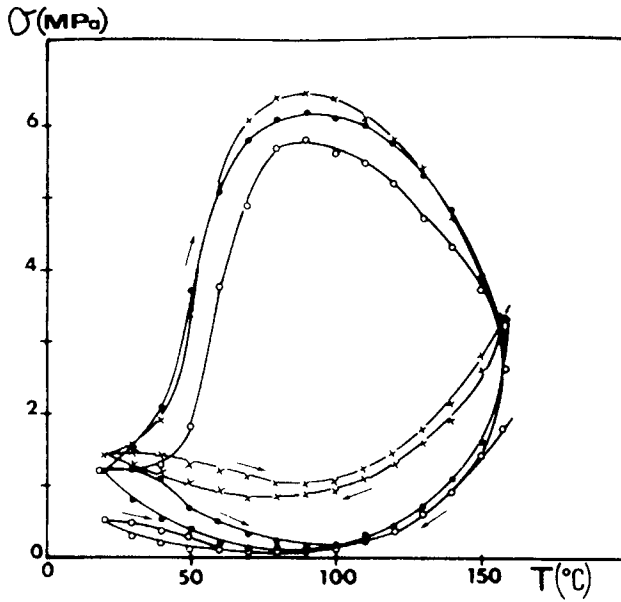


Fig. 3. The retractive stress cycle (first heating and cooling, the second heating after 24 h relaxation at room temperature) of the sample with $\lambda = 7$ at a heating rate 0.5 (○), 1.0 (●) and, 2.0 (X) K/min.

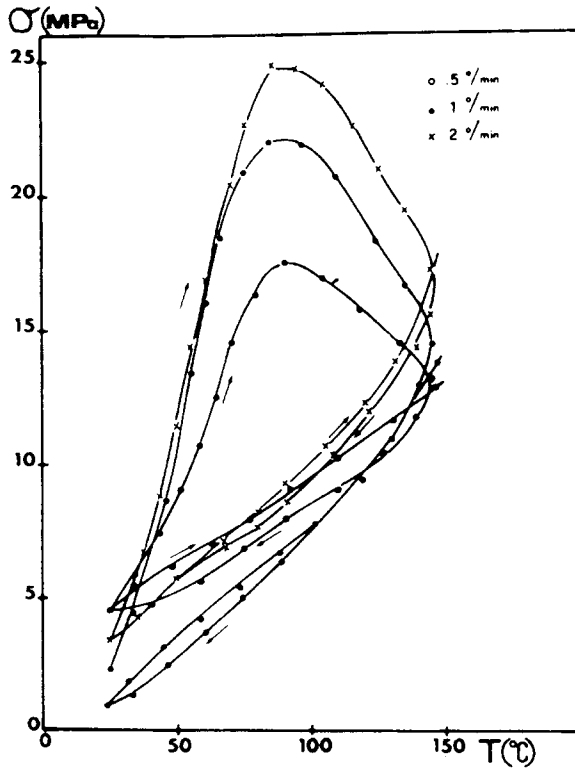


Fig. 4. The retractive stress cycle of the sample with $\lambda = 11$ at the same conditions as in Figure 3.

or from 40 to 140°C (Fig. 4) and cooled back to the starting temperature. The second heating was performed after the sample relaxed at room temperature for 1 day, i.e., for 24 h.

The sample drawn to $\lambda = 7$ (Fig. 3) and heated or cooled by 0.5 K/min did not return to the initial point of the curve. This was mainly caused by the long standing at the highest temperature, 160°C, of the first run that so much relaxed the sample. The other two rates, 1 and 2 K/min, without any prolonged standing at the highest temperature did not produce any such effect. The first heating in all cases yielded a high retraction stress maximum of about 6 MPa at 90°C. The cooling of the first cycle went through a minimum. The curve nearly coincided with subsequent heating and cooling curves, the former being a little higher than the latter ones. The cooling curves have a minimum at 80°C while the heating curves have it at 100 and 90°C with the heating rates 1 and 2 K/min, respectively.

The higher draw ratio = 11 (Fig. 4) shows a substantial increase of the retraction force and a clear cut dependence on the heating rate. If one goes from 0.5 to 2.0 K/min, the maximum retraction stress increases from 17.4 to 22.2 MPa. The influence of the heating rate is rather small on the initial increase and the final retractive stress at 40°C after completing the cycle. Most likely the differences observed at lower temperatures are caused by small but unavoidable measurement errors in the first heating and cooling curves. Hence they do not require a special explanation.

The maximum of the retractive stress in the first run is shown in Figure

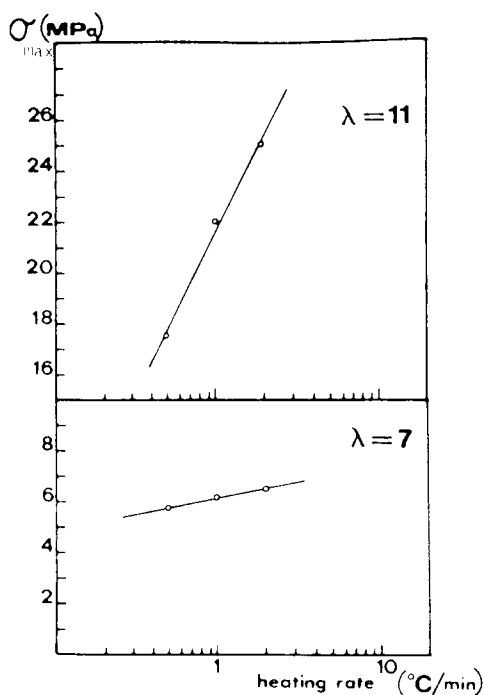


Fig. 5. The maximum retractive stress σ_{max} of the samples with $\lambda = 7$ and 11, respectively, as a function of the logarithm of the heating rate.

5. It turns out that the maximum stress is a linear function of the logarithm of the heating rate. One may write

$$\sigma_{\max} = A + B \log(\Delta T/\text{min}) \quad (1)$$

with $A = 6.2$ and $B = 1.33$ for $\lambda = 7$ and $A = 22.0$ and $B = 12.0$ for $\lambda = 11$, respectively. All the quantities σ_{\max} , A and B are expressed in MPa. The location of the maximum is almost constant at $T = 90^\circ\text{C}$ for $\lambda = 7$ and 11. But the value increases with increasing draw ratio and heating rate.

The influence of the draw ratio on the retractive stress during heating is shown in Figure 6. The heating rate was 1 K/min. The curves are steeper and higher with increasing draw ratio λ . The flat beginning up to 50°C of the samples with $\lambda = 6$ and 7 gradually disappears with higher draw ratio. At $\lambda = 11$ the increase of the retractive stress starts already at 30°C and later gradually diminishes with approaching the maximum. Note also the much greater increase from the curve corresponding to $\lambda = 9$ to the curve of $\lambda = 11$ as compared with the almost constant but substantially smaller increase of the retraction stress of samples with $\lambda = 6, 7, 8$, and 9. One has the feeling that between the draw ratios 9 and 11 something more happens to the drawn LPE sample than at lower draw ratios.

The maximum of the retractive stress moves consistently to lower temperatures if the draw ratio increases. The position of the temperature corresponding to the maximum retractive stress at different draw ratios is

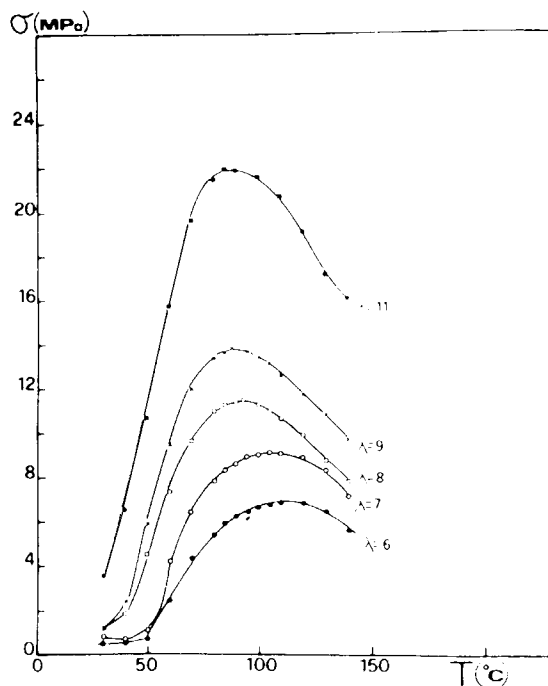


Fig. 6. The influence of the draw ratio λ on the retraction stress of the first heating up to 140°C with the heating rate of 1.0 K/min.

presented in Figure 7. It rapidly drops with increasing draw ratio, but it levels off between $\lambda = 9$ and 11 in full agreement with the above statement about the absolute value of the retraction stress. Since the retractive stress increases but the relative shrinkage decreases with the draw ratio, one may conclude that the resistance of the sample, i.e., its stability, increases faster with the draw ratio than the retractive stress.

At each temperature the retractive stress as a function of time, shown in Figure 8, first rapidly increases to a maximum as a consequence of the gradual heating of the sample and subsequently drops to a limiting value $\sigma_{\infty}(T)$. The whole time dependence of the retractive stress is an interplay of the temperature distribution in the heated sample. In the first 5 or 10 min the retractive stress of each volume element varies with time. No simple and straightforward relationship between the heating temperature and the intrinsic thermomechanic stresses of the sample may be deduced either from the value of the maximum stress or from its position in time. One only knows that the observed stress depends not only on thermodynamic properties of the volume element of the drawn material but also on the geometry and temperature conductivity of the sample. But since the drop from the maximum σ_{\max} to the final value σ_{∞} may be observed up to at least 200 min, the short heating process of 5–10 min duration may be completely neglected.

The maximum is followed by a slow drop. The retractive stress approaches a limiting value $\sigma_{\infty}(T)$ shown in Figure 9. This value changes very little with the temperature between 70 and 100°C and drops nearly linearly at higher temperature. The not measured drop after 140°C to zero value at the melting temperature seems to be still faster. The retraction force should disappear in a completely melted material, i.e., above 165°C. The effects also disappear at room temperature, although the sample is far from equilibrium. After the sample stands for a sufficiently long time at room temperature, it does not change at all because the retractive forces stay constant or even decrease, but the viscous resistance is prohibitively high. Hence the limiting retractive forces were not measured below 70°C.

The limiting retractive stress³ shows very much the same behavior as formerly observed in the retractive stress during the first heating, shown

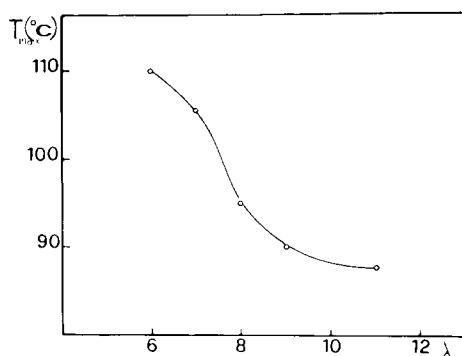


Fig. 7. The temperature T_{\max} of the curves in Figure 6 as a function of the draw ratio of the heated sample.

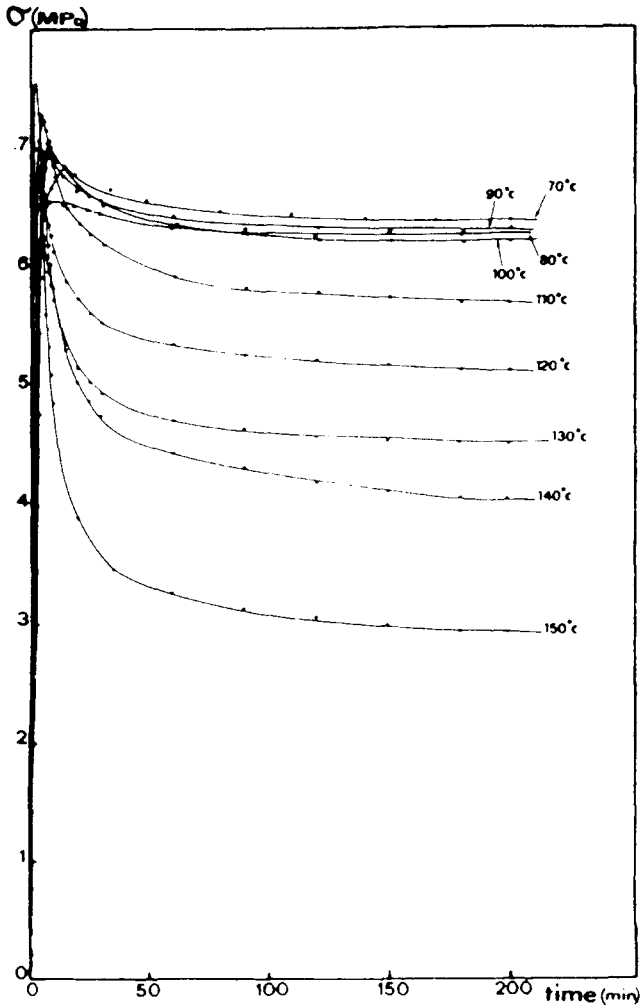


Fig. 8. The time dependence of the retractive stress at constant temperature between 70 and 150°C of a sample drawn to $\lambda = 7$.

in Figures 3 and 4. The steepest reduction in time yields a "relaxation" time τ of annealing at a temperature T_A :

$$\tau = \lim_{t \rightarrow 0} t / \ln \{ [\sigma(t_0 - t/2) - \sigma(t_0 + t/2)] / \sigma(t_0) \} \quad (2)$$

where t_0 is the time of the steepest descent and t is the time distance of retractive force measurement before and after t_0 . It is plotted as a function of T_A shown in Figure 10 for $\lambda = 7$. In the beginning, at small T_A , this "relaxation" time rapidly drops with increasing temperature of annealing. After $T_A = 120^\circ\text{C}$ it remains almost constant. It has a limited physical meaning for the material investigated because it partially measures also the influence of the shape of the sample.

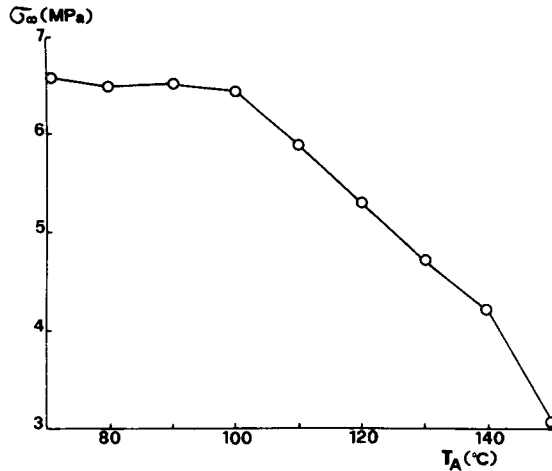


Fig. 9. Equilibrium retractive stress σ_∞ of the heated sample with $\lambda = 7$ of Figure 8.

DISCUSSION

What may be derived from Figures 1-10 and what conclusions may be supported by them? The explanation model must follow directly from the molecular mechanisms during drawing and annealing. In a great many cases one forgets about this most basic requirement and constructs the model that best reproduces the observed data without paying enough attention to the possibility of molecular formation of such a structure.

The discussion of the shrinkage and restoring force will be given in terms of the microfibrillar model of the fibrous structure that was mainly based on the experiments of drawing of linear PE of medium molecular weight and of iPP.⁸ The model seems to be sufficiently realistic for the straightforward explanation of the newly observed effects on drawn iPP.

According to this model, the axial strength of the microfibrils caused by the great many intramicrofibrillar TTM which were all formed at the de-

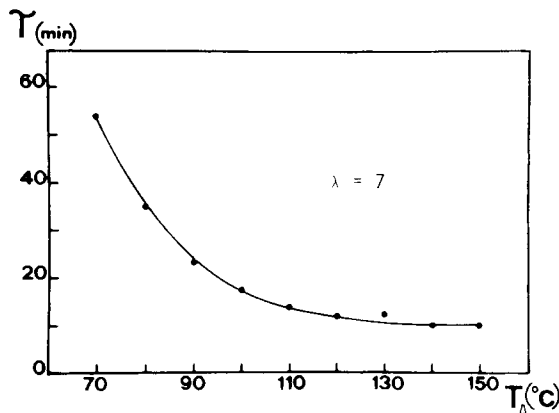


Fig. 10. The temperature dependence of the "relaxation" time τ of the retractive stress of the sample with $\lambda = 7$ of Figure 8.

struction of the original lamellar structure. The drawn sample contains also extended intermicrofibrillar and interfibrillar TTM. Their number per amorphous layer increases almost linearly with the draw ratio of the microfibrillar structure. The aligned TTM crystallize and hence form crystalline bridges over the amorphous layers if the temperature T of the sample is so low that the supercooling $\Delta T = T_m - T$ permits this in a reasonable time. As a consequence of the extreme surface-to-volume ratio of the bundled TTM, the melting temperature T_m is far below the melting temperature of the infinite crystal. The crystalline bridges do not exert a measurable retraction stress on the whole sample, although they mightily compress the less than 100 Å thick amorphous layers between the crystal blocks in each single microfibril. As soon as they melt, the TTM behave like free macromolecules in a liquid environment. The resulting retraction stress on the bulk sample becomes measurable.¹³

The retractive force of a single macromolecule depends on the ratio of the end-to-end distance h and the contour length L_c of the mobilized section between the blocks it is anchored in. According to Kuhn and Gr \ddot{u} n,¹⁴ one has

$$F = \frac{kTL_c}{h_0^2} \mathcal{L}^{-1}\left(\frac{h}{L_c}\right) = \frac{3kT}{h_0^2} h \left(1 + \frac{3h^2}{5L_c^2} + \dots\right) \quad h/L \rightarrow 0 \quad (3)$$

$$= \frac{kT}{h_0^2} \frac{L_c^2}{L_c - h} \quad h/L \rightarrow 1$$

where $L_c = nA$ and $h_0 = \sqrt{nA}$ with A the length of the statistically independent segment of the macromolecule and n the number of such segments. The random conformation yields an equilibrium root mean square (rms) length h_0 . The length A decreases slightly with the temperature if one takes properly into account the temperature dependence of the potential energy of the mutual orientation of the consecutive CC bonds that are at a valency angle $\beta = 109.47^\circ$ with a limited rotation among the trans, gauche, and gauche-prime conformations. \mathcal{L}^{-1} is the inverse Langevin function $\mathcal{L}(x) = \coth x - 1/x$. The molecular retractive force factor F/h is extremely small at $h/L_c \rightarrow 0$ and goes to infinity at $n \rightarrow L_c$. That means a high retractive force at the mobilization of the almost fully extended TTM that decays rapidly as by increasing L_c (pulling of some chain elements out of the crystalline blocks) or decreasing h (pulling the crystal blocks closer together) the ratio h/L_c becomes smaller. The initially TTM is gradually transformed in a lax tie molecule (TM) as found in rubber.

Under the influence of the retractive forces the sample shrinks. That depends on the magnitude of stress and the resistance of the drawn specimen against any shape change. Both change with λ , T_A , and time as seen in Figures 3–8. The shrinkage measures the displacement of the elements of the drawn sample under the influence of the retraction stress. Hence first the retractive stresses and subsequently the resulting shrinkage will be discussed.

The *retractive stress* is the average of all the retractive forces of the chains per unit area crossing a large enough plane perpendicular to the draw direction. The chains in the crystal lattice only transmit the forces exerted

on them by the amorphous layers. Their individual contribution to the retractive stress is practically nil. That applies also to the crystalline bridges formed from TTM crossing the amorphous layers. Their crystallization and melting point is enormously depressed by their high lateral surface-to-volume ratio. As soon as these bridges are melted by increasing the temperature, the mobilized TTM exert a large retractive force. According to eq. (3) the fully relaxed and randomly oriented chains in the amorphous layers contribute so little that they also may be completely neglected. The main contribution comes from the almost fully extended just mobilized TTM having the ratio h/L_c a little below 1. They exert so strong forces on their segments fixed in the crystals that they may be pulled out of the crystal lattice thus increasing L_c and lowering the important ratio h/L_c .

At room temperature the retractive stress cannot be measured since it is borne completely by the deformation of the sample, i.e., by the amorphous component which is softer than the almost completely rigid crystals. As soon as one increases the temperature, some crystalline bridges of TTM melt. The thus mobilized TTM are exerting a strong additional retractive stress that may be actually measured. The force of each mobilized TTM is pulling some segments out of the crystal lattice. This, as already mentioned, reduces h/L_c and hence the force. At constant temperature the retractive stress ought to decrease steadily with time.

By increasing the temperature some new TTM are mobilized since one melts new crystalline bridges between the blocks and on the lateral side of the blocks, i.e., between microfibrils and fibrils. Their number very rapidly increases with time because even the melting of the very thin crystalline bridges requires a short but finite time. The relaxation of the retractive force of all the mobilized TTM lasts longer because the pulling of additional chain segments out of the crystal blocks also requires some time. The former increase seems to be faster than the latter decrease because the curves of lower heating rate where the sample had more time for relaxation are below those with higher heating rate.

In the beginning the contribution of the newly mobilized TTM is larger than the decrease of the retractive force of the formerly mobilized TTM (Figs. 3-6). At the stress maximum the changes of both contributions are equal. After that the decrease is predominant, bringing the retraction stress to zero at the complete melting of the specimen.

This explains well the first heating curve. The stress of the first cooling curve would be proportional to absolute temperature if all TM have an equal h/L_c ratio. As soon as they partially crystallize and thus reduce the fraction of TM and their ratio h/L_c , one has a steeper descent. This is supported by the greater steepness of the descent, 85 kPa/K for $\lambda = 11$ and 35 kPa/K for $\lambda = 7$ compared with 36 and 12 kPa/K of a thermal decrease of the stress in the rubbery state. The effect may be reversed. The descent may be less steep or even transformed into an increase if the non-crystallized sections of the TM assume a larger h/L_c than before partial crystallization. But no repair of the unfolding of chains in the crystal blocks seems possible.

In the second run one starts with a sample that differs completely from that before the first run. One has the impression that the second heating does not mobilize a great many new TM that were not yet mobilized at the

highest temperature of the first cycle and frozen during the subsequent first cooling. The difference between the first cooling and the second heating are mainly caused by the usual slow crystallization and melting of different groups (index i) of TTM that obtained their ratio of end-to-end distance h_i and contour length L_{ci} at the highest temperature of the first cycle. The rate of the temperature change certainly affects that ratio since at each temperature h_i and L_{ci} slowly but independently increase as a consequence of shrinkage (h_i decreases) and pulling of chain segments out of the crystal blocks the TTM is anchored in (L_{ci} increases). With increasing rate of heating and cooling one does not achieve complete equilibration even at the highest temperature of the experiment. At lower temperature with higher relaxation time τ (Fig. 10) one is still farther away from equilibrium.

In the case $\lambda = 7$ all the cooling and subsequent heating curves have a minimum. Its existence and the increase of the retractive stress to the initial value at 20°C may be a consequence of chain stiffening, i.e., of gradual increase of the ratio h/L_c from 0 towards the upper limit 1. We are unable to give a credible explanation why this effect so conspicuous with the sample drawn to $\lambda = 7$ is missing at $\lambda = 11$. It was also not found with drawn linear² and branched³ PE.

The first heating curve yields a higher retractive stress with higher λ (Fig. 6) since the fraction of TTM is an almost linearly increasing function of the draw ratio. The increase of the stress between $\lambda = 6$ and 9 is nearly constant and supports this view. But between 9 and 11 it is more than twice as high, which would correspond to twice as large change in the draw ratio. One gets the impression that between these two draw ratios something happens to the drawn specimen. The samples with $\lambda = 11$ and higher differ in their structure from those below or at $\lambda = 9$. Very likely in this region either the smectic phase disappears or the transformation of the initial lamellar structure into the final microfibrillar structure is completed. The same conclusion may be derived from the temperature position of the maximum retractive force (Fig. 7). The temperature of the maximum gets substantially reduced up to $\lambda = 9$ but hardly changes between 9 and 11.

The drop of the retraction stress from its maximum σ_{\max} to the final limiting value σ_{∞} is best characterized by the "relaxation" time τ of the fastest decrease as shown in Figure 10. The higher the temperature of annealing the more rapid is this decrease as seen from the rapid drop of τ with the temperature. But rather soon a limiting value is found that does not decrease any more with increasing temperature. It is about 9 min at the highest temperature of the experiment, 150°C, and becomes substantially larger, 55 min, at the lowest temperature, 70°C. That means that the softening of the crystal lattice very rapidly increases with the temperature of heating.

It is questionable whether the levelling off of τ at high λ that starts at $\lambda = 9$ agrees with the inception of a larger increase of the retractive stress with the draw ratio. One has the feeling that in the range from $\lambda = 9$ to $\lambda = 11$ the sample changes more than in going with λ from 6 to 8 or from 7 to 9. From the transport properties of LPE,¹⁵ one knows that for the sample investigated (Fortiflex A60-500, Celanese trademark, $M_n = 5500$, $M_w = 80,000$) the transformation from the Lamellar to the microfibrillar structure seems to be completed for λ between 8 and 9. One may conclude

that our data on the retraction stress indicate a similar effect occurring in iPP at λ between 9 and 11.

More understandable is the increase of the retractive stress with the draw ratio as shown in Fig. 6. The higher the draw ratio, the larger the number of TTM. The increase is quite general in the whole spectrum of lengths of TTM so that the number of mobilized TTM at each temperature increases with λ . Hence the retraction stress in the first heating run starts earlier and reaches higher σ_{\max} the higher λ .

The subsequent runs are without a true maximum, the retraction force increases up to the highest temperature of heating, at least for $\lambda = 11$. The small initial maximum in the sample drawn to $\lambda = 7$ will not be discussed. The curves for the first cooling and the subsequent thermal cycles almost coincide as long as one does not surpass the highest temperature of the first run and one may neglect the relaxation effects at any temperature of the cycle.

The pulling of chain sectors out of the crystal lattice is the more efficient the higher the temperature which raises the retractive force and reduces the resistance of the crystal lattice since it expands with increased temperature. The resistance has a lower limiting value because the chain elements have to be pulled out of the potential energy minima of the crystal lattice. Before the energy for such a pulling out of the potential energy minimum is available, no displacement of the microfibrils and fibrils is possible. With increasing temperature the distance between chains increases. That flattens the potential energy curve and reduces the amplitude of the minima. The minimum is higher and the energy barrier is lower with increased distance the lattice assumes at higher T .

A simpler molecular situation is shown in Figure 8, where the isotherms of the retractive stress observed in a sample drawn to $\lambda = 7$ are plotted versus the time of heating. The steady decay after the maximum up to the final value σ_{∞} shows just the decrease in h/L_c of all the mobilized TTM since their fraction remains practically constant in time. The decrease of h/L_c is a consequence of the increase in L_c by pulling chain segments out of the crystal lattice of the blocks the TTM are anchored in. The final stress σ_{∞} (Fig. 10) drops rapidly with increasing T_A . It measures the resistance of the crystal lattice to the pulling out of the chain elements. With increasing temperature the crystals get softer and hence resist less the tendency of TM to increase their contour length by chain segments pulled out of the crystal block they are anchored in. The pulling out proceeds so long that the average resistance of the crystal lattice is just equal to the average of the pulling force of TM.

The *shrinkage* is a consequence of the displacement of sample elements by the retractive force of the mobilized interfibrillar and intermicrofibrillar TTM. By shear displacement of the microfibrils that contain the blocks they are anchored in they tend to bring these blocks closer together. The reduction of the end-to-end distance h of TM brings them closer to the equilibrium distribution rms length h_0 .

The retractive force is resisted by the viscous force of microfibrils that have to be displaced in the opposite direction to that during drawing if the interfibrillar or intermicrofibrillar TTM are to be shortened. Any such motion demands a shear displacement of adjacent microfibrils. The resist-

ance to such a displacement is proportional to the area between the adjacent microfibrils and the viscosity of shearing. The shrinkage at each temperature ceases as soon as the average of the retractive forces of all the connecting molecule acting on the blocks in a microfibril is opposed by an equally strong resistance force of the microfibril.

In the normal viscosity the shear motion would persist as long as any contracting force is applied. With time it would become slower but would end at all temperatures at the same average of the equilibrium conformations of all axially connecting molecules. Since one may neglect the relatively small decrease of A and increase of $n = (L_{c/h})^2$ with T , one would expect almost the same shrinkage at all temperatures. The observations (Fig. 2) show, however, an extremely small or no shrinkage at low temperature and a rapid increase with increasing temperature that is many times higher than, and opposite to, that caused by the decrease of A . Hence, one has to consider some other effect which is responsible for the effects observed.

Such an effect is inherent to the Bingham type viscosity. Below a certain limiting stress no shear motion may occur. This barrier ought to decrease with increasing temperature since it practically disappears in the melt. The existence of such a limiting retracting stress reduces more the amount of shrinkage at lower temperature where the fraction of mobilized TTM is smaller.

The decrease of the shrinkage at each temperature if one increases the drawn ratio λ from 7 to 11 definitely shows the larger stability of the sample with a larger draw ratio. This stability increases faster than the retractive force that is proportional to the steadily with λ increasing fraction of TTM. Such a behavior permitted to find by electron microscopy of annealed drawn PE samples the existence of fibrils¹⁶ and the difference in the draw ratio of adjacent fibrils. The smaller the draw ratio of a microfibril, the larger the effect of annealing.

That means that in the boundary layer between the microfibrils more chain elements of the interfibrillar and intermicrofibrillar TTM are located so well in the potential energy minima of the crystal lattice that the simultaneous lifting of the CH_2 and CH_3 groups from them requires a higher force than the less perfect location achieved at $\lambda = 7$. This increases the limiting stress of the Bingham type viscosity.

CONCLUSIONS

The higher the draw ration, the more stable the drawn sample is against the thermal effects of annealing. The TTM are longer and included in more crystal blocks and wider bridges. As a consequence of the smaller surface-to-volume ratio, they depress less the crystallization or melting point. At any temperature the probability of their melting during the annealing is less than with smaller λ . But their number and hence the number of melted bridges and the thus activated TTM increases with λ as seen from the increase of the restoring stress. The sample, however, shrinks less as a consequence of the higher stability as measured by the viscosity of the shear displacement of the fibrous structure. The Bingham type viscous resistance increases faster with λ than the retractive stress. Even at melting the

sample never again reaches the length of the original material if λ is high enough.

The TTM are almost fully stretched in the extremely thin quasiamorphous layer between adjacent microfibrils. They alternatively pass the crystalline blocks of each microfibril and the amorphous layers between the blocks. In most cases their stretching and orientation highly favor crystallization that is hampered by the large depression of the crystallization point caused by the large surface-to-volume ratio of the crystallizable TTM. The crystalline bridges over the amorphous layers increase the axial elastic modulus and the axial coherence length of the crystal blocks as derived from the radial width of the diffraction maxima of the wide angle X-ray scattering.¹⁷ Heating melts the bridges and hence mobilizes the affected TTM. They shrink the sample that is annealed with free ends and exert a retraction force on the sample with fixed ends.

The mobilized TTM exert a retractive force that increases extremely rapidly if the contour length L_c only slightly surpasses the end-to-end distance h . If the sample is free to contract, the retractive force pulls closer together the blocks the TTM are anchored in. The sample shrinks. If the ends are fixed, the retractive force of each mobilized TTM irretrievably pulls chain segments out of the crystal blocks the TTM is anchored in. Such an operation takes time. The longer the chain is mobilized, the larger the effect of pulling that gradually increases L_c . With the ensuing decrease of h/L_c the force exerted by the chain decreases drastically so that with increasing time the blocks at the end of the TTM may efficiently resist the pulling of the blocks closer together and the pulling of chain sections out of the block. After a time the sample looks stabilized.

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