Swelling, Deformation, and Retraction of Poly(4-methylpentene-1). II. Mechanical Properties in the Swollen State

Yoshimichi HASE* and Phillip H. GEIL

Division of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A. (Received February 6, 1971)

ABSTRACT: In relation to our previous morphological observations of swollen poly(4-methylpentene-1) (P4MP1), the mechanical properties of swollen P4MP1 have been studied both as a function of degree of swelling and in the fully swollen state. In the former case extrapolation of the observed values of yield stress, elongation at yield and initial modulus to zero swelling, leads to the value of the unswollen specimen; almost no effect of the initial degree of "preswelling" was observed in these mechanical properties. Cyclic extension—relaxation experiments in the fully swollen state indicates that the stress recovery at a given maximum strain increases with increasing maximum strain although it decreases as the number of cycles is increased. In contrast to stress recovery, the strain recovery decreases as the applied maximum strain is increased with a gradual decrease as the number of cycles is increased. Both stress and strain recovery is a time dependent phenomenon, the recovery increasing with longer rest period. Electron micrographs show that it is the fibrils formed during the initial elongation which undergo repeated extension and relaxation.

KEY WORDS Poly(4-methylpentene-1) / Swelling / Deformation / Mechanical Properties / Stress Recovery / Strain Recovery / Relaxation / Cyclic Extension /

The mechanical properties of swollen P4MP1, such as stress and strain recoveries in repeated extension-relaxation cycles and the yield stress, yield strain and initial modulus as a function of degree of swelling, have been studied. The objective of this experiment was to examine the relationship of these mechanical properties to our morphological observations¹ of the structure of P4MP1 in the swollen state and the changes in this structure during the deformation and retraction of the swollen polymer. From the morphological studies it was shown that (1) the swelling occurs in inter-lamellar or amorphous regions, (2) lamellar separation, caused by the swelling, reveals inter-lamellar links, (3) upon deswelling the pulled-out links decrease in length and increase in width, (4) under tensile stress, swollen P4MP1 undergoes multiple micronecking resulting in numerous regions of pulled-out fibrils alternating with lamellar fragments, and (5) upon release of the tension, retraction of the pulled-out fibrils as well as some interlamellar slip occurs.

EXPERIMENTAL

Sample Preparation

P4MP1 pellets were molded in either 1-mm or 0.8-mm thick sheets as described previously¹. The molded films were immersed in benzene at room temperature for sufficient time to obtain equilibrium swelling; generally they were allowed to remain in the benzene for a few days.

In order to examine the mechanical properties in the fully swollen state, $5 \text{ cm} \times 1.2 \text{ cm} \times 0.08$ cm specimens, already swollen to the equilibrium state at room temperature, were stretched at room temperature in an Instron using a specially designed adaptor which permitted the specimen to be strained and relaxed while completely

^{*} Present address: Teijin Limited, Plastic Research Laboratory, 37-19, 3 Chome, Oyama, Sagamihara, Kanagawa, Japan.

immersed in the swelling medium. The specimens were stretched to various strains, up to 150%, then immediately relaxed to zero strain; a strain rate of 20%/min was used for both elongation and relaxation (a 10%/min rate was used for the low elongation data; up to 20-% elongation). After this cycle, the specimen was relaxed at zero strain for various periods of time. In general, five such extension-relaxation cycles were carried out for a given sample. In some cases the strain in the second extension cycle was increased over that in the first one to examine any work-hardening effect. Also a short study of interrupted stretching has been carried out to examine whether the same workhardening effect as observed in poly(vinyl chloride) $(PVC)^2$ exists; *i.e.*, the stretching was interrupted at a certain strain for various periods of time and then continued to further strain.

In order to control the degree of swelling, specimens fully swollen either at room temperature or at 50°C were allowed to dry in the air for a certain period of time until they reached the desired degree of swelling. After complete deswelling the specimen returned to the original shape and clarity. The equilibrium degree of swelling at room temperature and at 50°C was 21.7 and 33.2% by volume (6.8 and 10% by length) respectively. These controlled specimens were stretched in air at 100%/min on the Instron in order to study the mechanical properties as a function of degree of swelling as well as the effect of initial degree of "preswelling." The shape of these specimens was $5 \text{ cm} \times 1.2 \text{ cm} \times$ 0.1 cm.

Electron Microscopy

In relation to the cyclic extension—relaxation experiments, morphological observations of the stretched films were carried out in an attempt to determine the region which undergoes deformation during the restretching process. After the first extension—relaxation cycle (either in the medium or in air) of a fully swollen specimen having a free surface, it was dried completely, with no tension, *in vacuo* and then shadowed with either Pt-C or Au (for gold decoration³). This shadowed specimen was restored, in benzene at room temperature, to the (new) equilibrium degree of swelling and then restretched more or less to the original strain either in the medium or in air and kept taut. After being dried completely the specimen was reshadowed with a thin carbon film and the resulting replica then stripped with poly(acrylic acid). It was anticipated that the region which underwent deformation in the second extension would show some kind of disruption of the original shadowing material.

RESULTS

Stretching and Relaxation in Fully Swollen State

Typical stress—strain curves for the extension relaxation cycles in benzene are shown in Figure 1. The stress recovery, the immediate strain recovery and the retarded strain recovery are defined as follows (see Figure 1).

Stress recovery
$$=\frac{\sigma_i}{\sigma_1}$$
 ,

where σ_i is the stress in the *i*-th cycle when stretched to the maximum strain in the first cycle and σ_1 is the stress at the end of the first elongation.

Immediate strain recovery=
$$\frac{\varepsilon_i}{\varepsilon_{\max}}$$
, and
Retarded strain recovery= $\frac{\varepsilon_i}{\varepsilon_{\max}}$,

where ε_{\max} is the maximum strain applied and the value of ε_i depends on the period of rest at zero strain between the cycles, ε_i increases with longer rest periods whereas ε_i' does not depend on the rest periods.

The data shown in Figures 2 and 3 clearly indicate that the stress recovery increases with increasing maximum strain although it decreases as the number of extension—relaxation cycles is increased. The stress recovery during the second and fifth elongation cycles, as a function of maximum strain, shown in Figure 3, reemphasizes that the stress recovery is low at low elongation but is pretty good at high elongation. Although no stretching could be carried out reproducibly above 150-% strain, the stress recovery seems to level off at the higher elongations. It should be noted that, although at low strain cyclic extension the data fluctuate a bit, the second

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Figure 1. Typical stress—strain curves for the extension—relaxation cycles of swollen P4MP1 in benzene. The stress recovery, the immediate strain recovery, and the retarded strain recovery are described in the figure.



Figure 2. Stress recovery of swollen P4MP1 in benzene at various maximum strains. The extension—relaxation cycle was repeated 5 times with no rest period between the cycles.



Figure 4. Stress recovery at various maximum strains. The extension—relaxation cycles were repeated 5 times with rest periods between 0 and 5 min.

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Figure 3. Stress recovery, σ_2/σ_1 and σ_5/σ_1 , as a function of maximum strain with no rest period between cycles.

stress above 100-% cyclic extension exceeded the first value quite consistently. Since more and more fibril structures are formed as the specimen is stretched more, the pulled-out fibrils must have responsibility for this recovery phenomenon.

If the specimens are relaxed at zero stress for a certain period of time before they are restretched in the following extension cycle, the stress recovery at any extension cycle increases at all strains as shown in Figures 4 and 5. At low strain cyclic extension the stress recovery increases rapidly in the first several minutes relaxation period while it increases more gradually at short times for the large strain cyclic exten-



Figure 5. Stress recovery, σ_2/σ_1 , as a function of rest period between the cycles.



Figure 6. Immediate strain recovery, $\epsilon_1'/\epsilon_{max}$, at various maximum strains. The extension—relaxation cycle was repeated 5 times with no rest period between the cycles.



Figure 7. Retarded strain recovery, $\epsilon_2/\epsilon_{max}$ for the same experiments as in Figure 6.



Figure 8. Immediate strain recovery, $\epsilon_1'/\epsilon_{max}$ and $\epsilon_5'/\epsilon_{max}$, as a function of maximum strain.



Figure 9. Retarded strain recovery, $\epsilon_2/\epsilon_{\max}$ and $\epsilon_5/\epsilon_{\max}$, as a function of maximum strain with no rest period between the cycles.

sion (Figure 5). For both cases it tends to level off for long relaxation times. These data, both with and without relaxation periods, strongly suggest that the pulled-out fibrils have been drastically reorganized during the relaxation process. The molecules in the fibril regions would appear to be straightened out more completely giving a higher stress in the second extension. The reorganization process is quite time dependent.

In contrast to the stress recovery, both the immediate and retarded strain recovery decreases as the applied strain is increased, as shown in Figures 6–9. Again in this case the strain recovery decreases gradually as the number of extension-relaxation cycles is increased. The retarded strain recovery increased as the specimen was relaxed for longer periods at zero strain between the cycles. The effect of the relaxation periods on retarded strain recovery was quite similar to that for stress recovery, *i.e.*, a sudden increase in recovery in the first several minutes and levelling off in the case of low strain, with a rather gradual increase with time up to 120 min followed by a levelling off in the case of large strain (Figure 10).



Figure 10. Retarded strain recovery, $\varepsilon_2/\varepsilon_{max}$, as a function of the rest period between cycles.

When the strain in the second extension exceeded the first one, the stress—strain curve showed a new yield point although it was smaller than in the first cycle the yield stress was higher than the stress at the maximum strain in the first cycle even if the first strain was applied far beyond the first yield point (Figure

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Figure 11. Typical stress—strain behavior of swollen P4MP1 in benzene when the strain in the second extension exceeded that in the first extension.

11, solid line). If the first strain was not greater than the normal yield strain (shown as a dotted line in Figure 11) the yield in the second extension can be attributed to a normal yielding process; the lower value of the yield stress on second extension is believed to be due to some kind of plastic deformation such as polygonization of the lamellae or inter-lamellar slip during the first extension cycle. The new yield point observed during the high-strain experiments suggests that a new deformation process had to be initiated in the fragments of the lamellae left-over from the first extension.

When the stretching was interrupted at 80-%, 120-%, or 180-% strain for about 5 min, the stress dropping to about 50%, and then continued to further strain, no stress-hardening effect such as reported for PVC² was observed. Instead the stress after interruption appeared to fall on an



Figure 12. A typical stress—strain curve of swollen P4MP1 in benzene when the stretching was interrupted at 80, 120, and 180-% strain for about 5 min and then continued to further strain.

extrapolation of the first stress—strain curve (Figure 12). This is in contrast to the case where the sample was relaxed and a new yield point was observed, suggesting that relaxing the stress permits reorganization of the molecules in the pulled-out fibrils.

Mechanical Properties as a Function of Degree of Swelling

In an attempt to examine the effect of initial degree of swelling, the quenched films were swollen with benzene at room temperature (Q-RT) and at 50° (Q-50) giving an equilibrium swelling of 21.7 and 33.2% respectively and then allowed to dry to varying degrees before being strained. It was expected that the highly swollen specimen (Q-50) would show larger elongation at yield and lower values of initial modulus and yield stress at a given degree of swelling when compared to Q-RT specimens; for a given final degree of swelling the Q-50 film was originally swollen to a greater extent and therefore relaxed more than the Q-RT film during the deswelling process. However both specimens showed the same value of both yield stress and initial modulus at a given degree of swelling (Figures 13 and 14), indicating that the swelling-deswelling process is quite reversible. For the elongation at yield, the effect although not large was opposite that one would expect; i.e., Q-RT specimens showed a slightly higher value than Q-50 specimens at all



Figure 13. Yield stress as a function of degree of swelling. The error bars indicate the maximum fluctuation of the observed values. The quenched P4MP1 films were swollen with benzene at room temperature (Q-RT) and at 50° C (Q-50) and allowed to dry to various degrees of swelling.



Figure 14. Initial modulus as a function of degree of swelling for the same specimens as shown in Figure 13.



Figure 15. Elongation at yield as a function of degree of swelling for the same specimens as shown in Figure 13.

degrees of swelling (Figure 15).

Another peculiar effect is that the swollen Q-RT specimen, when stretched in benzene, showed smaller elongation at yield (about 23%) than a similar sample stretched in air (about 35%). We have also observed a decrease in elongation at

yield of poly(vinylidene fluoride) (PVF_2) when stretched in a swelling medium; the yield elongation was about 40% for a specimen swollen with and stretched in dimethylformamide (DMF) whereas there was no apparent yield point when a fully swollen sample was stretched in air. In addition to a difference in elongation at yield, the deformation of the swollen specimen in the swelling medium is different from that in air for both P4MP1 and PVF₂; in the swelling agent the samples develop more cracks, look more opaque during deformation and fail at a lower elongation. On the other hand the microscopic surface morphology of stretched P4MP1 is similar for both cases, *i.e.*, micronecking occurs. Since there can be no significant difference in degree of swelling in the two cases and the samples drawn in air can still be wet with swelling agent, it may be that the differences arise from surface interactions with excess agent but the exact mechanism is unknown.

Extrapolation of the observed values of yield stress, elongation at yield and initial modulus to zero swelling, leads to the value of the unswollen specimen which was measured separately; *i.e.*, the values of the unswollen specimen were the same as those of specimens which were fully swollen and then completely deswollen, indicating complete reversibility of the swelling. These data strongly suggest that the reorganization of the molecules in the pulled-out fibrils is pretty perfect; they are quite consistent with the perfect stress recovery in the second elongation observed for P4MP1 previously stretched to a high strain and relaxed in benzene.

Electron Microscopy

Electron micrographs of the replicas with Pt/Cshadowing prepared by the method mentioned in the experimental section are shown in Figures 16 and 17. Figure 16 shows a restretched area, with 140-% elongation, which was initially stretched 120% and relaxed to 60%; both first and second stretchings were carried out in benzene. Figure 17 shows a restretched area, at 300-% elongation, which was initially stretched to the same extent; both first and second strechtings were carried out in air. In both cases they clearly indicate that no change occurred in the lamellar region during the restretching process, that it was the fibril region which underwent the restretching. The very weak contrast and vague image in the fibril region in Figure 16 was probably caused by washing out of the shadowing material during the restretching pro-



Figure 16. Electron micrograph of a restretched area, with 140-% elongation, which was initially stretched 120% and relaxed to 60%; the first and second extensions were carried out in benzene. The specimen was shadowed with Pt-C in the relaxed state and then coated with C after the second extension.



Figure 17. Electron micrograph of a restretched area, with 300-% elongation, which was initially stretched to the same extent; both first and second elongations were carried out in air. The specimen was shadowed with Pt-C in the relaxed state and then coated with C after the second extension.

cess in benzene. It is reasonable to assume that the contact between the shadowing material and the polymer can easily be loosened when the substrate polymer undergoes large deformation, especially when it is immersed in a liquid medium. Little washing effect was observed on the fibril regions when the specimen was restretched in air as shown in Figure 17. The washing out effect was enhanced for Au decorated samples; gold particles appear to be released and washed away during the reswelling process alone. Several stretched and dried taut samples (A) and stretched and dried free samples (B and C) were decorated with gold at the same time; sample A was then carbon coated while sample B was carbon coated after reswelling and free drying and sample C was carbon coated after reswelling and restretching either in the swelling medium or in air. The carbon coatings with the Au remaining on the samples at the time of coating were then removed. Although many rather uniformly distributed gold particles are observed in sample A, both in fibril and lamellar regions, few particles were seen on samples B and C indicating that washing out of the particles occurred even during the reswelling process. Somewhat similar effects have been reported for polyethylene crystals washed with xylene after Au decoration: Keller⁴ reported that Blundell, Keller, and Sadler⁵ observed that the decoration density was coarser on the interior of a uniform monolayer polyethylene crystal and that the density difference was enhanced by flooding the previously decorated crystal with xylene; a coarser distribution of Au developed in the interior with little or no change in the fine distribution on the exterior. They concluded that a portion of the surface was mobilized by the swelling agent; they attribute this to amorphous material possibly in the form of loose loops and cilia.

DISCUSSION AND CONCLUSIONS

At present we find it difficult to explain some of the above results; a number of the effects are opposite to those one would expect in terms of either a lamellar model or a two phase model for the structure of the bulk polymer and the fibrils. In addition we know of very few similar measurements on other crystalline polymers, restricting comparative evaluation.

Consider first the effect of preswelling on the mechanical properties. In one previous piece of work on P4MP1, the effect on mechanical properties of blending petroleum jelly with the P4MP1 before molding was reported.⁶ For comparable amounts of additive, smaller changes were observed in modulus, elongation at yield, and yield stress than in our samples. These results were interpreted in terms of plasticization of the crystalline regions. In our samples X-ray diffraction showed the majority of the crystalline regions to be unaffected (changes, if any, in a few percent of the crystals probably would not be observable).

The large changes in mechanical properties of our samples with increasing degree of swelling, i.e., the exponential decrease of yield stress and modulus and linear increase in elongation at yield could possibly be explained in terms of plasticization of interlamellar amorphous regions. Electron micrographs show this is where the swelling takes place, the fibrils observed spanning interlamellar cracks on fractured swollen samples possibly arising from this material since the lamellae themselves do not appear disturbed even when there are cracks on both sides of a single lamella (Figures 5-7, ref 1). However this interlamellar material must be closely tied to the lamellae by interconnecting molecules $(e.g., \text{ cilia}^7)$ in order to give rise to the fibrils. If the interlamellar region consisted only of segregated atactic materials one would not expect fibrils to form. Since the mechanical properties of samples deswollen to various degrees extrapolates, for zero residual swelling, to the values measured on the original unswollen sample, the results suggest a complete reversibility in the morphological features associated with the swelling, *i.e.*, a complete relaxation and randomization of the molecules stretched out into the craze fibrils. This is emphasized by comparison of the samples swollen at RT and 50°C. One might have expected the Q-50 sample, which had been swollen to a greater extent, to have a higher value of elongation at yield than the Q-RT sample at any given degree of swelling; it had previously been swollen to a greater extent. Instead it always had a slightly lower value, with nearly the same modulus and yield stress.

Several aspects of the stress and strain recovery during cyclic extension of the swollen polymer are also difficult to explain. For instance the stress recovery σ_i/σ_1 increases with increasing maximum strain; i.e., on the second (or any subsequent) cycle the stress σ_i required to obtain the original maximum elongation is closer to the stress required to obtain that elongation in the first cycle (σ_1) the greater the original strain. The fact that engineering stress rather than true stress is plotted in the graphs does not affect the relative values since the cross sectional area at maximum strain in all cycles is the same. One might at first suggest that this effect, particularly the 100% or better recovery for large elongations, could be explained in terms of a recovery and reformation of the original morphological structure during the relaxation portion of the cycle. However, both the electron microscope observations and the stress-strain curves themselves show this is not the case. Electron microscopy shows that it is the fibrils, which are not present in the original sample, that undergo the relaxation and extension in subsequent cycles. The large hysteresis observed in the first cycle can be attributed to plastic deformation, *i.e.*, micronecking and fibril formation; the smaller hysteresis in subsequent cycles suggests a more elastic deformation and is seen to result from the extension and relaxation of the fibrils (see Figure 1). Thus the stress recovery phenomena must be attributed to a reorganization of the molecular arrangement in the fibrillar regions, a reorganization that is time dependent since the stress recovery increases as the sample is permitted to remain at zero stress for increasing periods of time.

The strain recovery, *i.e.*, the degree of retraction, also increases with increasing rest period but decreases with increasing maximum strain and increasing numbers of cycles. Thus, although increasing strain results in a greater portion of the material being converted to presumably similar fibrils, the retractive ability of these fibrils decreases with increasing numbers and/or length. The greater strain recovery at small elongation cannot be attributed solely to a high degree of elasticity in interlamellar slip since the total elongation attributable to this effect is only 10% or less.

Possibly related data for semicrystalline polymers are extremely limited; we know of only

one report on structure changes during the deformation and relaxation of swollen polymers; Oda and Kawai⁸ reported that the c-axis orientation of the crystalline phase of a low-density polyethylene film swollen with xylene and stretched to a given strain is lower than for a film stretched to a greater strain and then relaxed to the same Recently, however, several reports of strain. "elastic" semicrystalline polymers have been published, all of which appear to involve polymers in which, by various fabrication techniques, a morphology has been produced consisting of lamellae oriented normal to the fiber axis. These lamellae are presumably tied together at various isolated points, as in Davis' micrographs of the surface of an annealed, injection molded sample of poly(oxymethylene)⁹ and deformation and relaxation occur by an elastic bending of the lamellae.¹⁰ These reports include that by Quynn and Brody¹⁰ in which this model is suggested, and reports by Foglia¹¹ on poly(1-butene) and Mitsuhashi¹² on poly(isobutylene oxide). In the paper by Quynn and Brody¹⁰ elastic samples of poly(oxymethylene) and polypropylene were prepared by a high rate of crystallization from the melt under a high applied stress. The immediate strain recovery of the "elastic" poly(oxymethylene) sample from 50-% elongation, for instance, was about 97%. The "elastic" polybutene sample was prepared by a tubular extrusion process so arranged "as to promote machine direction orientation in the melt." Such crystallization from an oriented melt leads to a shishkebab structure, *i.e.*, a similar morphology to that required for the model. It should be noted that elasticity in both cases was observed only when the sample was stretched along the machine direction. The poly(isobutylene oxide) sample was prepared by drawing a sample 500% and annealing it taut. Since annealing drawn polymers results in the formation of lamellae normal to the draw direction¹³ this material may also have a morphology similar to the model. Wideangle X-ray diffraction and infrared spectroscopy, however, indicate it contains a mixture of oriented and misoriented crystallites (*i.e.*, possibly fibrils and undeformed lamellae).

For the above-mentioned materials only one cyclic stress—strain curve was reported;¹⁰ thus

a close comparison of the elastic properties is not possible. However, despite the somewhat similar elastic response in the first cycle, we believe the nature of the elasticity in our samples differs from that for the samples described above, except possibly for the poly(isobutylene oxide) sample. There is no evidence in our samples from either small-angle X-ray diffraction or electron microscopy (Pt shadowed or Au decorated) of any periodicity or lamellar structure in the individual fibers; the elasticity is in the ca. 200-Å diameter individual fibrils. The new yield point observed when the strain in the second extension exceeded that in the first extension is probably due to the initiation of a new deformation process; after all the fibrils responded elastically to the applied stress, in the lamellar region left-over from the first extension.

Except for samples fabricated in such a manner as to give rise to a shish-kebab structure as mentioned above, we know of no directly related cyclic mechanical measurements on crystalline polymers. However, somewhat similar results on repeated elongation have been obtained for a styrene-isoprene block copolymer¹⁴ and a styrene—butadiene—styrene block copolymer.^{15,17} Henderson and his coworkers^{14,16} concluded that reformation of the continuous polystyrene phase occurred during the recovery process. This suggests that the deformation processes occurring at the yield point are reversible although the yielding phenomenon itself and stress softening are attributed to partial destruction of the polystyrene structue. Beeche, et al.,17 observed a complete recovery of stress-strain behavior for a styrene-butadiene-styrene block copolymer when it was restretched following several months relaxation in the unstretched state at 25°C after a previous elongation of up to 100%. These results appear to be strong evidence for the mobility and reorganization of the rigid structure as well as a retraction of the flexible amorphous regions.

As in the case of the process of swelling and deswelling it seems reasonable to attribute the elasticity in the fibrils to a retraction of strained amorphous regions in a two phase fibril model. Although there appears, in these fibrils, to be no necessity or reason to assume the presence of chain folds, they, of course, are also not ruled out. Measurements of the relative size of the crystalline and amorphous regions in the fibrils as well as the relative amount of left-over lamellae and fibrils at a given elongation are needed for quantitative discussions; however, the amount of shrinkage appears attributable in magnitude to a coiling up of previously oriented (or aligned) molecules in amorphous regions. For discussion purposes we can consider the average maximal dimensions of a given length molecule, *i.e.*, the average distance between the two segments of the chain furtherest apart as being given by $1.4 \times$ $\langle r^2 \rangle^{1/2}$ where $\langle r^2 \rangle^{1/2}$ is the root-mean-square endto-end distance. The ratio of the length of the molecule in the fully extended state to this value would give an idea of the shrinkage of strained amorphous regions. According to Flory and Jernigan¹⁹ $\langle r^2 \rangle^{1/2}$ for a realistic polyethylene molecule can be expressed as $\langle r^2 \rangle^{1/2} = \alpha^{1/2} N^{1/2} l$, where N is a number of segments in a molecule, *l* is a bond length and α is a function of *N*. The values of these parameters for P4MP1 have not been described; the results should qualitatively be similar, however. For relatively small numbers of segments ($N \leq 200$), the maximal dimensions (l_{max}) calculated from the values given by Flory and Jernigen¹⁹ are listed below.

Lª,Å	α^{b}	$\langle r^2 \rangle^{1/2}$,Å	l_{\max} ,Å	l_{\max}/L
63	6.5	22	31	0.49
125	6.9	33	46	0.37
188	7.0	40	56	0.30
250	7.2	47	66	0.26
	<i>L</i> ^a ,Å 63 125 188 250	$\begin{array}{c c} L^{a}, \mathring{A} & \alpha^{b} \\ \hline 63 & 6.5 \\ 125 & 6.9 \\ 188 & 7.0 \\ 250 & 7.2 \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

- ^a Length of fully extended chain in a planar zigzag conformation.
- ^b Values estimated from the graph given in ref 19.

Thus according to these calculations, an extended molecule of about 200 Å can be coiled back to about 60-Å length, *i.e.*, 70-% shrinkage. From the same area electron micrographs,¹ approximately 30-% shrinkage was observed in the fibril regions. This is in reasonable agreement with the above calculation under the assumption that the size of the amorphous region in the fibrils is on the order of 200 Å in length and the crystallinity of the fibrils is about 50%;

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although not measured a crystallinity of 50% in the fibrils is reasonable in terms of literature values for unoriented polymer.^{20,21}

As indicated above the elastic nature of the fibrils can be explained in terms of a retraction and coiling of the amorphous regions in a two phase fibril model. The block copolymers would appear to be a suitable model system; most of the deformation and retraction being in the amorphous regions. Interlamellar slip (and corresponding retraction) may occur in the crystalline regions of the fibrils, corresponding to disruption and reformation of the rigid regions. In neither material, however, is the reformation step to be taken as indicating a reformation of the same structure as in the original but rather that a similar structure reforms having nearly identical physical properties as the original structure.

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REFERENCES

- 1. Y. Hase and P. H. Geil, *Polymer J.*, 2, 558 (1971).
- 2. P. I. Vincent, Polymer, 1, 7 (1960).
- G. A. Bassett, D. J. Blundell, and A. Keller, J. Macromol. Sci., B1, 161 (1967).
- A. Keller, *Reports on Progress in Physics*, *Part-*2, 31, 623 (1968).
- 5. D. J. Blundell, A. Keller, and D. M. Sadler, cited in ref 4; to be published.
- J. McCann and C. Geacintov, J. Appl. Polym. Sci., 13, 2383 (1969).
- A. Keller, D. J. Priest, J. Macromol. Sci. (Phys.), B2 (3), 479 (1968).
- 8. T. Oda and H. Kawai, Reports on Progress in Polymer Physics in Japan, 10, 219 (1967).
- 9. H. A. Davis, J. Polym. Sci., Part A-2, 4, 1009 (1966).
- 10. R. G. Quynn and H. Brody, J. Macromol. Sci. (Phys.), in press.
- 11. A. J. Foglia, J. Appl. Polym. Sci., Appl. Polymer Symposia, 11, 1, (1969).
- S. Mitsuhashi, Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.), 72, 2159 (1969).

- K. Kobayashi, "Polymer Single Crystals," P. H. Geil Ed., Interscience Publisher, New York, N. Y., 1963, p 474.
- J. F. Henderson, K. H. Grundy, and E. Fischer, J. Polym. Sci., Part C, 16, 3121 (1968).
- 15. D. M. Brunwin, E. Fischer and J. F. Henderson, J. Polym. Sci., Part C, 26, 135 (1969).
- 16. E. Fischer, and J. F. Henderson, J. Polym. Sci., Part C, 26, 149 (1969).
- 17. J. F. Beecher, L. Marker, R. D. Bradford and

S. L. Aggarwal, J. Polym. Sci., Part C, 26, 117 (1969).

- M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience, New York, N. Y., 1963.
- P. J. Flory and R. L. Jernigan, J. Chem. Phys., 42, 3509 (1965).
- 20. A. E. Woodward, Polymer, 5, 293 (1964).
- M. Takayanagi and N. Kawasaki, J. Macromol. Sci. (Phys.), B1 (4), 741 (1967).