

Polyacrylonitrile Fiber Behavior. I. Mechanisms of Tensile Response

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Synopsis

The behavior of polyacrylonitrile fibers has been studied by a number of methods over a wide range of temperatures. At the glass transition temperature T_g , in the vicinity of 100°C. by linear thermal expansion, creep, and dye sorption experiments, the break extension was found to rise abruptly, while an initial, stiff response disappeared. The tensile recovery as normally measured was incomplete at all temperatures; below T_g , however, all extensions were completely reversible when the kinetic conditions for retraction were provided. The main extension below T_g is attributed to the straightening of twisted molecules against the intramolecular repulsion of adjacent dipoles, the small initial extension up to the "yield" knee to an increase in volume required for the operation of the main response. The additional extension(s) above T_g appear(s) to involve permanent relative displacement of fiber elements. Water depressed T_g by 30-35°C.

The tensile behavior of fibers has been the subject of many investigations.¹⁻³ In comparison to the behavior of rubbers and amorphous plastics, it is complicated by uniaxial orientation along the fiber axis and usually by partial crystalline order. It appears to have become generally accepted that increases in covalent bond lengths or angles cannot account for even a significant part of the strain at the stress levels normally encountered. In most cases, the origin of the stresses or strains has been sought within the polymer molecule or in its interaction with its immediate neighbors, although explanations in terms of interactions at higher morphological levels can also be found. Details of the interpretation of the tensile behavior of different fibers have varied in accordance with known features of fiber structure and behavior in each case. They are most often based on a straightening of rubberlike molecules coiled by their tendency to assume a random conformation, a stretching of "intermolecular bonds," or a combination of these.³

The dominant characteristic in the polyacrylonitrile molecule is the strongly polar nitrile group. Solubility of the polymer is confined to a number of highly polar solvents. This, as well as the high melting point, was long attributed (and usually still is) to high intermolecular attractive forces, exerted mainly through the very strong nitrile dipoles, possibly by

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hydrogen bonding to the tertiary hydrogen atoms on adjacent molecules. A high solubility parameter, reported by Walker,⁴ appeared to lend specific experimental support to the interpretation. The low heats and entropies of fusion extrapolated more recently by Krigbaum and Tokita⁵ from concentrated solution measurements indicated, however, that the severe requirements for fusion and solution reflect molecular stiffness rather than strong intermolecular interactions. The findings are supported⁶ by a high unperturbed end-to-end distance obtained from dilute solution measurements and attributed to intramolecular repulsion of adjacent nitrile dipoles which twist the molecules into a helical conformation so as to minimize the repulsive potential. Such a conformation can account for intermolecular distances in drawn fibers as estimated from equatorial x-ray reflections by Bohn, Schaeffgen, and Statton⁷ or for the length per monomer unit obtained by Lindenmeyer and Hosemann⁸ from a combination of x-ray and density measurements. It also proved of major pertinence to the work reported here.

Much of this work originated in an effort to find simple methods for the determination of glass transition temperatures T_g on fibers. T_g is usually determined on unoriented bulk samples of fiber-forming polymers, but Brown⁹ has described measurements based on the tensile recovery of stretched fibers. Since T_g may depend on morphological features, such as crystallinity, which are affected by a number of steps subsequent to polymerization, measurement on the final fiber will evidently give a more direct characterization of that fiber.

A number of observations made in the course of testing the validity of findings appeared to afford some insight into the molecular structure of the fibers and the ways in which the fibers can respond to an imposed stress. Specific work was then done with a view to gaining a better understanding of fiber tensile behavior.

EXPERIMENTAL

Except for the effect of environment, for which an experimental instrument described by Crane and Wharff¹⁰ was used, the tensile and recovery experiments were carried out on an Instron Model TTB. The fibers were mounted on Mylar tabs which were attached to a hooked rod suspended from the sensing cell and to a pin on a gooseneck clamp connected to the crosshead, respectively. They were completely surrounded by the desired fluid in a beaker provided with heating coils. The temperature was sensed by thermocouples placed close to the fiber and controlled within $\pm 0.5^\circ\text{C}$. To eliminate the possibility of effects due to the (epoxy) mounting medium, curves were obtained on completely different fibers and on wires. Silicone oil was regarded as the "dry" medium; the assumption that behavior in it is equivalent to that in air at all temperatures was not fully tested but appears reasonable. In the results shown in the present paper a point represents an average of three to five experiments. To study the effect of plasticizers only one curve was obtained for any one temperature and com-

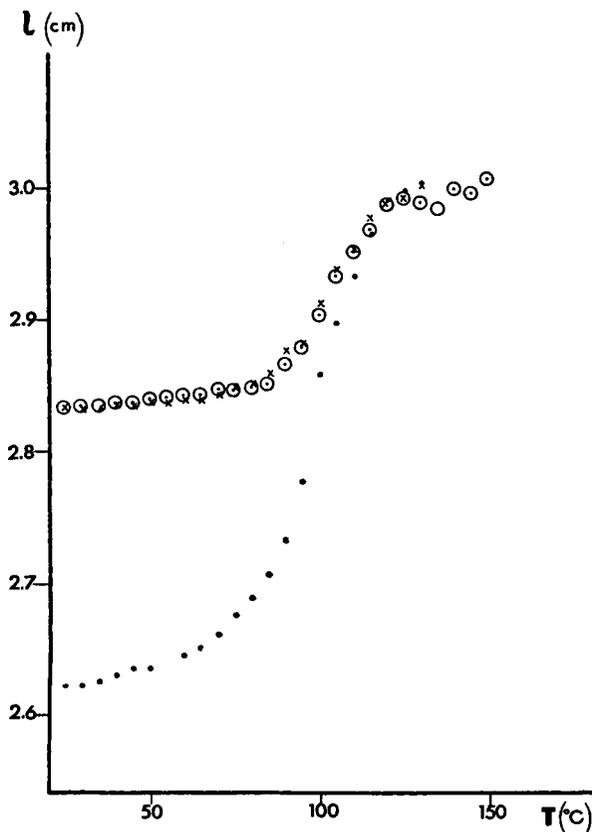


Fig. 1. Measurement of axial thermal expansion: (●) first heating; (○) second heating; (×) cooling.

pound. For the purpose which they made to serve here, this should not be a serious limitation. A constant rate of extension of 100%/min. was used in all experiments.

For the measurement of axial thermal expansion, a single fiber was mounted between a lower stationary clamp and an upper mobile clamp attached to a Statham strain gauge fixed on a traveling stage. To take a reading of fiber length, the stage was moved by manual turning of a lead screw until the load reached $1/50$ g./den. Although this could be considered negligible, the jaw separation was decreased to the point where the fiber was slack immediately after the length had been read visually on a sensitive dial and recorded, so as to eliminate to the utmost complications due to creep. The fiber was immersed in the fluid desired which reached above the mobile clamp at all times and which was contained in an open beaker provided with heating coils. A constant rate of heating of 3°C./min. was obtained by means of a programmed pyrometer controller (West Guardsman), which was also used (reversed) during the subsequent cooling cycle.

Following the cooling (with ice water pumped through copper coils), heating was repeated at the same rate. Curves shown in the text are all based on the second heating cycle. A curve was used only if it could be regarded as (essentially) identical to the preceding cooling curve. In most cases this was so, the curves in Figure 1 being representative. The first heating curve invariably showed a major divergence from the other two and always in the direction shown. The initial length l_0 used for the other curves is the length at the beginning of the second heating cycle.

Creep was measured similarly but with continuous recording of the change of length with time, as described earlier.¹¹

Most of the polyacrylonitrile fibers currently available contain a small amount of plasticizing ester comonomer. Experimental results actually shown here are for fibers from a homopolymer (designated as H) or from a copolymer (C) with 5 mole-% methyl acrylate, the comonomer in most of the fibers now made. Although these are termed "acrylic" up to 15% by weight of comonomer, in practice they all appear to contain much less than that; the two fibers shown here are thought to represent the extremes in the composition range available. While there were differences in the detailed properties, the basic behavior discussed was similar for the two, as well as for a large number of diverse acrylic fibers examined (except for one feature, discussed in the text). The effect of environment was examined on only one fiber, but in view of the similarity in other respects, it is reasonable to assume that the results there are also of general validity. Experimental fibers were wet spun from concentrated aqueous $ZnCl_2$ solution.

RESULTS AND DISCUSSION

T_g and Tensile Behavior

The break extension of polyacrylonitrile fibers increases slowly at first with increasing temperature (Fig. 2), then the slope rises sharply over a narrow temperature interval. All other features of the load elongation curve are also affected by the changes, attributed to a glass transition, taking place at this temperature, but the break extension was found to be the most sensitive for tensile measurement of T_g . The fibers cease to be glassy or brittle by the unfreezing of an additional mechanism of response. Creep rates also show a distinct change at the same temperature (Fig. 3). Independent justification for attributing the changes to a glass transition was provided by dye diffusion^{11,12} and thermal expansion¹³ results. Water quite generally decreased T_g by 30–35°C. For most properties, wet and dry (silicone oil) plots could be superimposed by a shift of 30–35°C. along the temperature axis. The one clear exception was the initial modulus, which was relatively insensitive to water near room temperature.

Load elongation curves at different temperatures are shown in Figures 4–6. The discussion will be facilitated by the generalized diagram in Figure 7. Three regions of extension can be distinguished. The knee

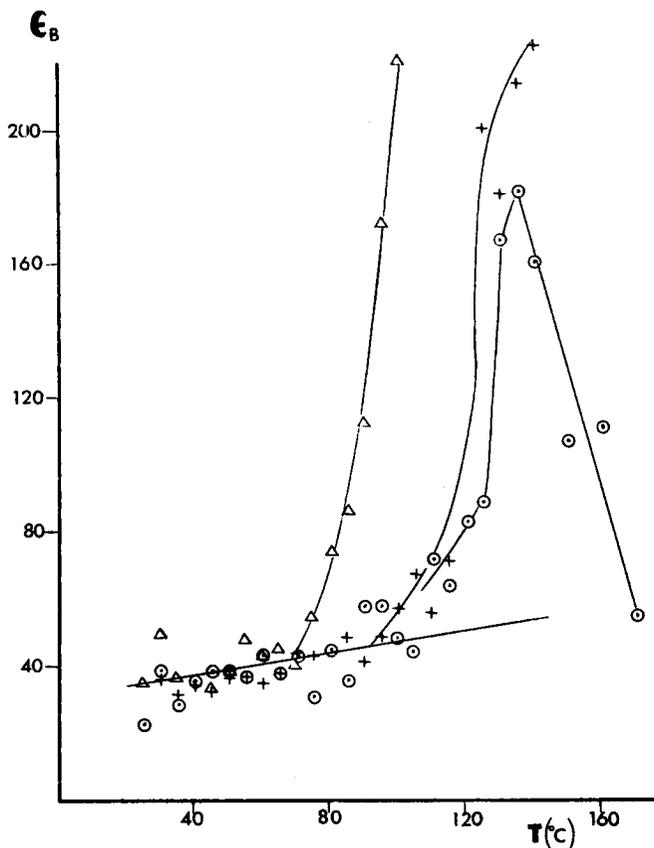


Fig. 2. Variation of break extension with temperature: (O) homopolymer (H) in silicone oil; (+) 5 mole-% methyl acrylate copolymer (C) in silicone oil; (Δ) 5 mole-% C in water.

separating *B* and *C* is not always well pronounced, but, even where it is not, basic similarity in behavior is indicated by the similar abrupt increase in break extension above T_g . *C* is absent below T_g , *A* above it. Disappearance at T_g of the "yield point" separating *A* and *B* has been noted by Bryant.¹⁴ The ratio of the initial slopes of *A* and *B* should then decrease with increasing temperature and reach a value of one at T_g . Such plots are often linear over a substantial range below T_g . In those cases, it provides a simultaneous, independent measurement of T_g ; like the break extension, it does not require strict constancy or even measurement of fiber denier (which is usually not very precise). Where the linearity holds, there is reasonable agreement of T_g with that from break extensions.

As noted earlier, the basic features discussed here were found to be generally valid for "normal" experimental fibers and all other acrylic fibers examined. The more specific effects of copolymerization and other ways of modifying the detailed properties of the fibers are treated in Part

II,¹³ as is the effect of water and other polar compounds. The three extension regions in Figure 7 are attributed to the existence of (at least) three different mechanisms of tensile response which will be discussed in this paper.

When fibers were subjected at room temperature to different extensions short of break, followed by immediate unloading, part of the extension

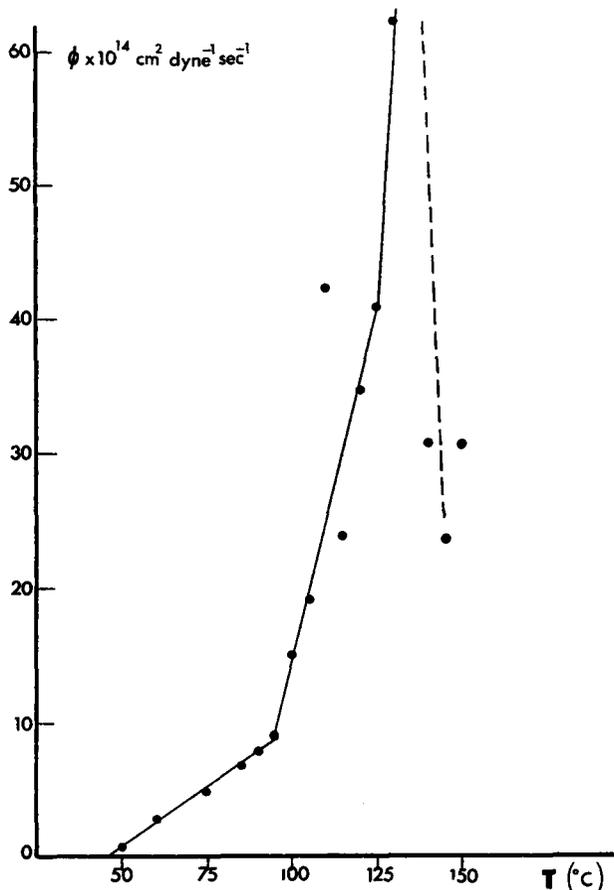


Fig. 3. Variation of creep rate ϕ with temperature. C in silicone oil; ϕ based on total relative change in length between 0.5 and 30 min.

was recovered during the unloading, as shown by the crosses in Figure 8. Most of the extension not recovered immediately was still recorded as set after a week. After heating the fibers without tension in saturated steam at 130°C., however, the total recovery was as shown by the circles in Figure 8. Fibers that exceeded the average break extension of 37% recovered even that very last extension. There was essentially no permanent set. Similar behavior is shown in Figure 9 for fibers from homopolymer. Results

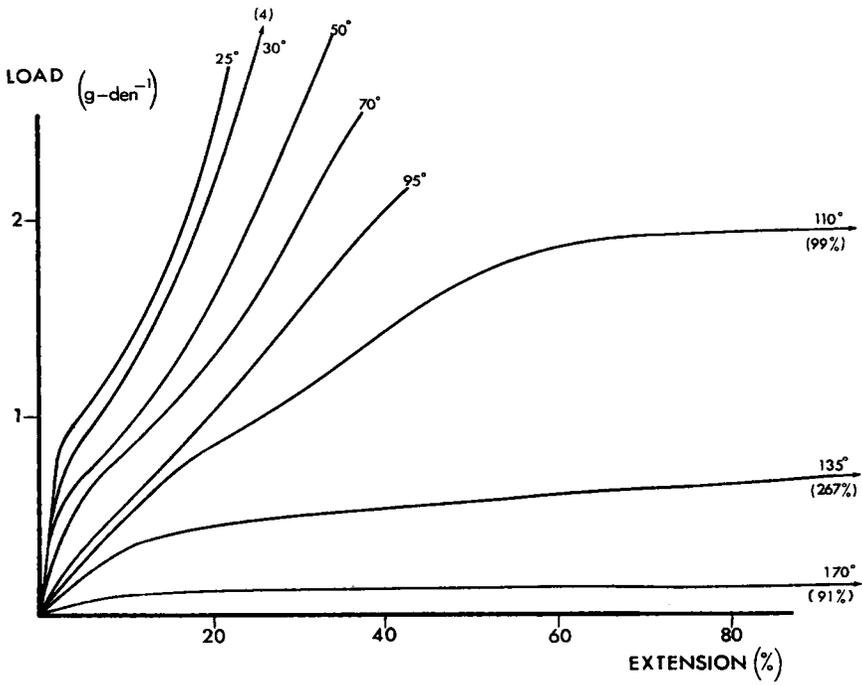


Fig. 4. Effect of temperature on load-extension curve; H in silicone oil.

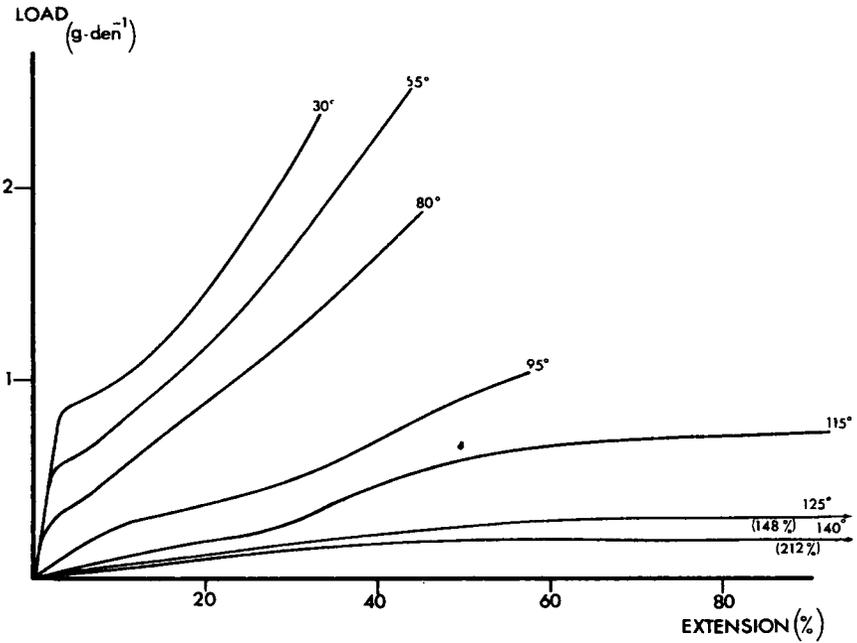


Fig. 5. Effect of temperature on load-extension curve; C in silicone oil.

for extensions carried out above T_g , at 95°C. in water are plotted in Figure 10. Even at relatively low extension the total recovery was incomplete.

Main Extension (*B*) below T_g

It is proposed that the main extension below T_g is made possible by short-range straightening of individual molecules twisted out of a straight

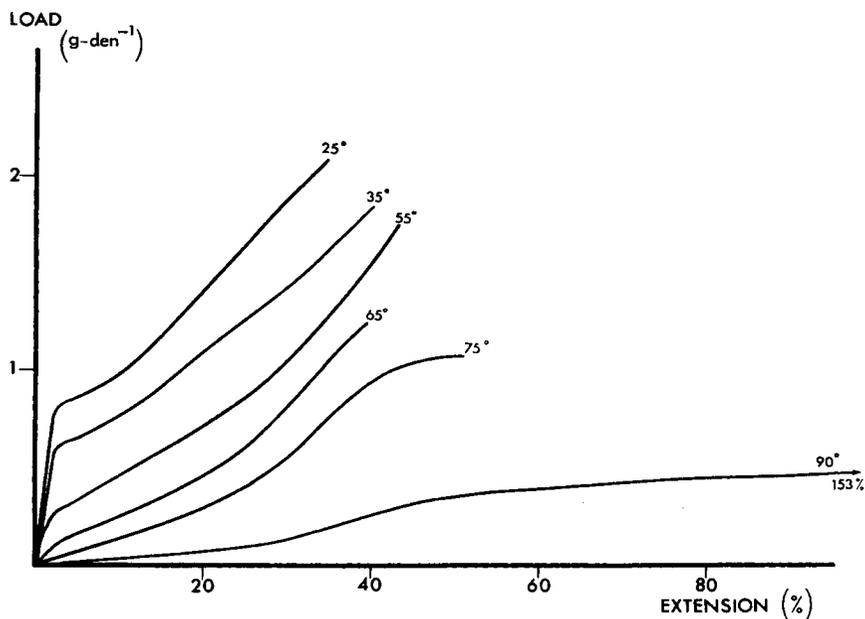


Fig. 6. Effect of temperature on load-extension curve; C in water.

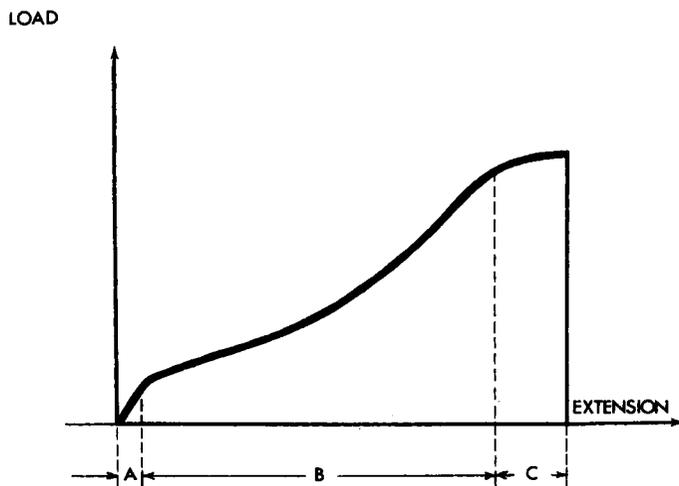


Fig. 7. Diagram of generalized load-extension curve.

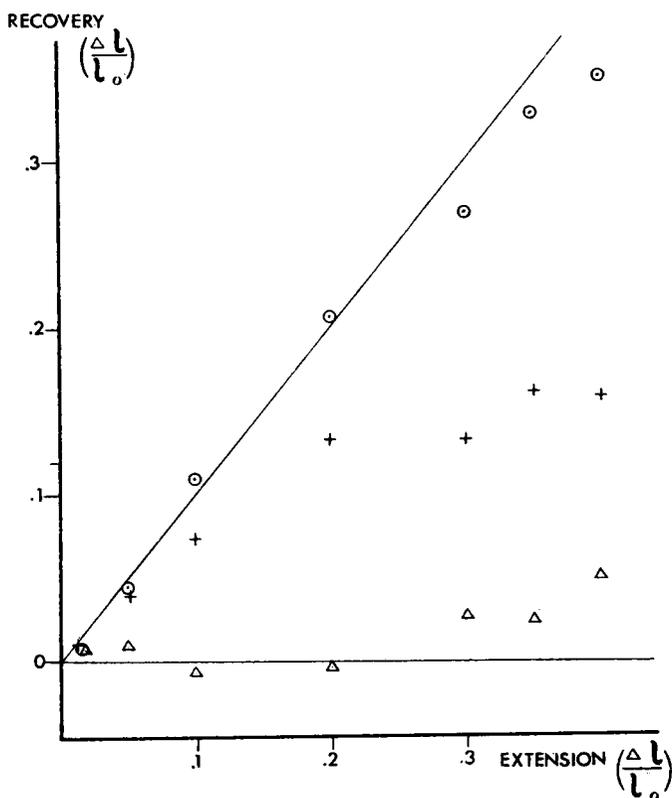


Fig. 8. Tensile recovery after extension at 25°C., H in water: (+) immediate recovery; (○) total recovery after steam relaxation; (Δ) residual set.

zigzag conformation by the repulsive forces between adjacent dipoles. Such a mechanism will be shown to accord well with the evidence presented as well as with the published data. Other mechanisms considered, which have or might be suggested, showed serious conflict with experimental behavior.

There is substantial evidence to show that the extension does not result from a straightening of rubberlike chains against the tendency of flexible molecules to assume a more probable conformation. Dart¹⁵ has examined the contribution to the force f of the two terms in

$$f \simeq (\partial E / \partial l)_T - T(\partial S / \partial l)_T = (\partial E / \partial l)_T + T(\partial f / \partial T)_l$$

over a wide range of extensions for a number of fibers by measuring the temperature dependence of the force at constant length l near room temperature. For a polyacrylonitrile fiber, he found that the entropy S actually decreased with increase in length, indicating that the resistance to tensile deformation is due entirely to an increase in internal energy E . Although there can be objections to quantitative use of the relation, the

qualitative aspects of Dart's findings appear to be valid. The positive coefficients of linear axial thermal expansion shown in Part II¹³ and their comparison to nylon provide limited independent support. Apart from any specific evidence, moreover, it may be stated quite generally that the motion of segments of a rubber should be negligible below T_g . Also, all these fibers have x-ray orientation angles (usually substantially) less than 30° . Further alignment of molecules already so parallel to the direction

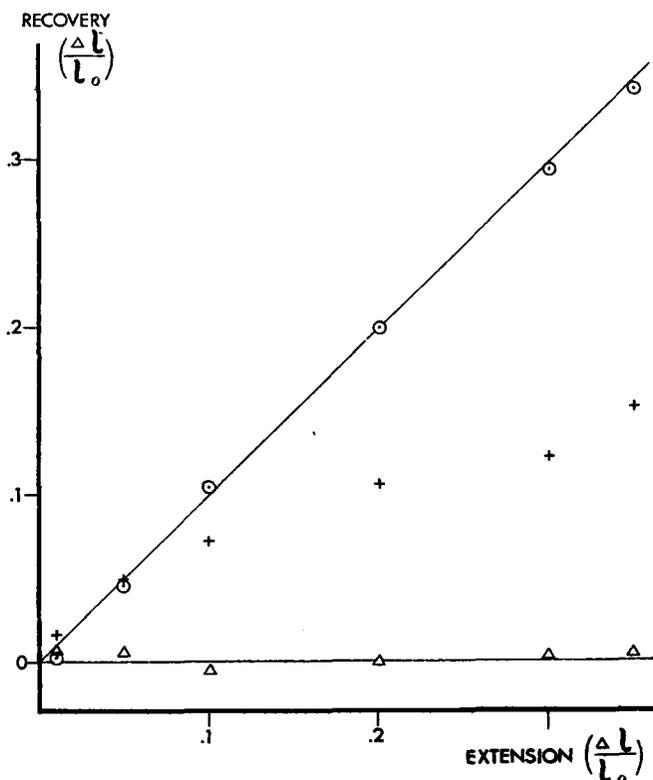


Fig. 9. Tensile recovery after extension at 25°C ., C in water: (+) immediate recovery; (○) total recovery after steam relaxation; (Δ) residual set.

of stress can hardly account for such high extensions. A satisfactory mechanism has to enable at least about 40% reversible extension below T_g .

The latter consideration applies not only to the rubberlike deformation, but also to any other explanation by alignment of fiber elements on a higher morphological level, such as fibrils or crystallites with axes tilted with respect to the fiber axis. In order to account for the reversible extensions shown in Figures 8 and 9, a consistent tilt angle of about 45° would be required. With an angle of 30° the maximum extension would be 15%. There also appears to be no other evidence to suggest the presence of such tilted fiber elements.

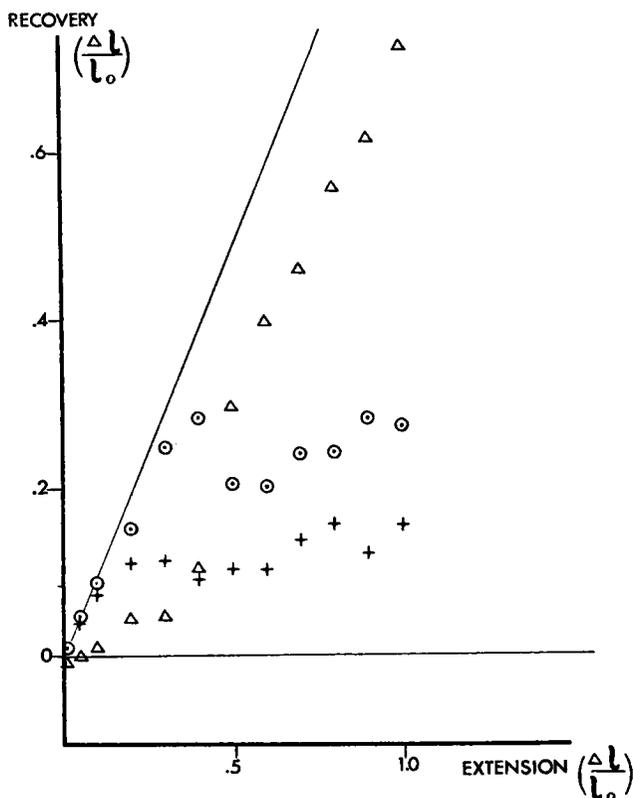


Fig. 10. Tensile recovery after extension at 95°C., H in water: (+) immediate recovery; (○) total recovery after steam relaxation; (Δ) residual set.

A common explanation for fiber extensions is that intermolecular bonds are being stretched.³ This would satisfactorily give rise to an increase in energy. No description of the strained fiber for this model has been encountered in the literature which is explicit enough for evaluation. It is hard to see, however, how small reversible relative displacements of adjacent chains of high molecular weight can possibly add up to such large macroscopic deformations.

Viscous flow of molecules past one another can be discarded on the basis of the complete recovery. The same applies to the permanent displacement of other fiber elements.

The inability of these general mechanisms to account for the available evidence makes it necessary to seek a more specific explanation. Quantitative description of the untwisting mechanism suggested here requires more information on details of molecular conformation and configuration than is available at present. A rough estimate indicates the feasibility of extensions of 40–50%, enough to account for all the deformation at room temperature. It is also in line with the other evidence cited. The external

stress counteracts the repulsive potential between the dipoles so that, by rotation around the C—C bonds in the backbone chain, closer mutual approach of the dipoles becomes possible, and the molecules straighten out. This results in an increase in internal energy, in agreement with Dart's findings. Also, if the twisted form has only a small number of low energy states available, the entropy could increase on stretching. The incomplete recovery at room temperature can be understood in conjunction with the discussion of extension *A* in the last section. No permanent relative displacements are involved, so that the extension should be reversible, if kinetic conditions for the resulting decrease in energy exist. This is provided by steam treatments above T_g , which allow complete recovery. The unexpectedly strong plasticizing action of water was explained by a decrease in the repulsion forces due to an increase in dielectric constant; this will be discussed further¹³ with additional experimental evidence.

While still of a speculative nature, the mechanism can hardly be regarded as far-fetched, in view of the similarity to the $\alpha \rightarrow \beta$ transformation in protein fibers.¹⁶ Of all mechanisms considered, the only other one that is not clearly incompatible with the experimental results is the straightening of molecules folded in a manner that has recently been demonstrated extensively¹⁷ in polymer single crystals, with the folds parallel to the fiber axis. The usual increase in fold length with temperature^{18,19} could also account for the high axial thermal expansion. At present this mechanism appears less likely, partly because of the difficulty of visualizing the course of extension or recovery. For the latter, especially, it would appear that motion of segments of the same size as in a rubber would be required; this would make it difficult to account for the substantial, though incomplete, recovery below T_g . Also, no evidence for the existence of such folded sequences in drawn polyacrylonitrile fibers has been encountered.

Additional Extension (*C*) above T_g

From both the shape of the load extension curves and the extremely high break extensions above T_g it is clear that an additional mechanism becomes available here. This extension is probably the most difficult to characterize. The high extensions—at least 350% have been recorded—appear to be a feature unique to fibers from acrylonitrile polymers. The results in Figure 10 would indicate that irreversible flow forms the major part of this deformation. Again the only possible single alternative appears to be chain unfolding, which looks much more likely here than below T_g . Recoverable extensions of at least 75% have been obtained.

The high, though incomplete, recoveries at extensions below 40% make it appear reasonable that the main mechanism for extension *B* below T_g also provides the initial response above T_g . Rubberlike extension of incompletely oriented molecules may also contribute here. It should be noted that the very high break extensions would be impossible if the molecules passed through (more than one) crystallites which acted as effec-

tive crosslinks. It is quite likely that the units involved in the flow are on a supramolecular morphological level, such as crystallites or fibrils.

Initial Extension (*A*)

In an earlier section it was shown that the motion required for complete recovery cannot take place below T_g . On the other hand, it is suggested that the converse (untwisting) motion is possible. The apparent discrepancy is removed by assuming that the function of *A* is to provide the free volume required for the onset of extension *B*. Increases of free volume with strain in glassy polymers have been treated by Ferry and Stratton.²⁰ Bryant has made a similar assumption earlier.¹⁴ His further suggestion, (for modacrylic fibers) that the extension at the yield point ending *A* is that at which the resulting increase in free volume has lowered T_g to the temperature of the experiment, cannot be supported by the present work for a number of reasons (e.g., it would be impossible then to detect T_g by measurement of any feature following that point, such as the break extension).

The extensions covered by *A* are very small, approximately 2–3%. One reasonable way to visualize the course of the volume expansion is to consider that in the unstrained state, two adjacent (and presumably twisted) molecules lower their energy by bringing together a maximum number of groups that can interact favorably (and consistent with other factors). This results in close mutual approach. Relative shifting in the axial direction pulls the interacting groups out of registration, with a resultant increase in intermolecular distance and volume. When, below T_g , a sample has been pulled well into region *B* and the stress is released, some motion is possible at first; gradually a state of reasonably good interaction is reached, the free volume decays, and the recovery remains partial, unless the temperature is now raised above T_g .

More direct indication of the function performed by *A* was obtained from the dependence of the tensile behavior on the molecular size of the testing medium (Part II¹³).

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Résumé

On a étudié le comportement de fibres de polyacrylonitrile au moyen d'un certain nombre de méthodes et dans un large domaine de températures. A la température de transition vitreuse T_g , aux environs de 100° , on a trouvé par des expériences de dilatation thermique linéaire, de fluage et de sorption de colorants que l'extension de rupture augmente brusquement, tandis qu'une réponse initiale rigide disparaît. Le rétablissement de tension, comme on le mesure normalement, est incomplet à toutes les températures; au-dessous de T_g , cependant, toutes les extensions sont complètement réversibles lorsque toutes les conditions cinétiques pour la rétraction sont fournies. L'extension principale en-dessous de T_g est attribuée au redressement des molécules tordues en dépit de la répulsion intramoléculaire des dipôles adjacents; la faible extension initiale, s'étendant jusqu'à la limite de viscoélasticité linéaire, est attribuée à une augmentation du volume. Les extensions additionnelles situées au-dessus de T_g semblent impliquer un déplacement relatif permanent des fibres. L'eau abaisse T_g de $30-35^\circ$.

Zusammenfassung

Das Verhalten von Polyacrylnitrilfasern wurde nach verschiedenen Methoden in einem weiten Temperaturbereich untersucht. Bei der Glasumwandlungstemperatur T_g in der Nähe von 100° wurde durch lineare thermische Ausdehnungs-, Kriech- und Farbstoffsorptionsversuche ein abrupter Anstieg der Bruchdehnung gefunden, während eine anfängliche starre Reaktion verschwand. Die in der üblichen Weise gemessene Spannungsrückbildung war bei allen Temperaturen unvollständig; unterhalb T_g waren jedoch bei Einhaltung der kinetischen Retraktionsbedingungen alle Dehnungen vollständig reversibel. Der Hauptanteil der Dehnung unterhalb T_g wird auf die Streckung verdillter Materialien gegen die intramolekulare Abstossung benachbarter Dipole zurückgeführt, die kleine Anfangsdehnung bis zum "Grenz" knie auf eine für den Ablauf des Hauptverhaltens erforderliche Volumszunahme. Die zusätzliche Dehnung oberhalb T_g scheint mit einer permanenten relativen Verschiebung der Faserelemente verknüpft zu sein. Wasser setzt T_g um $30-35^\circ$ herab.

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