Polyacrylonitrile Fiber Behavior.   II.   Dependence on Structure and Environment

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Synopsis

The effect of comonomer, draw ratio, and annealing temperature on the glass transition temperature T_g and on a number of properties of polyacrylonitrile fibers has been examined.   The coefficients of axial thermal expansion above T_g were found to be positive and unusually high.   In water, they increased with increasing draw ratio and annealing temperature, but these effects could not (or hardly) be observed in decalin. The axial thermal expansion is compared with that of polyamide fibers, where the coefficient was positive on unstretched fibers but negative on drawn ones throughout the temperature range (25-150°C.) examined.   Implications for the structure of polyacrylonitrile fibers and a number of peculiarities in their glass transition are discussed.   Most of the results were in line with a structure based on stiff molecules twisted out of a straight conformation by intramolecular repulsive interaction between adjacent dipoles. An unexpectedly large proportion of compounds examined were found to exert a plasticizing action which could be related most readily to the dipole moments.   The effect is attributed to a reduction in molecular stiffness and is compared with the solution behavior of the polymer.   An increase in "yield point" with increasing molecular size of tensile testing medium provided evidence for an increase in volume during initial extension.

General aspects of the temperature dependence and tensile response of polyacrylonitrile fibers have been discussed in Part I.[1]   It was suggested that there are at least three different mechanisms of tensile response, one of which is absent above the glass transition temperature T_g, another below. T_g can therefore readily be measured from the load–elongation behavior. The main, completely recoverable, extension (B) below T_g was attributed to the untwisting of molecules against the intramolecular repulsions of adjacent nitrile dipoles,[2] the small initial extension (A) up to the "yield point" to an increase in volume required for the operation of the main mechanism.   Water was shown to exert a strong plasticizing action.   Here, the effect of copolymerization, stretching, and annealing of the fibers and plasticization by polar compounds is examined.

Effect of Copolymerization, Drawing, and Annealing

Introduction of a small amount of ester comonomer, as well as a number of annealing treatments, have a very pronounced accelerating effect on

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internal motions in the fiber.   Dyes diffuse much faster,[3,4] the fiber becomes more easily deformed at elevated temperatures, e.g., under dyeing conditions, and low temperature brittleness is decreased substantially.

The effect of copolymerization can be attributed to a decrease in T_g. Temperatures almost anywhere between 39°C.[5] and 180°C.[6] have been reported for the glass transition temperature of polyacrylonitrile; most commonly the values lie in the range of 80–110°C.[2,6−11] For copolymers, T_g is generally[12] intermediate between that of the two homopolymers. This appears to hold in the results of Mead and Fuoss[13] for copolymers of acrylonitrile with ethyl acrylate.

According to Kolb and Izard,[7] 5% styrene comonomer caused a T_g of 69°C., well below that of either homopolymer. A minimum in the variation of T_g with composition for copolymers with methyl methacrylate was found by Kolesnikov et al.[14] Such abnormal decreases of T_g with copolymerization might be expected where a comonomer intervenes between two acrylonitrile units to provide a flexible link by disturbing the
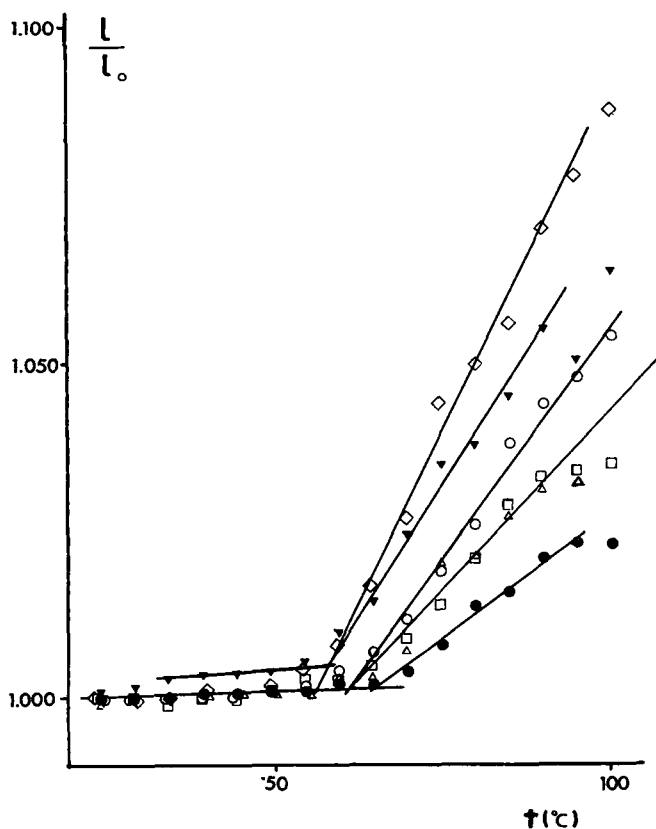

Fig. 1. Axial thermal expansion in water of fibers annealed at different temperatures: (●) 100°C.; (△) 108°C.; (□) 115°C.; O 126°C.; (▼) 130°C.; (◊) 138°C.
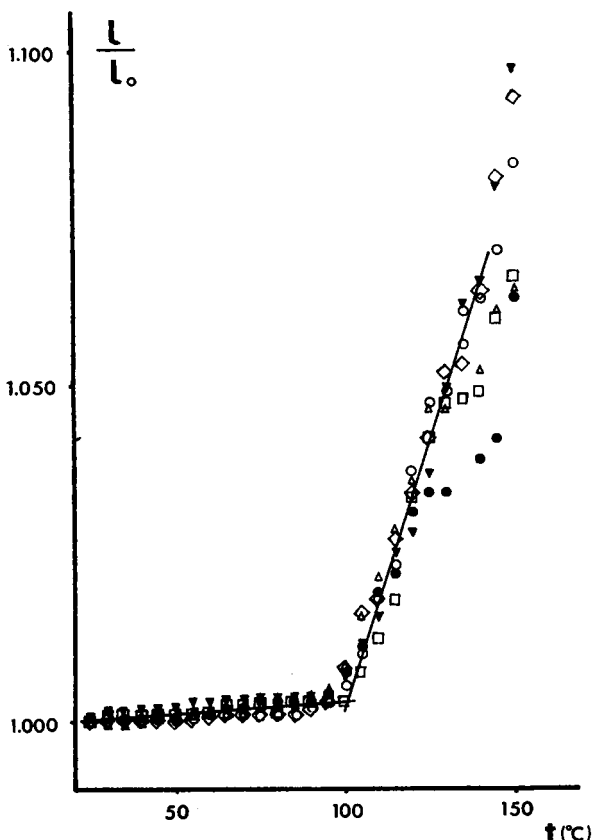
Fig. 2. Axial thermal expansion in decalin of fibers annealed at different temperatures: (●) 100°C.; (△) 108°C.; (□) 115°C.; (○) 126°C.; (▼) 130°C.; (◊) 138°C.

stiffening action of the nitrile dipole repulsion. It should not (or hardly) occur where the comonomer is present in a distinct polymeric form. Beevers and White[11] indeed found glass transition temperatures for block copolymers with methyl methacrylate intermediate between those of the homopolymers, but a minimum in the curve for the random copolymers.

Work done here on the effect of variation in comonomer content randomly distributed in the polyacrylonitrile chain has been less systematic than a number of the published investigations. It has tended to confirm the findings of most of the latter that T_g is reduced continuously by increments in acrylate comonomers at least up to about 5 mole-%. Abnormally low values have often been measured on experimental homopolymer fibers, however. This appears to accord with the findings of Howard[10] and with several reports[7,9] of T_g for dry polyacrylonitrile substantially below 100°C. At least in most of these cases, it is thought to be due to highly strained morphological states, with free volume occluded when the fiber was formed under conditions akin to fast quenching from the melt.[15] This will tend

to occur more readily with the less mobile homopolymers and is more difficult to anneal out there.   The data shown in the following were obtained on fibers made from a copolymer with 5 mole-% methyl acrylate. The basic points made appear to be similar for the homopolymer fibers tested, but it is much more difficult to obtain systematic data of corresponding validity for these.   The evidence in this laboratory was pre-
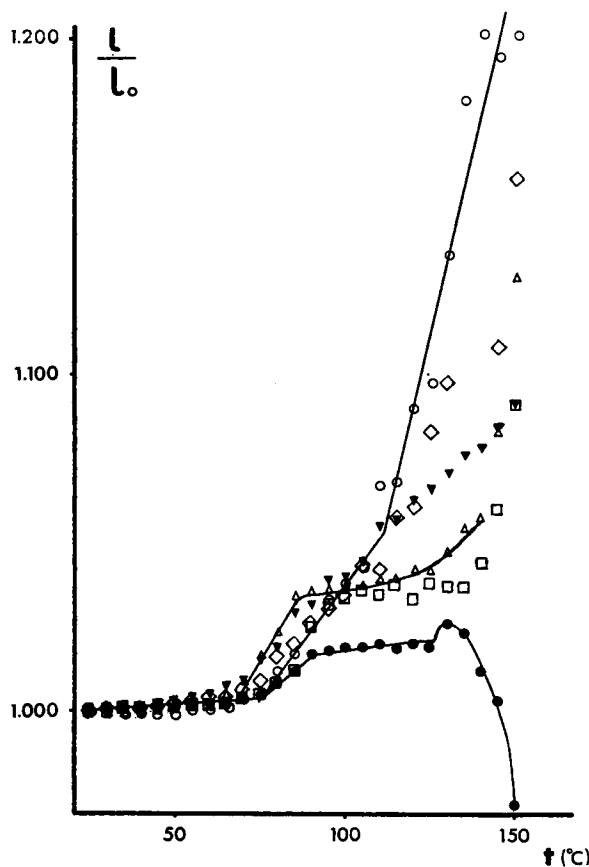

Fig. 3. Axial thermal expansion in ethylene glycol of fibers annealed at different temperatures: (●) 100°C.; (△) 108°C.; (□) 115°C.; (O) 126°C.; (▼) 130°C.; (◊) 138°C.

dominately in favor of T_g (dry) close to 110°C. for acrylonitrile homopolymer and a decrease of about 1°C. per (low) mole per cent methyl acrylate comonomer.   The considerations outlined may well be responsible for the difference between the result of 104°C. by Krigbaum and Tokita[2] which was obtained by extrapolation from concentrated solution, in which relaxation should be complete, and the considerably lower ones of Howard obtained on disks which are probably difficult to anneal.
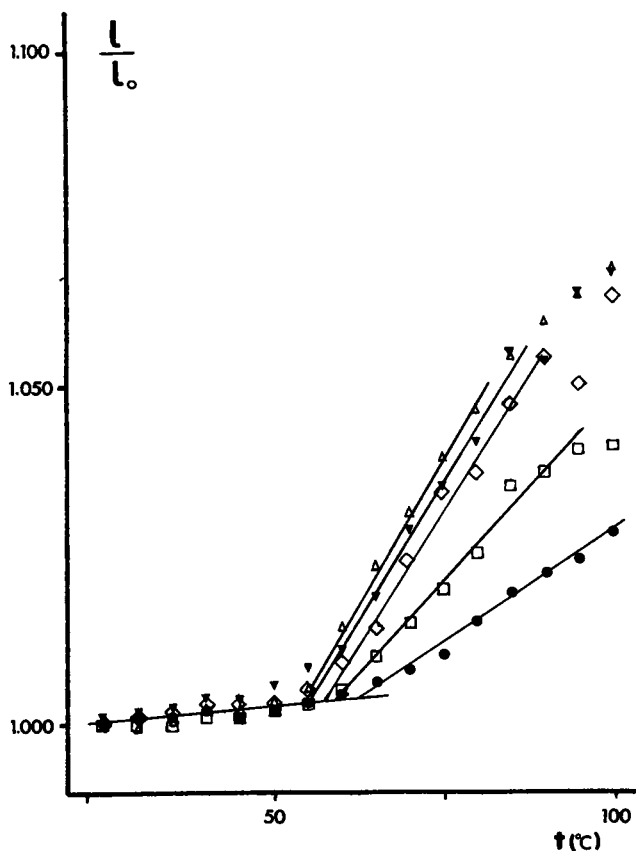
Fig. 4. Axial thermal expansion in water of fibers of different draw ratio: (●) 1× (unstretched); (□) 5×; (◊) 10×; (▼) 14.8×.

Figure 1 shows the variation in water of the linear axial thermal expansion of fibers that had been subjected to saturated steam for ten minutes at different temperatures. Similar results obtained in decalin and ethylene glycol with the same fibers are shown in Figures 2 and 3, and corresponding results for the effect of draw ratio are given in Figures 4–6. T_g is obtained with good definition, by an easy measurement, in satisfactory agreement with the tensile and dyeing results.[1,17] The method is related closely to the most common one of volume expansion. The geometrical factors that make measurement of the latter difficult in fibers make for ease and sensitivity along the direction of the fiber axis.

Coefficients of linear thermal expansion in a corresponding temperature range are usually of the order of 10^{-4}, most of which may be expected to originate from motions normal to the axis of the molecules or their segments. If covalent bonds of oriented molecules in a straight zigzag conformation had to be expanded, the coefficient $\alpha_{\parallel}$ (parallel to the fiber axis) measured here should be much smaller even than that. In practice, it was about an
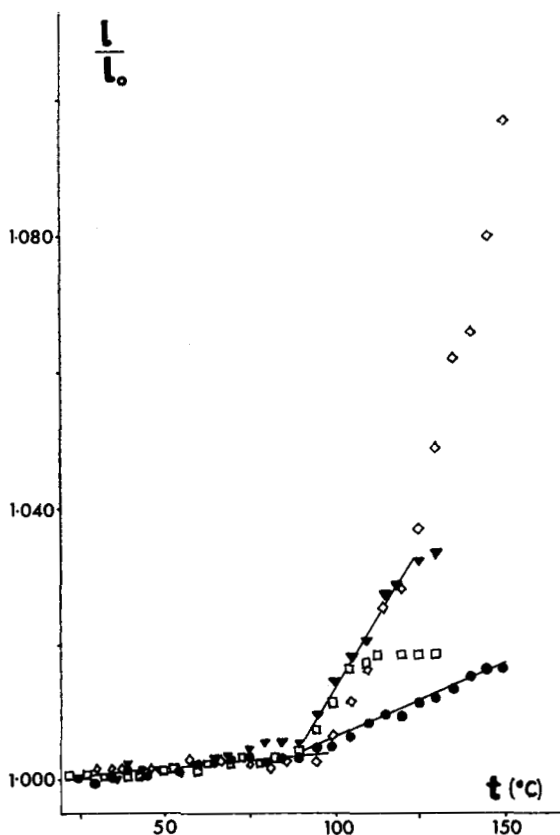
Fig. 5. Axial thermal expansion in decalin of fibers of different draw ratio: (●) 1×
(unstretched); (△) 2.9×; (□) 5×; (◊) 10×; (▼) 14.8×.

order of magnitude higher, suggesting a special degree of freedom.   This
would be well explained by an expansion of the pitch of the twist in the
polyacrylonitrile molecule.

The detailed results in water appeared to provide confirmation of re-
markable simplicity: $\alpha_\parallel$ increased with increasing draw ratio, as though
drawing represented merely an alignment of twisted rods in the direction
of the fiber axis (and possibly straightening of long-range coiling).   The
increase of $\alpha_\parallel$ with increasing annealing temperature is also expected, since
the higher temperatures provide the kinetic conditions for more perfect
twisting to the lowest energy possible.   It is hard to see, however, why the
same effects should not have been observed in decalin.   Highly stretched
fibers had a higher $\alpha_\parallel$ than unstretched ones, but there was no continuous
variation (this was also confirmed with an additional fiber series).   Dif-
ferences in behavior in the different fluids were not surprising in themselves,
since water may penetrate the helices (see also next section).   What is
most difficult to fit into the framework of the present discussion is the ab-
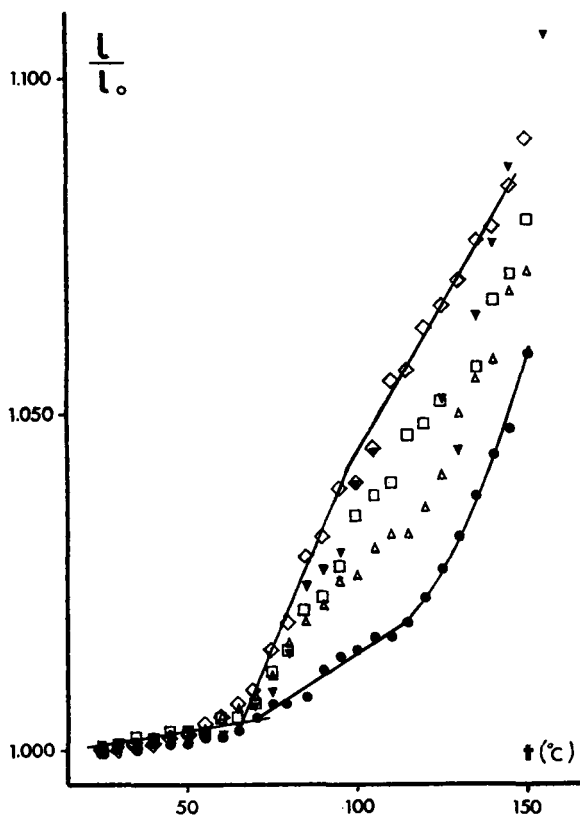
Fig. 6. Axial thermal expansion in ethylene glycol of fibers of different draw ratio: (●) 1× (unstretched); (△) 2.9×; (□) 5×; (◊) 10×; (▼) 14.8×.

sence of any effect at all of annealing temperature on $\alpha_\parallel$ in decalin (except far above T_g). The drastic increase in dye diffusion rates in water is consistent with the decrease in T_g, which was small, however. In addition, the relaxation times at T_g may also be decreased. Some indication of differences in estimates of this quantity on different fibers was obtained from the temperature dependence of dye diffusion.[17] They may be assumed to originate in a subtransition[15] affected by annealing, as reflected also by the lower brittleness below T_g of the more thoroughly annealed fibers. The latter, however, can also be observed on dry fibers, which should be well represented by those in decalin. The insensitivity of the behavior in decalin to annealing temperature will have to be explained, if the description is to be internally consistent. To a lesser extent, these remarks apply to the draw ratio results. The behavior in ethylene glycol was intermediate (predictably, see next section).

In view of the inadequacies in the above interpretation, it may be well to consider alternatives. The high $\alpha_\parallel$ could conceivably measure the expansion of transfer liquid (or air) occluded in voids elongated in the di-
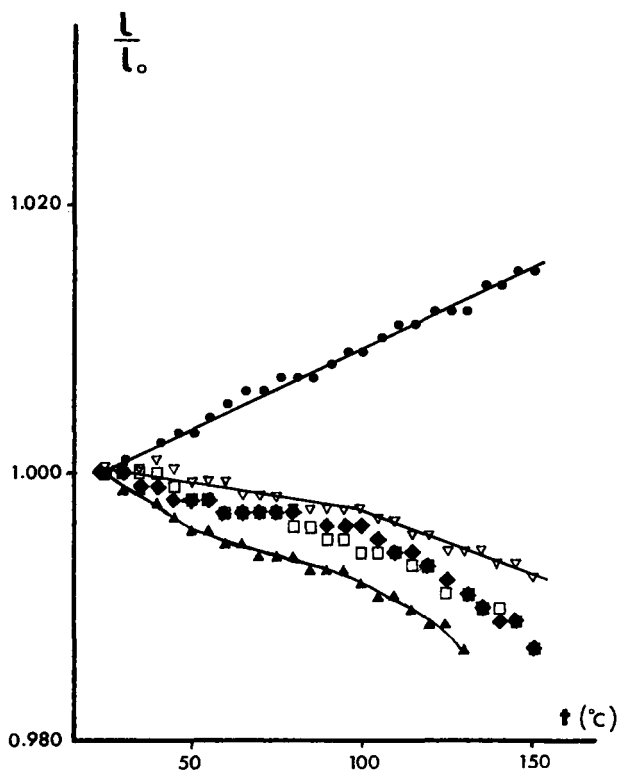
Fig. 7. Axial thermal expansion in decalin of nylon 6 fibers of different draw ratio: (●) 1× (unstretched); (▲) 1.5×; (▽) 2×; (□) 3×; (◆) 4×.

rection of the fiber axis. The observation of the glass transition in the measurement need not exclude that possibility, since below T_g the transmission of the expansion of the fluid may be prevented by the immobility of the polymer. Fibers which show the high coefficients have, however, given no indication of such voids by other measurements.[18] It should also be noted that the high $\alpha_\parallel$ is compatible with a structure based on molecules folded in the direction of the fiber axis. Fold lengths in single crystals of polymers have been shown to increase with increasing temperature.[19,20]

The linear axial thermal expansion of most of the common natural and artificial fibers has been measured by the same procedure. None of these had such high positive values of $\alpha_\parallel$, including those in which helical molecular conformations have been well established, such as polypropylene or wool. The closest in behavior was a poly(ethylene terephthalate) fiber.

Of special interest here was the behavior of nylon. The results in Figure 7 are in good accord with a fiber model made up of separate crystalline and amorphous regions. The stretched nylon 6 fibers contracted with increasing temperature (less thorough results with nylon 66 were similar), as rubber under tension. This can be attributed to the tendency of rub-

bery amorphous parts under an axial strain by the crystalline parts to assume a more probable conformation.   Since

$$(\partial f/\partial T)_l = - (\partial f/\partial l)_T (\partial l/\partial T)_f$$

where f is force, T is temperature, and l is length, the linear thermal expansion at zero outside force is given (see Part I[17]) by eq. (1).

$$(\partial l/\partial T)_f = (\partial E/\partial l)_T / T(\partial f/\partial l)_T \tag{1}$$

Both the temperature and the modulus are positive.   An increase of length with decreasing temperature thus indicates a decrease of internal energy E with increasing length, which could come about by reformation of crystalline "bonds" or the relieving of retractive stresses in a continuous crystalline network.   The undrawn nylon had a positive $\alpha_{\parallel}$, as has rubber not held under external strain.   The results show clearly that the polymer was above T_g at room temperature, a point which continues to be a subject of controversy.[15]   This was further confirmed (for fibers in water) by the finding that dyes can diffuse into nylons at room temperature (which is regarded as a diagnostic test of good validity[17]).   If the function ascribed to the initial extension region (A) in polyacrylonitrile fibers is of more general validity, it should, then, be absent in nylon at room temperature; this is the case, judging by the absence of the "yield point" and the low initial modulus.

In evaluating the implications of the comparative behavior of nylon and polyacrylonitrile fibers, it must be borne in mind that the positive expansion coefficients of the latter can support and extend Dart's finding[21] of a positive $(\partial E/\partial l)_T$ only at very small strains.   Further, the dissimilarity in the respective behavior of the two fibers is not complete.   About 30–50°C. above the glass transition temperature of polyacrylonitrile, $\alpha_{\parallel}$ usually begins to level off or even to decrease.   This may be indication of eventual negative coefficients at still higher temperatures (such have indeed been observed in a number of cases).   There is presumably a relation here to an irreversible disorienting contraction which predominates at still higher temperatures.   The decrease in $\alpha_{\parallel}$ with increasing temperature above T_g was one of a number of findings, apparently related to early observations by Kolb and Izard,[7] which can best be fitted by a description in which polyacrylonitrile ceases to be glassy at what has been designated as T_g here and elsewhere, but becomes rubbery only at higher temperatures.   Creep and break extension also usually[1] level off or exhibit a maximum in the same temperature range.   One might speculate more specifically that the change at T_g is from a glass to a viscous liquid, still made up of relatively straight, stiff rods which can readily slide past one another.   With increasing temperature above T_g, the greater frequency with which the barriers to rotation can be overcome results in a smaller effective segment length or a more flexible, rubbery molecule, hence in a decrease in $\alpha_{\parallel}$ and, by increasing entanglement, in the other effects cited. It would seem, indeed, that utilization of the predictable decrease in ef-
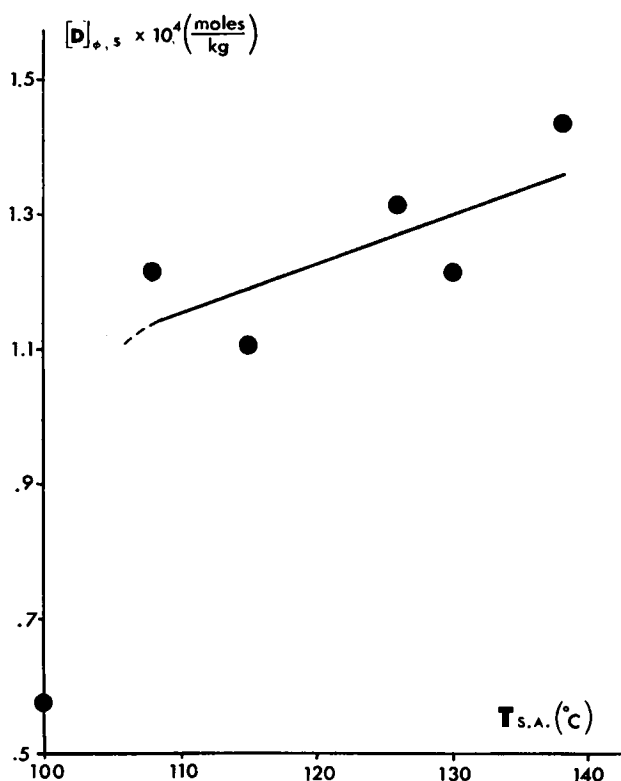
Fig. 8. Variation of pseudoequilibrium uptake of dye by outer fiber surface with fiber annealing temperature.

fective segment length with increasing temperature in a hindered polymer chain for the treatment of temperature dependence of kinetic processes above T_g should be explored more systematically for polymers in general.

The effect of annealing temperature on the uptake of dye on the outer fiber surface, which can be measured below T_g[22] was of interest (Fig. 8). In spite of the scatter, there can be little doubt about the effect, which has also been observed in a number of nonsystematic experiments. Cationic dye uptake (by the fiber as a whole) takes place on a very limited number of sulfonate sites derived from either initiator fragments or added comonomer. The increase in the surface equilibrium uptake below T_g with increasing annealing temperature could indicate that more sites are brought out to the surface. The magnitude of the uptake is often high enough to account for all the sites that should be present over a distance of several hundred Angstrom units from the surface on the assumption of complete homogeneity. There could be a number of explanations, but the most interesting possibility was that the chains near the surface orient in a radial direction, with the sulfonate groups at the surface. There is no further

support for this.   While it might be suggested alternatively that the annealing treatment results in a surface which can acquire a more negative electrokinetic potential by somehow adsorbing more anions, this appears less likely at present, since the fibers used for Figure 8 showed no systematic differences in streaming potential.

Effect of Environment

The strong plasticization by water (Part I) was surprising in view of the hydrophobic reputation of the polymer.   The latter is presumably based on the behavior of the unstrained fiber which is substantiated by the insensitivity of the initial modulus to water, but once enough free volume has been created by strain or temperature to, allow the entrance of water into the fiber, it exerts a strong plasticizing action.

The possible implication that the high dielectric constant of water reduces the postulated electrostatic resistance to extension was tested by examining the temperature dependence of the load-elongation behavior of a fiber in a large number of liquids over temperature ranges determined mainly by boiling or decomposition temperatures.   The results are summarized in Table I.   The last column indicates whether any plasticizing action Δ was observed.   The detailed data are too voluminous to be pre-

TABLE I
Physical Properties of Liquids and Plasticizing Action

| Solvent	M.W.	Molecular volume V_m, A.^{3}	Dielectric constant ϵ	Solubility parameter δ	Dipole moment μ	Active H	Plasticizing effect Δ
Decalin	138.2	258	2.17–2.20	8.27–8.73	0	−	−
Water	18.0	29.9	78.54	23.47	1.84	+	+
Methyl alcohol	32.0	67.1	33.1	14.54	1.66	+	+
Ethyl alcohol	46.1	97.0	24.3	12.83	1.7	+	+
Isopropyl alcohol	60.1	127	18.3	12.89	1.68	+	−
Benzyl alcohol	108.1	171	13.1	12.38		+	+
Ethylene glycol	62.1	92.6	37.7	16.96		+	+
Glycerol	92.1	121	42.5	16.5	2.67	+	−
Acetonitrile	41.1	87.1	37.5	12.33	3.4	−	+
Propionitrile	55.1	117	27.7	10.87	3.57	−	+
Acrylonitrile	53.1	110	38	10.72	3.6		+
Aniline	93.1	151	6.89	11.88	1.53	+	+
Phenol	94.1	146	9.78	12.90	1.6	+	+
Anisole	108.1	181	3.6–4.3		1.25	−	−
Nitrobenzene	123.1	169	34.8	9.58	3.98	−	+
Acetic acid	60.1	95.1	6.15	8.90	1.63	+	+
Oleic acid	282.5	526	2.46			+	−
Stearic acid	284.5	557				+	−
Dimethylformamide	73.09	127	26.6	12.5	3.82		+
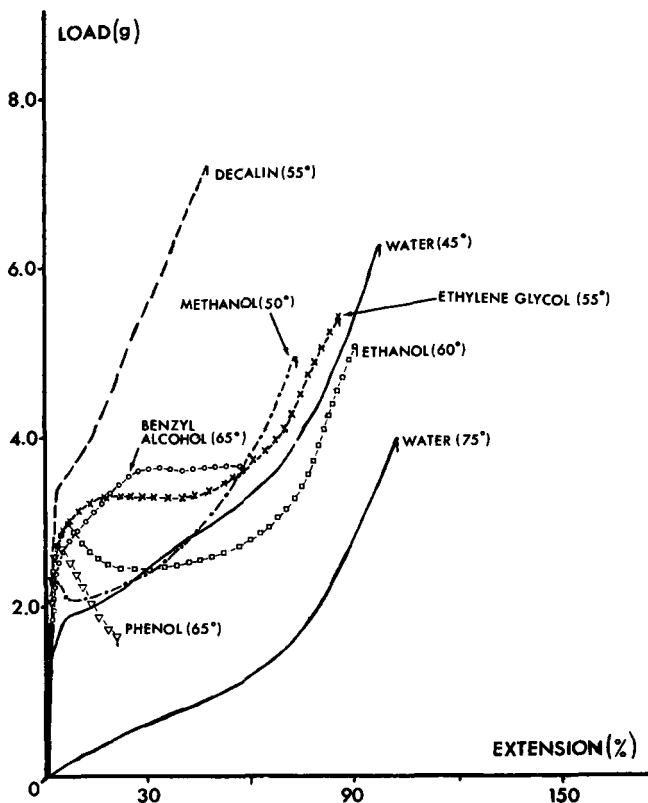
Fig. 9. Load–extension curves in hydroxylic plasticizing media.

sented here; selected representative curves obtained on fibers immersed in the hydroxy compounds are given in Figure 9, while Figure 10 shows specific features obtained in different other media.

Plasticization is meant here to denote any decrease by the liquid of the resistance of the fiber to an imposed stress. In most media, there was a decrease in load immediately following the yield point. The only possible indication that an active hydrogen may be necessary for plasticization was the elimination of the effect by substitution of the active phenol hydrogen by a methyl group (anisole), but this is explained as readily by any of the other possible factors. Correlation with dielectric constant ϵ is also unsatisfactory. The macroscopic ϵ indeed cannot be expected to provide a valid measure of intramolecular shielding. If the plasticizing action were due to separation by the solvent of favorably interacting polymer chains, or simply to an increase in free volume by the presence of diluent, then proximity of the solubility parameter to that of the polymer (15.4 according to Walker[23]) should be decisive. Although there is some correlation, e.g., the inactivity of glycerol, it is not good (e.g., acetic acid and propionitrile on the one hand, isopropanol on the other).

His findings may thus be compatible with solution by a reduction in molecular stiffness due to compensation of the polymer dipoles by those of the solvent.

It should be pointed out that a cohesive energy as high as that cited for polyacrylonitrile would not be in accord with the considerations of Krigbaum and Tokita[2] or Bohn, Schaefgen, and Statton.[9] Walker,[23] however, clearly relates the cohesive energy density to dipole moment of solvent.
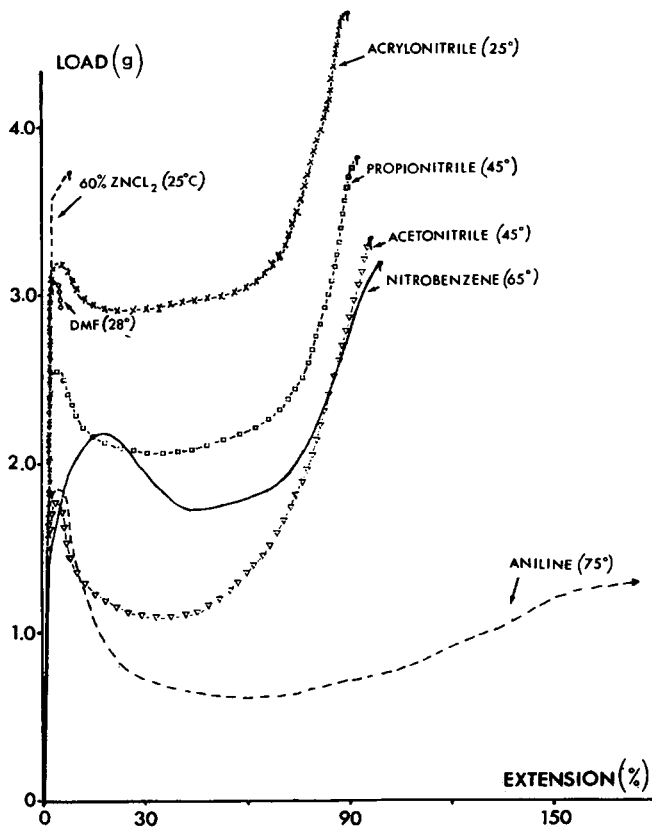

Fig. 10. Load–extension curves in different plasticizing media.

The dipole moment μ appears to provide the best single measure of plasticization effectiveness, especially if allowance is made for specific features. Thus, the inactivity of glycerol might derive from insolubility in the polymer, that of isopropanol from steric shielding of the hydroxy dipole. In Table I all effective compounds have a dipole moment above 1.6 D. The alcohols were considerably less effective than the corresponding nitriles. The dipole of the latter is much stronger, probably more accessible and more readily aligned alongside, but in an opposite sense to a fiber dipole, the repulsive effect of which thus becomes neutralized. A high dipole moment alone is evidently inadequate, however, for a complete explana-

tion of plasticizing action, and the interrelations between the factors cited make it difficult to differentiate their contributions.

While this experiment provided only indefinite support for the mechanism proposed for the main extension region (B), good substantiation was obtained for a volume expansion during the initial extension (A). The initial modulus was hardly affected by variations in test medium. Even in the solvents for polyacrylonitrile (60% ZnCl₂, N,N-dimethylformamide) the same curve was followed until the fibers suddenly dissolved at, or near, the yield point. It is possible that phenol, a nonsolvent, became a solvent for the fiber under load; in several cases no broken halves of the fiber could be found; this does not appear unreasonable, since the energy stored in the extension will make the free energy of solution of the stressed fibers more negative.

The length of extension region A (or the yield point) was decreased by the smaller plasticizers. The reduction and sharpness of the yield point (at least within a given class of compounds) increased with decreasing molecular diameter. Our data are not adequate for rigorous treatment with a possible view to estimating polymer segment size, but they provided the most direct evidence obtained up to now for an increase in volume during A. Efforts toward direct confirmation by actual measurement of volume changes are under way in this laboratory.

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Résumé

On a examiné l'influence du comonomère, du rapport d'étirage et de la température de recuit sur la température de transition vitreuse T_g et sur un certain nombre de propriétés des fibres de polyacrylonitrile. Les coefficients d'expansion thermique axiale au-dessus de T_g sont positifs et inhabituellement élevés. Dans l'eau, ils augmentent avec l'augmentation du rapport d'étirage et de la température de recuit, mais ces effets n'ont pas pu (ou difficilement) être observés dans la décaline. L'expansion thermique axiale a été comparée avec celle des fibres de polyamide, où le coefficient était positif pour les fibres non-étirées mais négatif pour les fibres étirées dans le domaine de température étudié (25–150°C). On discute des conséquences de cela sur la structure des fibres de polyacrylonitrile et sur un certain nombre de particularités de leur transition vitreuse. La plupart des résultats sont en accord avec une structure basée sur des molécules rigides déroulées en une conformation linéaire par interaction intramoléculaire répulsive entre les dipôles adjacents. Une grande proportion de composés examinés exercent une action plastifiante, qui pourrait être reliée le plus facilement aux moments du dipôle. L'effet est attribué à une réduction de la rigidité moléculaire et est comparé avec le comportement du polymère en solution. Une augmentation du "point de rendement" avec une augmentation de grandeur moléculaire du milieu soumis à l'essai en tension met en évidence une augmentation de volume pendant l'extension initiale.

Zusammenfassung

Der Einfluss von Comonomeren, Dehnungsverhältnis und Temperungstemperatur auf die Glasumwandlungstemperatur T_g und auf eine Anzahl von Eigenschaften von Polyacrylnitrilfasern wurde untersucht. Die Koeffizienten der thermischen axialen Expansion sind oberhalb T_g positiv und ungewöhnlich gross. In Wasser nahmen sie mit steigendem Dehnungsverhältnis und steigender Temperungstemperatur zu, in Decalin konnten jedoch solche Effekte nicht (oder kaum) beobachtet werden. Die thermische Axialexpansion wird mit derjenigen von Polyamidfasern verglichen, bei welchen der Koeffizient bei ungestreckten Fasern positive, aber bei gereckten im ganzen untersuchten Temperaturbereich (25–150°) negativ war. Schlüsse auf die Struktur von Polyacrylnitrilfasern sowie eine Anzahl von Eigentümlichkeiten ihrer Glasumwandlung werden diskutiert. Die Mehrzahl der Ergebnisse entsprach einer Struktur von steifen, durch intramolekulare Abstossung benachbarter Dipole aus der gestreckten Konformation gedehnten Molekülen. Eine unerwartet grosse Zahl der untersuchten Verbindungen zeigte eine Weichmacherwirkung, die am einfachsten zu den Dipolmomenten in Beziehung gesetzt werden konnte. Diese Wirkung wird einer Heabsetzung der Molekülsteifigkeit zugeschrieben und mit dem Lösungsverhalten des Polymeren verglichen. Eine Zunahme der Streckgrenze mit steigender Molekülgrösse des Zugtestmediums lieferte einen Hinweis auf eine Volumszunahme während der Anfangsphase der Dehnung