Change of Orientation by Thermal Contraction of Polyacrylonitrile Fiber

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Synopsis

Polyacrylonitrile polymer powder was dissolved in 70% nitric acid and spun into isotropic filament through a glass nozzle of 0.5 mm. diameter in a coagulating bath of 30% nitric acid. Stretching was carried out in two stages: the first stretching was done in water at 20°C. followed by drying, and the second stretching was done in a boiling saturated solution of ammonium sulfate. The total stretching ratio was 23. These filaments were shrunk freely in water at 70–180°C. The change in orientation factors was traced by x-ray, infrared dichroism, visible dichroism, and sonic modulus methods. The relation between the reciprocal absolute temperature of thermal contraction and the logarithm of fiber length is a straight line which has two inflection points at 93 and 175°C. The orientation factors by x-ray and infrared dichroism remain unchanged up to 175°C. On the contrary, the orientation factors by visible dichroism and sonic modulus drop suddenly at about 90°C. This indicates the occurrence of relaxation of the amorphous chain at the glass transition temperature and shows the polymer is not perfect single-phase material. Orientation of crystalline and amorphous phases is stable from 100 to 170°C. in spite of considerable thermal contraction. The stability of orientation can be explained by the growth of a folded structure in the polymer.

INTRODUCTION

According to Bohn et al.,[1] the wide-angle x-ray diffraction patterns of oriented polyacrylonitrile show discrete diffraction only on the equator and lack the amorphous halo which is always seen in the diffraction patterns of normally crystalline polymer; this would indicate that polyacrylonitrile is 100% laterally ordered material as a single phase combining some of the properties of both crystalline and amorphous phases.

When this polymer exists as a single phase, it would be expected that the various orientation factors should behave in the same way with a change of orientation by thermal contraction.

The relations between variously obtained orientation factors and the temperature of thermal contraction of polyacrylonitrile fiber were studied.

EXPERIMENTAL

Preparation of Polyacrylonitrile Fiber

Spinning. Polyacrylonitrile polymer powder (molecular weight 97,000) was dissolved in 70% nitric acid (polymer concentration 12 wt.-%) and

spun into an isotropic filament through a glass nozzle of 0.5 mm. diameter into a coagulating bath of 30% nitric acid. In order to prevent hydrolysis of the polymer, the temperature of the spinning apparatus was kept at about 0°C. The filament was washed free of nitric acid with cold water and stored in cold water.

Dyeing for Visible Dichroism. The swollen isotropic filament can be dyed very easily by aqueous Congo Red solution at room temperature as already reported.[2-6] The affinity of Congo Red for polyacrylonitrile fiber is rather high, and the Congo Red is very slightly desorbed by washing with water. Of course, once the fresh filament is dried, the swelling of the fiber drops so much that dyeing becomes difficult. Dyeing was carried out with two direct dyes, Congo Red (C.I. 22120) and Durazol Grey RG (C.I. 27720).

Stretching. The dyed swollen filament was stretched twice its swollen length in water and dried. The dried fiber was again stretched thirteen times its dried length in a boiling saturated solution of ammonium sulfate. The total stretching ratio was 23.

Thermal Contraction. Stretched filaments were sealed in glass ampules with sufficient water and contracted freely at various temperatures by dipping the ampules in an oil bath. The per cent shrinkage of the filament was measured.

Measurement of Orientation Factors

The change in orientation factors at room temperature was determined by x-ray, infrared dichroism, visible dichroism, and sonic modulus methods.

X-Ray Diffraction Method. The x-ray orientation factor f_x was measured from the azimuthal scanning at $2\theta = 16.8°$ by the usual method.[8]

Visible Dichroism. Parallel and perpendicular absorbances were measured by a microscope photometer, care being taken to cut out stray light. The orientation factor by visible dichroism f_D was calculated from the ratio D of these absorbances.

$$f_D = (D - 1)/(D + 2) \tag{1}$$

As Congo Red has no absorbance at a suitable wavelength in the direction perpendicular to the long axis of the dye molecule, the visible dichroism of perfectly aligned polymer dyed with Congo Red is unity.[7]

Infrared Dichroism. The observed transmission coefficient incorporates error caused by imperfect polarization of the incident beam, and the infrared microscope introduces another sort of error caused by divergence of the induced beam. The former was corrected as described in the preceding report[8] and the latter according to the Fraser's principle.[9] The orientation factor by infrared dichroism f_{ir} is given as

$$f_{ir} = [(D - 1)/(D + 2)]/[(3 \cos^2 \phi - 1)/2] \tag{2}$$

where $(D - 1)/(D + 2)$ is the observed and corrected dichroism and ϕ is the angle between the polymer chain axis and the direction of vibration of the band.

The angle ϕ can be obtained by combining infrared dichroism and other orientation factors for the same samples. When the mean orientation of x-ray and visible dichroism is obtained by taking into consideration the crystalline fraction as a measure of the average polymer alignment, the eq. (3) is valid:

$$f_x X + f_D (1 - X) = [(D - 1)/(D + 2)]/[(3 \cos^2 \phi - 1)/2] \quad (3)$$

where X is degree of crystallinity by the x-ray method.

For the calculation of the angle ϕ, four highly oriented specimens were prepared by stretching in saturated ammonium sulfate solution at 108°C. and drying at the same stretching ratio. The orientation of these specimens and infrared dichroism of the CN stretching vibration at 2237 cm.$^{-1}$ are given in Table I. The angle ϕ is calculated to be about 70° and

TABLE I
Calculation of Angle ϕ Between the Polymer Chain Axis
and the Direction of Vibration at 2237 cm.$^{-1}$

Draw ratio[a]	f_x	f_D	X	$f_x X +$ $f_D (1 - X)$	$\dfrac{D - 1}{D + 2}$ [b]	ϕ
5.5	0.744	0.618	0.321	0.659	−0.209	70
8.0	0.822	0.725	0.358	0.759	−0.244	70
13.0	0.853	0.816	0.449	0.833	−0.277	70.5
13.0	0.900	0.839	0.475	0.867	−0.297	71

[a] Draw ratio in boiling saturated ammonium sulfate.
[b] Infrared dichroism at 2237 cm.$^{-1}$.

there is a slight tendency for the angle to increase at high stretching ratios. This tendency agrees with the Bohn's result, in spite of the difference of the method used for preparation of the fiber.[10] Thus, the orientation factor by infrared dichroism at 2237 cm.$^{-1}$ is

$$f_{2237} = [(D - 1)/(D + 2)]/(-0.325) \quad (4)$$

on taking 70° for ϕ.

Sonic Modules. Sonic velocity was measured with a pulse preparation meter (H. M. Morgan Co., Inc). Sonic velocity in fiber gives an orientation factor α, defined as

$$\alpha = 1 - C_u^2/C^2 \quad (5)$$

where C_u is the sonic velocity of isotropic fiber and C is the sonic velocity of the sample.[11]

RESULTS AND DISCUSSION

The relation between the reciprocal absolute temperature of thermal contraction and the logarithm of per cent shrinkage of fiber length follows a straight line which contains inflection points at 93 and 175°C. (Fig. 1).

It appears that 93°C. is the glass transition temperature in the wet state and 175°C. is the softening temperature, i.e., that temperature at which melting or decomposition of the crystalline phase begins. These temperatures are correlated with the change of orientation factors in Figure 2.
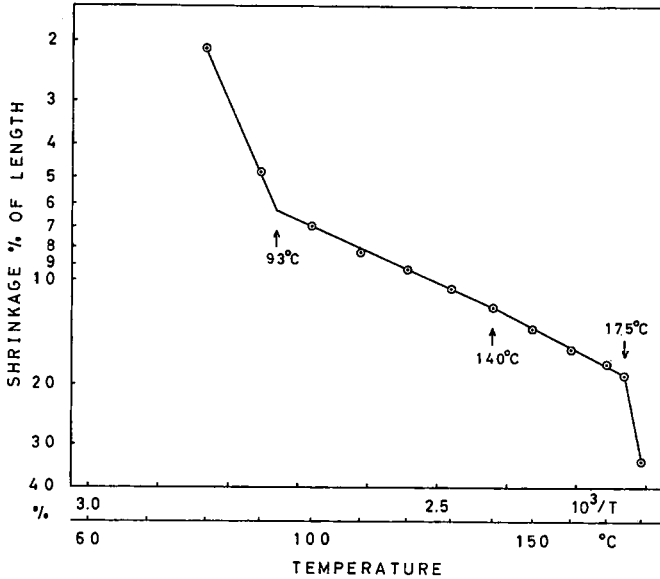

Fig. 1. Relation between the reciprocal absolute temperature of thermal contraction and the logarithm of per cent shrinkage of fiber length.
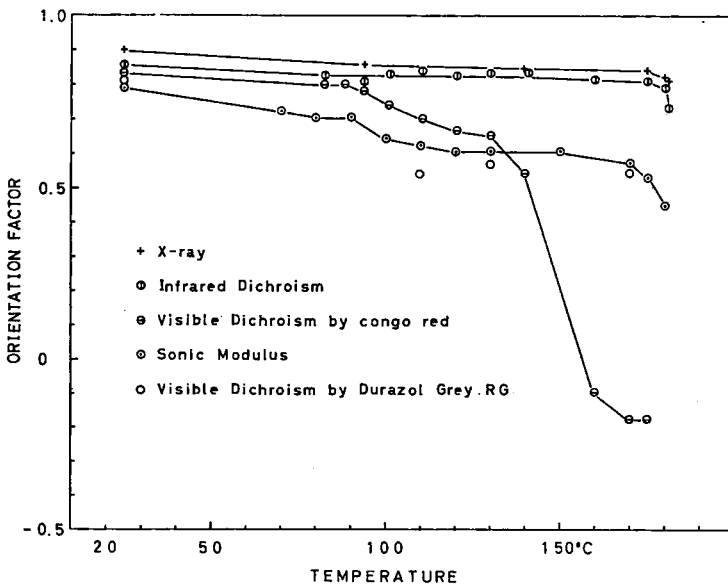

Fig. 2. Relations between the orientation factors and the temperature of thermal contraction.

The relation between the orientation factors and the temperature of thermal contraction is given in Figure 2. All four orientation factors, i.e., those obtained by x-ray, infrared dichroism, visible dichroism, and sonic modulus methods, decreased slightly from 25 to 90°C. nearly in the same ratio. The orientation factors obtained by x-ray and infrared dichroism are stable from 90 to 175°C. but begin to decrease at 180°C. On the contrary, the other two orientation factors decrease suddenly at about 90°C. The orientation factor from sonic modulus measurements is stable at temperatures from 100 to 170°C. and begins to decrease at 175°C.

The orientation factor by sonic modulus is taken to be a measure of the average orientation of all molecules in the sample regardless of the degree of crystallinity, i.e., this factor reflects the total molecular orientation.[11,12] The orientation factor by visible dichroism is related to the orientation of the amorphous phase in polymer, as the dye molecules are believed to be absorbed mainly in the amorphous phase. The sudden drop of this factor at about 90°C. shows the movement of amorphous chains at the glass transition temperature.

The orientation factors obtained by x-ray and infrared dichroism measurements are more stable at about 90°C. The orientation factor measured by sonic modulus begins to decrease at 175°C., i.e., about 5°C. lower than the temperature at which the decrease is apparent by the x-ray or infrared dichroism methods.

If a polymer is 100% single phase material, a similar change in the several orientation factors on thermal contraction would be expected. The results, however, indicate that this polymer is not single phase material, though the difference between the thermal stability of crystalline and amorphous phases is smaller than that of normally crystalline polymer.

Infrared dichroism at 2237 cm.$^{-1}$ is a measure of the average direction of stretching vibration of all nitrile groups, i.e., the orientation factor by infrared dichroism is considered to be the total molecular orientation. In Figure 2, however, the orientation determined by infrared dichroism is very similar to the x-ray orientation or crystalline orientation over the whole range of thermal contraction.

At this point, the results are in accord with a single phase model, or with a two-phase system in which the amorphous chain is bent, to keep the direction of the nitrile groups the same at the sudden drop of amorphous orientation at about 90°C. For such a bending mechanism to hold, the infrared dichroism of the nitrile group would not be related to the inclination of the polymer chain.

The method of measuring visible dichroism with Congo Red shows a peculiar drop in the orientation factor at temperatures over 140°C. At this temperature, Congo Red molecules begin to isolate from polymer and to coagulate into irregular particles in the filament. The visible dichroism was measured with the transparent part at the outer side of the dye particle. When Congo Red molecules are isolated from polymer and are in random orientation, dichroism should approach zero; however, the observed

dichroism has a negative value at 160–170°C.   This means that Congo Red molecules in transparent parts of the polymer are aligned perpendicular to the fiber axis.   As the length of the Congo Red molecule is about 26 A., it is difficult to conceive that the polymer should have an opening or crack of this width.   A possible interpretation is the preferential absorption of Congo Red on the fold surface, if this polymer has sharp crystalline fold plane at right angles to the fiber axis.

Another dichroic dye, Durazol Grey RG, did not coagulate in polymer at 170°C., and the pattern of change of orientation by dichroism with this dye is similar to that by the sonic modulus method.   This can be explained by the fact that the Durazol Grey RG molecule is longer than Congo Red and thus may move with difficulty in the polymer.

Orientation of both crystalline and amorphous phase is stable at 100–170°C. in spite of the considerable thermal contraction of fiber length (about 10%, i.e., $17\%_{170°C.}$–$7\%_{100°C.}$).   If the thermal contraction is related to the relaxation of extended polymer chains, the orientation of amorphous phase should decrease, but this is not the case.   Stability of orientation can be explained by the growth of folded structures in the polymer.

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Résumé

La poudre de polyacrylonitrile polymère a été dissoute à 70% d'acide nitrique et filée en un filament isotrope à travers une filière en verre de 0.5 mm de diamètre dans un bain coagulant contenant 30% d'acide nitrique.   L'étirement a été effectué en deux étapes, le premier étirement dans l'eau à 20°C, suivi du séchage, et le second étirement a été effectué dans une solution saturée bouillante de sulphate d'ammonium.   Le rapport d'étirement total était de 23.   Ces filaments sont rétrécis librement dans l'eau entre 70 et 180°C.   Les variations des facteurs d'orientation ont été déterminées au moyen de la méthode aux rayons-X, par dichroïsme infrarouge, par dichroïsme dans le visible et par le module du son.   La relation entre l'inverse de la température absolue de contraction thermique et le logarithme de la longueur de la fibre s'exprime par une ligne droite qui a deux points caractéristiques à 93 et 175°C.

Zusammenfassung

Pulverförmiges Polyacrylnitril wurde in 70%iger Salpetersäure gelöst und durch eine Glasdüse von 0,5 mm Durchmesser in ein Fällbad aus 30%iger Salpetersäure zu einem isotropen Faden gesponnen.   Die Verstreckung wurde in zwei Stufen ausgeführt und zwar die erste Verstreckung in Wasser bei 20°C mit darauffolgender Trocknung und die zweite Verstreckung in einer siedenden gesättigten Ammonsulfatlösung.   Das Gesamtstreckverhältnis betrug 23.   Diese Fäden wurden einer freien Schrumpfung in Wasser bei 70°–180°C unterzogen.   Die Änderung des Orientierungsfaktofs wurde mit der Röntgenmethode, Infrarotdichroismus, Dichroismus im Sichtbaren und Schallmodul verfolgt.   Die Beziehung zwischen reziproker absoluter thermischer Kontraktionstemperatur und Logarithmus der Faserlänge liefert eine gerade Linie mit zwei Knickpunkten bei 93°C und 175°C.