Morphological Changes in Twisted Nylon Monofilament

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Synopsis

The changes in structure of oriented nylon monofilaments due to an applied twisting action was investigated using wide angle x-ray scattering analysis and microscopy. The surface layer of the twisted filaments changes to a single texture after being repeatedly twisted in one direction at high temperature. Simultaneously, kink bands were produced on their surface. Characteristic features of kink bands are observed on the surface layer of the filaments first twisted in one direction and then twisted in the opposite direction at high temperature. X-ray diffraction patterns of the surface layer also changed remarkably. These changes in surface layers are related to the twist direction, the repeated number of twists, and the temperature of untwist. At lower temperatures, kink bands are not formed and a structural change to a single texture does not occur spontaneously.

INTRODUCTION

The structure and mechanical properties of oriented semicrystalline polymers subjected to twisting have been reported by Cooper, McKinnon, and Prevorsek,[1] Hien, Cooper, and Koutsky,[2] G. Sze, Spruiell, and White,[3] J. L. White, Cheng, and Duckett,[4] Kitao, Spruiell, and White,[5] and Kurokawa, Konishi, and Fijii.[6] It is generally accepted that oriented filaments consist of a bundle of fibrils, which, when twisted, undergo a helical deformation. Changes in wide angle x-ray diffraction (WAXS) patterns and mechanical properties have been explained in terms of these models of helically twisted fibrils.

The strain sustained by a twisted filament is proportional to the radial distance from its center. Hence, under severe twisting, fibrils in the surface layer of the filaments may be plastically extended to a helical form. Upon forceful untwisting, these extended fibrils will be compressed to their original state. Also the axial stress produced by twist contraction would act along the filament axis if the distance between two grip ends of the specimen does not vary during twisting and untwisting.

Zaukelies[7] has observed the development of kink bands in the oriented semicrystalline nylon 610 filaments compressed along the chain direction, and he interpreted them in term of the (010)(001) slip mechanism. These conditions for the formation of kink bands would be satisfied by the fibrils in the surface layer of the nylon filaments forcibly untwisted under suitable conditions. Their formation is affected by the tortional strain, number of repeated twists and untwists, and the temperature of untwisting.

Upon twisting, the oriented nylon filament hydrogen bonded sheets [the (002) planes in nylon 6 and the (010) planes in nylon 610] assume radial orientation. Upon untwisting, these planes tend to return to their initial randomly oriented

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state.[1] Repeated twisting and untwisting makes this recovery of orientation incomplete.

It seems plausible to expect that there exists a relationship between the change of morphology and that of structure. We have examined these changes with the help of wide angle x-ray diffracion, small angle x-ray diffraction (SAXS), and optical and scanning electron microscopy.

EXPERIMENTAL

Three kinds of oriented nylon monofilaments were used in the work: (1) commercial highly oriented nylon 610 filaments with 1.075 g/cm^3 density and 0.6 mm diam, (2) oriented nylon 610 monofilaments drawn to a draw ratio of four at 30°C with 1.07 g/cm^3 density and 0.62 mm diam, and (3) oriented commercial nylon 6 filaments with 1.146 g/cm^3 density and 0.5 mm diam. Three oriented filaments were repeatedly twisted and untwisted in a silicon oil bath at temperature which varied from 30 to 190°C. The specimen was fixed at a length of 20 mm during twisting and untwisting. Pieces of the surface layer were sliced from the twisted or untwisted filaments with a razor blade and then mounted on the specimen holder of a micro-x-ray camera (Rigaku Denki Co.: slit diam 0.1 mm, camera length, 10 mm). Each sample used for SAXS analysis was made up of four pieces of razor-sliced samples piled up in the same direction. The x-ray used was Ni-filtered Cu-K_α and the direction of x-ray beam was perpendicular to the surface layers. Morphological changes in the surface layer were observed by ordinary, polarized, and scanning electron microscopes.

For the indication of twisted or untwisted filaments, we shall use notation such as $S25(6)Z1(6)$, where S and Z denote the direction of twist, and 25 and 1 represent the number of turns per unit length (turn/cm). In order to denote the twist specimen the number $\frac{1}{2}$ is used. For example, $S25(1/2)(6)$ is the filament subjected to 25 cycles of twist and untwist which is then finally twisted 6 turns/cm toward the S direction (as indicated by 1/2).

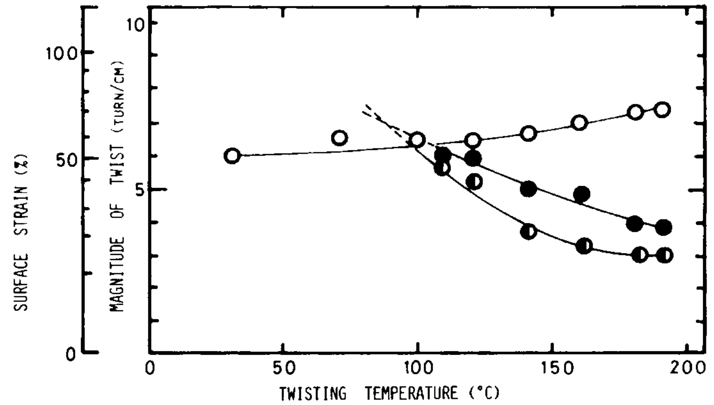
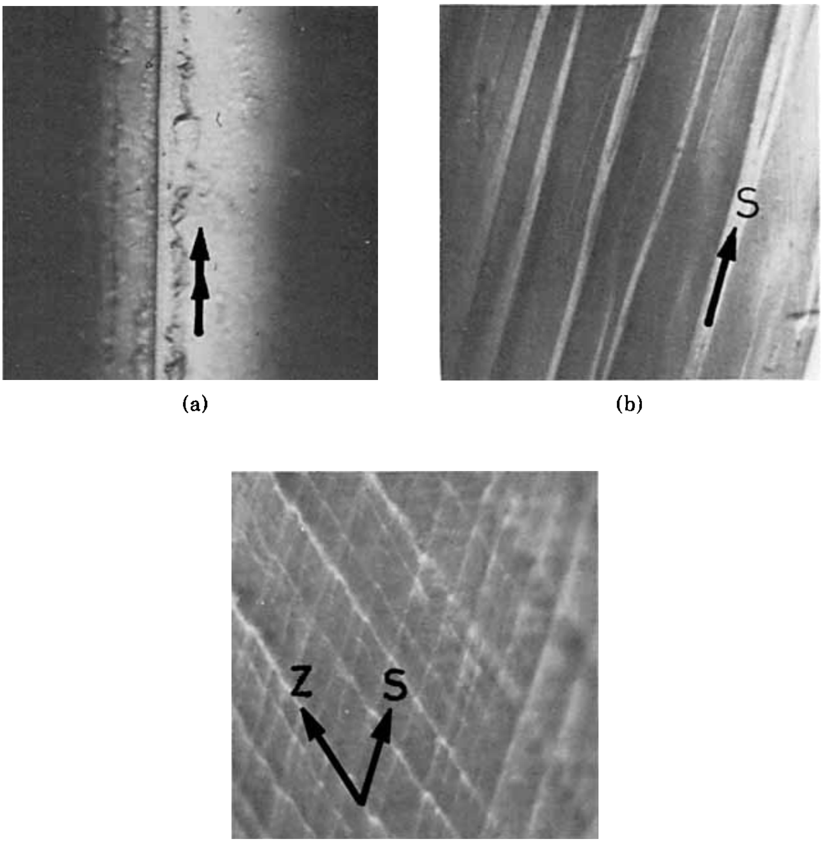


Fig. 1. Temperature dependence of twist strain (numbers of twist/cm) necessary to produce kink bands and twist strain at break for oriented nylon 6 monofilaments. ●, twist strain necessary to produce kink bands in one S twist; ○, in 10 S twists; ◐, at break.



(a) (b)

(c)

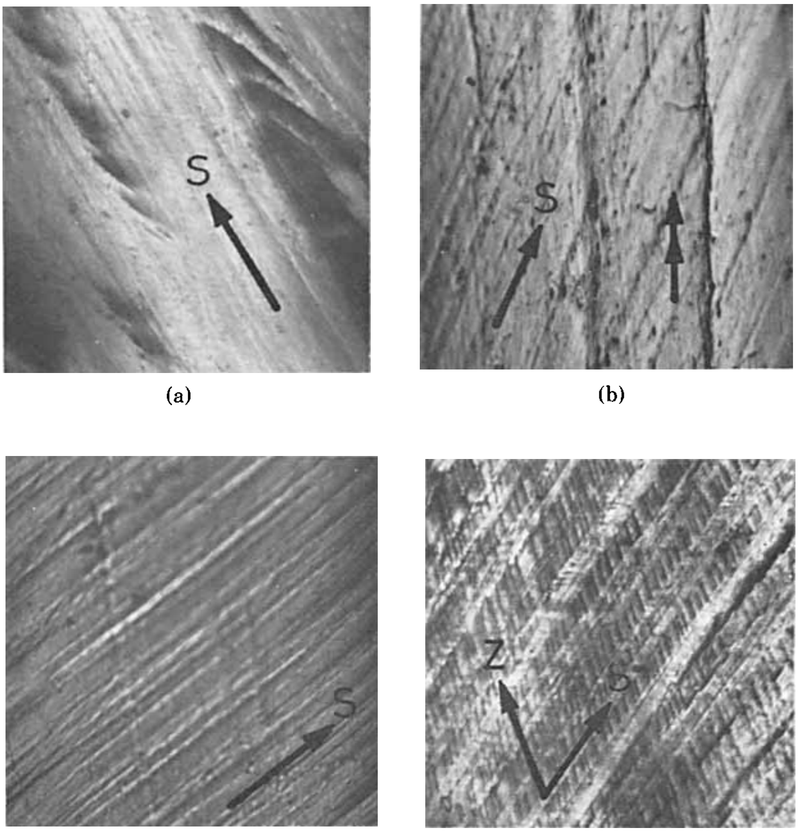
Fig. 2. Ordinary (a) and polarized [(b), (c)] micrographs of the surface of twisted nylon 610 monofilaments. Filament axis is vertical and → *S*, → *Z* show direction of *S*, *Z* kink bands. (a) Original oriented filament; (b) *S*1(6) filament twisted and untwisted of turns/cm in *S* direction at 180°C; (c) SZ10(6) filament subjected to 10 cycles of twist and untwist of 6 turns/cm in alternately *S* and *Z* direction at 180°C. (×150).

RESULT

Microscopic Observation

In the previous report,[6] it was shown that, when oriented nylon 610 filaments were twisted strongly and then forcibly untwisted at a temperature above 100°C, kink bands formed on their surface. Fig. 1 shows the temperature dependence of twist strain (number of turn/cm) necessary to develop the kink bands and twist strain at break (number of turn/cm) for the oriented nylon 6 monofilaments. Kink bands can not be produced for the filaments untwisted below 100°C, because the breaking strain at twist become smaller than the twist strain necessary to form the kink bands. These kink bands are inclined at about 25° at advanced sides of the fibrils on the filament surface in the direction of untwist [Fig. 2b]. This angle is nearly equal to the kink angle for the oriented nylon samples.

If the untwisted filament with kink bands are further twisted in the other direction, fibrils may again be extended helically and kink bands disappear. Upon further untwisting, the other set of kink bands is produced. Kink bands vanish



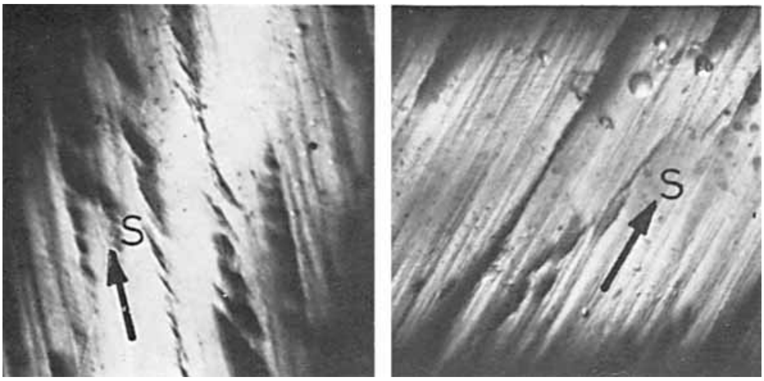
(a) (b)

(c) (d)

Fig. 3. Ordinary [(b), (c)] and polarized [(a), (d)] micrographs of surface of oriented nylon 610 monofilaments subjected to 25 cycles twist of 6 turns/cm [(b) $S26(6)$ sample], then twisted 6 turns/cm towards S direction [(a) $S25(1/2)(6)$ sample] or towards Z direction [(c) $S25(6)Z(1/2)(6)$ sample] and untwisted [(d) $S25(6)Z1(6)$ sample] at 180°C. Filament axis is vertical, ↗S shows the direction of S kink bands, ↟ shows scratch on surface parallel to filament axis. (×150).

during repeated twisting, but insufficient S and K kink bands crossing each other are observed on the filament twisted alternately in the S and Z direction [Fig. 2(c)].

Figures 2 and 3 show micrographs of the surface layer for highly oriented nylon 610 filaments twisted and untwisted 6 turns/cm at 180°C. $S1(6)$ and $S(25)$ samples show the typical S kink bands corresponding to the S twist. Insufficient recovery of structure upon untwisting produces the permanent change in surface layers as the number increases and this change influences the deformation produced by further twisting or untwisting. The $S25(6)Z1(6)$ sample shows a characteristic feature with strong S kink bands and fine Z kink bands which may be restrained by S bands. S bands are steps on the filament surface, but fine Z bands lie under the surface. We can thus observe S bands but not Z bands with a scanning electron microscope. The Z bands disappear following a Z twist but do not disappear completely following an S twist. Traces of S bands are observed on repeatedly twisted filaments and their tilt angle to the filament axis in the twisted state is different in the S and Z twist, because of the inclination of S bands in untwisted filament $S25(6)$ and $S25(6)Z1(6)$ [Figs. 3 and 4].

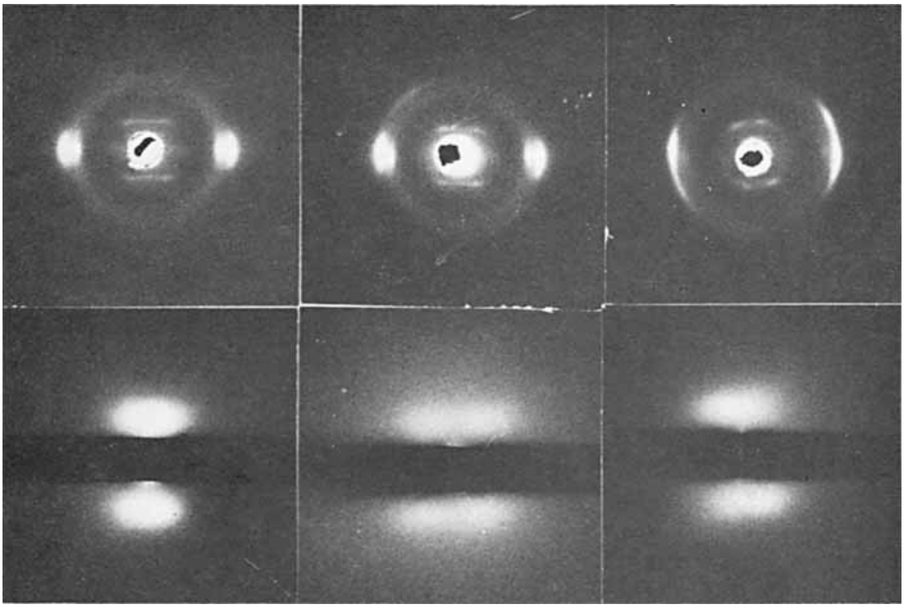


(a) (b)

Fig. 4. Ordinary photomicrographs of surface of oriented nylon 610 monofilaments subjected to 25 cycles of S twist, 1 cycle of Z twist of 6 turns/cm, then further twisted 6 turns/cm toward S direction [(a) $S25(6)Z1(6)S(1/2)(6)$ sample] or Z direction [(b) $S25(6)Z1(1/2)(6)$ sample]. Filament axis is vertical and ↗S shows direction of S kink bands. (×150).

X-Ray Diffraction

Figures 5 and 6 show the WAXS and SAXS patterns for the surface layers of the same specimens as shown in Figures 2 and 3. The fiber axis in the twisted state, as shown by WAXS patterns, tilts about 46° to the filament axis. This value is nearly equal to the calculated value of 48.5° The WAXS patterns of



(a) (b) (c)

Fig. 5. WAXS and SAXS patterns of twisted nylon 610 monofilaments corresponding to Fig. 2. (a) original oriented filament annealed at 180°C; (b) $S1(6)$; (c) $SZ10(6)$. Filament axis is vertical.

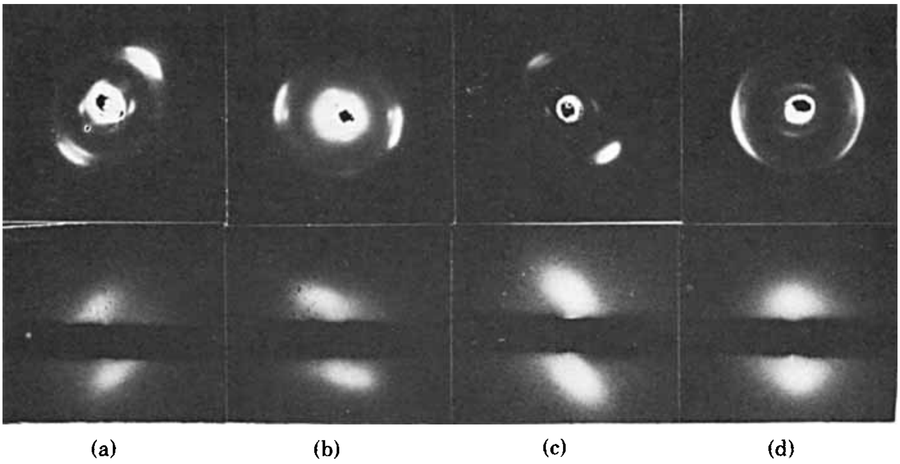

(a) (b) (c) (d)

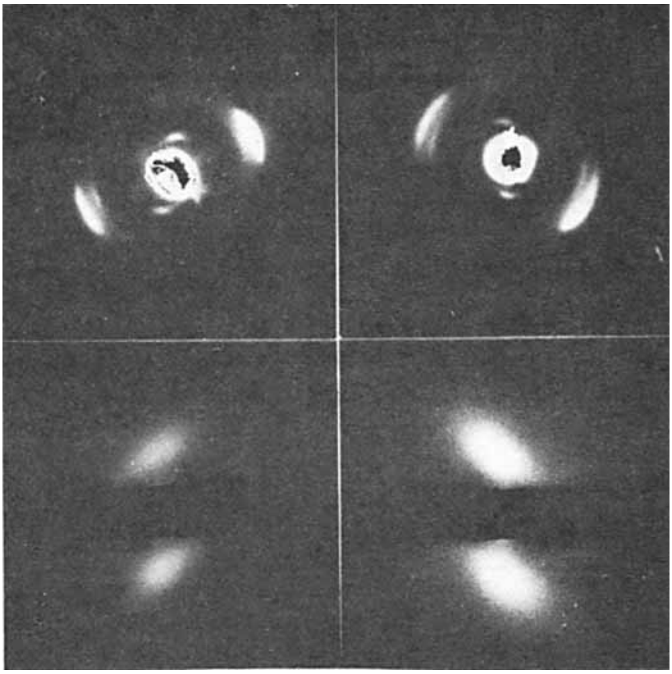
Fig. 6. WAXS and SAXS patterns of repeatedly twisted nylon 610 monofilaments corresponding to Fig. 3. (a) *S*25(1/2)(6); (b) *S*25(6); (c) *S*25(6)*Z*(1/2)(6); and (d) *S*25(6)*Z*1(6), respectively. Filament axis is vertical.

TABLE I
Long Periods, *L*, and tilt angles, ψ, of SAXS Pattern for Twisted Nylon 610 Monofilaments

Sample	Temp. of twisting, °C	Long period (*L*), (A)	Tilt angle of SAXS pattern (ψ),°
Original annealing at	100	88	0
	150	94	0
	180	98	0
*S*25(1/2)(5)	100	94	24
*S*25(1/2)(6)	150	110	31
*S*25(1/2)(6)	180	120	31
*S*25(5)	100	94	0
*S*25(6)	150	110	19
*S*25(6)	180	120	22
*S*25(5)*Z*(1/2)(5)	100	94	24
*S*25(6)*Z*(1/2)(6)	150	110	45
*S*26(6)*Z*(1/2)(6)	180	120	52
*S*25(5)*Z*1(5)	100	89	0
*S*25(6)*Z*1(6)	150	98	0
*S*25(6)*Z*1(6)	180	100	0
*S*Z10(6)	180	105	0

twisted samples show the preferred radial orientation of (010) planes [Figs. 6(a) and 6(c)]. For the samples repeatedly twisted in the *S* direction (010), reflections gradually split into two peaks with an increasing amount of repeated twisting [Fig. 6(b)]. The direction of split is the same as the direction of *S* kink bands, and the equilibrium angle between the two peaks is about 21° which is close to the kink angle.

The four-spot pattern of (001) reflection for the twisted samples displays asymmetry and the intense reflections change, depending on whether it is an *S* or *Z* twist [Figs. 6(a), 6(c), and 7]. The *S*25(6) sample gives the same asymmetry

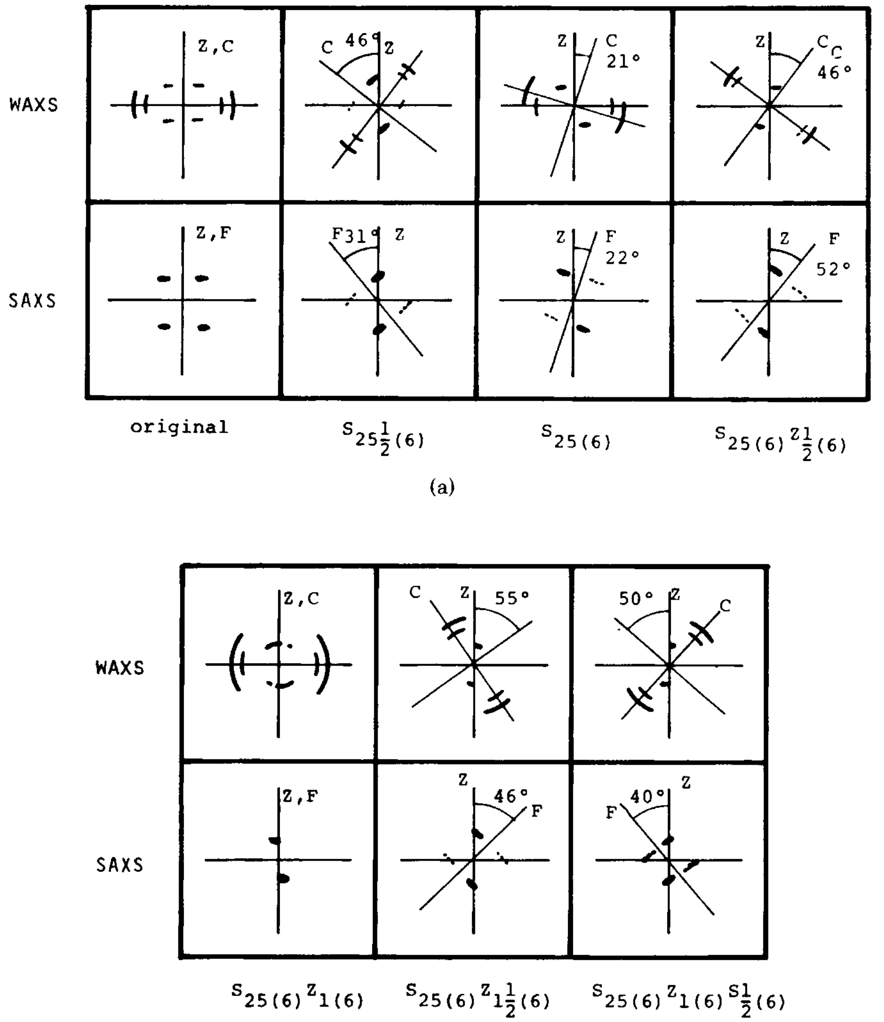


(a) (b)

Fig. 7. WAXS and SAXS patterns of twisted nylon 610 monofilaments corresponding to Fig. 4. (a) $S25(6)Z1(6)S(1/2)(6)$; (b) $S25(6)Z1(1/2)(6)$, respectively. Filament axis is vertical.

as (001) reflections of *Z* twist samples, though it is not twisted towards the *Z* direction. This asymmetry will be associated with the split (010) reflection arcs which display a nearly asymmetrical pattern and (001) spot rotate toward the meridian [Fig. 6(d)].

One reflection of the original four-point SAXS pattern intensifies, while the other grows fainter and eventually disappears as the number of repeated *S* twists increases. At the same time, the direction of layer lines gradually tilts from the direction perpendicular to the filament axis. The direction of twist determines which reflection of the SAXS pattern intensifies and to which direction it is inclined (Figs. 6 and 7). Their tilt angle χ and long period L increase with an increasing number of twists and reach the nearly equilibrium values after about 10 repeated twistings. Measured values of χ and L are shown in Table I; they change according to the twist strain, number of repeated twists, and temperature of untwist. Directions of tilt in SAXS patterns have the same dependence on the twist direction as the symmetric (001) reflections. The SAXS pattern of the $S25(6)$ sample tilts about 22° in the same direction as that of the *Z* twist sample $S25(6)Z1(6)$, similar to the asymmetric (001) reflection of the $S25(6)$ sample. The SAXS pattern of the $S25(6)Z1(6)$ sample changes to the two-point pattern on the meridian and its long period decreases [Fig. 6(d)]. If this filament is further twisted towards the *S* or *Z* direction, its SAXS pattern and long period return to the same shape and value as that of $S25(1/2)(6)$ or $S25(6)Z(1/2)(6)$ though their tilt angles are different (Fig. 7).



(a) (b)

Fig. 8. Schematic diagrams of WAXS and SAXS patterns corresponding to Figs. 5–7. *Z*, direction of filament axis, *C*, chain direction of crystallites and probably fibrillar direction; *F*, direction of stacks of lamellae of single texture.

DISCUSSION

Figure 8 represents the schematic diagrams to explain the WAXS and SAXS patterns for the surface layers of twisted samples. Pope and Keller[8,9] reported that, when the oriented polyethylene samples were deformed by shear compressive force during annealing at high temperature, it was changed to the single texture. Point et al.[10,11] investigated the single texture of polyethylene[10,11] and nylon.[12] We can conclude that the deformation occurring in the surface layers of the twisted filaments is similar to the deformation they reported and that the surface layers assume the single texture, the sheared direction of which changes according to the direction of twist. Fibrils in the surface layers are deformed helically and simultaneously take on the preferred radial orientation of (010)

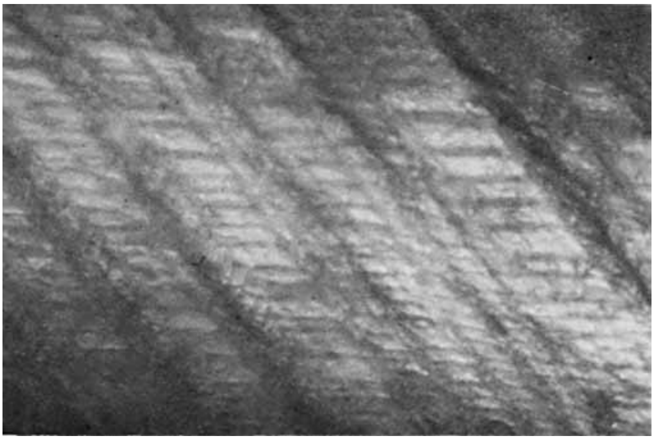


Fig. 9. Polarized micrographs of surface of oriented nylon 610 monofilament subjected to 25 cycles of S twist of 5 turns/cm and then 1 cycle of Z twist 5 turns/cm at 100°C. Filament axis is vertical (×150).

planes upon twisting. Upon untwisting, the preferred orientation partially recovers and formation of kink bands occurs. Repeated S or Z twist changes the surface layer to single texture. These changes, especially the change from the single texture by S twist to that by Z twist, are the causes of the structural changes related by the WAXS and SAXS patterns.

The tilt angle found in the SAXS pattern for $S25(1/2)(6)$ is a different form of $S25(6)Z(1/2)(6)$, as shown in Figures 6 and 8. This difference is similar to the difference in the inclination of S kink bands (Fig. 3). But for the $S25(6)Z1(6)$ sample, WAXS and SAXS patterns show that their symmetry improves, though their S kink bands are remarkably different from their Z bands. The tilt angle for further twisted samples $S25(6)Z1(6)S(1/2)(6)$ and $S25(6)Z1(1/2)(6)$ is nearly symmetrical with respect to the filament axis, as shown by WAXS and SAXS patterns (Fig. 7), but the traces of S kink bands show a different inclination then before (Fig. 4). The SAXS pattern and long period for $S25(6)Z1(6)$ sample change remarkably and (010) diffraction arcs broaden [Fig. 5(d)]. These changes resemble the thermal relaxation of structure which occurs during the annealing of the oriented filament at temperatures near the melting point. We suppose that the characteristic features of surface morphology for $S25(6)Z1(6)$ may be produced by the relaxation of structure which accompanies the change from an oriented fibrillar structure to the stacked lamellae.

When the temperature of twist is below 100°C, we can neither observe the split of (010) reflections in $S25(5)$ samples nor the change in SAXS patterns which represents the structural change to single texture and the formation of kink bands. We observed weak transverse lines similar to creases in the surface layer of the filament which had been twisted and untwisted repeatedly at near 100°C, but we observed no change in the filament twisted and untwisted at room temperature (Fig. 9).

The deformation mechanism of oriented semicrystalline polymer has been reviewed by several investigators,[13,14] and our results for twisted nylon filaments may be explained with this deformation mechanism, although the influence of morphological changes on the microstructure as revealed by WAXS and SAXS can not be determined accurately.

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