Synchrotron Wide-Angle X-Ray Diffraction of Single-Filament PPTA Fibers Under Stress

INTRODUCTION

Fibers of poly(*p*-phenylene terephthalamide) (PPTA) show high tensile strength, high Young's modulus, high thermal stability, and low creep,[1] due to the fully extended macromolecular chains. Unlike the usual crystalline polymers, the chains are highly extended with poor lateral order, in the so-called paracrystalline structure even in the noncrystalline zone.[2] Wide-angle x-ray diffraction (WAXD) and small-angle x-ray scattering (SAXS) have been used to study the lattice structure and the relation between the lattice structure, the morphology, and the macroscopic properties, with or without stress.[2-5] However, these studies employed fiber bundles exclusively. Only a very small angular change in the x-ray diffraction pattern could be observed because PPTA fibers attain very limited deformation before they are broken. Therefore, the stress distribution in each filament and the slight misalignment of the filaments could easily smear the results of WAXD. In a previous Communication,[6] we demonstrated successfully that the equatorial diffraction patterns of a *single* filament of Kevlar 49 (a DuPont trademark) fiber could be measured by taking advantage of the high-flux synchrotron x-ray source at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Here we present our results of the WAXD studies of the lattice deformation in a and b directions using a *single* filament each of the three PPTA fibers, with *c* being the fiber axis and the stretching direction.

EXPERIMENTAL

The PPTA fibers were obtained through the courtesy of Dr. E. Roche, E.I. du Pont de Nemours and Company, including the Kevlar 29 fiber, the Kevlar 49 fiber and a laboratory made PPTA fiber. The Kevlar 29 and 49 filaments have diameters of 12.7 and 13.1 μm, respectively, while the laboratory made PPTA filament has a diameter of 28.0 μm. The stress was induced by putting a known weight on one end of the filament. The weight was increased until the filament was broken.

The experiments were performed at the SUNY X-3A2 Beamline, NSLS/BNL. A modified Kratky block collimator was used to define the x-ray beam.[7] The wavelength was 0.154 nm. A linear position-sensitive detector was used to record the equatorial (200) and (110) diffraction patterns. The SAXS experiment was also performed using slightly modified geometry. The measured time was about 3000 seconds for each run. The Bragg equation was used to calculate the lattice dimensions in the a and b directions. More experimental details can be found in ref. 6.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the strain in both *a* and *b* directions upon the stress. The strain is defined as $(a-a_o)/a_o = \epsilon_a$ in the a direction and $(b-b_o)/b_o = \epsilon_b$ in the *b* direction with the subscript *o* denoting the dimension of the unit cell without stress: $a = 2d_{200}$, $b = a \cdot \tan(\mu)$ and $\mu = \sin^{-1}[d_{110}/(2d_{200})]$, with $d_{200} = \lambda/(2 \sin \theta_{200})$ and $d_{110} = \lambda/(2 \sin \theta_{110})$, where λ, θ_{200} and θ_{110} are, respectively, the x-ray wavelength, the Bragg angle for the (200) diffraction, and the Bragg angle for the (110) diffraction. From the plot, it is noted that the deformation in the a direction is greater than that in the b direction for all the three PPTA fibers, with the laboratory-made PPTA fiber showing the most obvious difference.

The unit cell in PPTA was found by Northolt and van Aartsen[5] to be monoclinic with dimensions $a = 0.787$ nm, $b = 0.518$ nm, c (fiber axis) $= 1.29$ nm, and $\gamma \simeq 90$ degrees. The molecular chains are parallel to the *c* axis. The benzene rings are not in the *b*–*c* plane because of competition between the stereo-hindrance and the conjugation. In the *b*–*c* plane, hydrogen bonds (N—H···O) exist between two adjacent molecular chains. In the *a*–*c* plane only the van der Waals force exists. The contraction in the b direction under stress implies either a change in the hydrogen-bonding angle or a change in the hydrogen-bonding length. The contraction in the a direction, however, implies simply that the van der Waals resistance becomes stronger when the distance between the molecular chains becomes shorter. Obviously, a stronger force is required to overcome the hydrogen-bonding resistance. This could be the reason for the difference of strain between the *a* and *b* directions.

The angle μ changes under the lattice deformation owing to the anisotropy in the dependence of the strain in *a*

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and b directions. Figure 2 shows that the μ value increases with increasing stress for all the three PPTA fibers, with the laboratory-made PPTA fiber showing the most obvious increase and Kevlar 29 fiber, the least. It has been reported[1] that the Kevlar 49 fiber is "harder" than the Kevlar 29 fiber (higher modulus and lower elongation to break). The structural difference under stress could then be correlated with some macroscopic properties of the fiber.

An error analysis is made because the diffraction peak shifts very slightly. From $a = 2d_{200} = \lambda/\sin\theta_{200}$,

$$\Delta\epsilon_a/\epsilon_a = \cos\theta_{200}/(\sin\theta_{200})\cdot\Delta\theta_{200}. \quad (1)$$

From $b = a\cdot\tan(\mu)$ and with the assumption that $\theta_{200} \simeq \theta_{110}$ and $\Delta\theta_{200} \simeq \Delta\theta_{110}$,

$$\Delta\epsilon_b/\epsilon_b \simeq 1.37\cos\theta_{110}/(\sin\theta_{110})\cdot\Delta\theta_{110}. \quad (2)$$

The uncertainty in determining the peak position is ±1 channel of the linear position-sensitive detector (LPSD). The sample-to-detector distance is 175 mm. Therefore with an LPSD pixel dimension of 0.0934 × 2 mm^2, we have $\Delta\theta_{200} = 1 \times 0.0934/175 \simeq 5.3 \times 10^{-4}$ rad, which gives rise to $\Delta\epsilon_a/\epsilon_a \simeq 0.13\%$ and $\Delta\epsilon_b/\epsilon_b \simeq 0.18\%$.

The maximum strain was less than 0.4%, implying that our WAXD experiment remained fairly low in precision. However, our single-filament result has better precision when compared with previous reports on fiber bundles,[3,4,8,9] thanks to the high-flux synchrotron x-ray source and the high resolution of our LPSD.

Finally, our SAXS experiment failed to detect any periodic spacing in equatorial or meridional directions with fiber bundles of all three PPTA fibers. Our SAXS set-up had an angular resolution down to 1 mrad, corresponding to a spacing of ca. 150 nm, implying that the paracrystalline zone, if it exists, may have very similar electron density to the crystalline zone.[2]

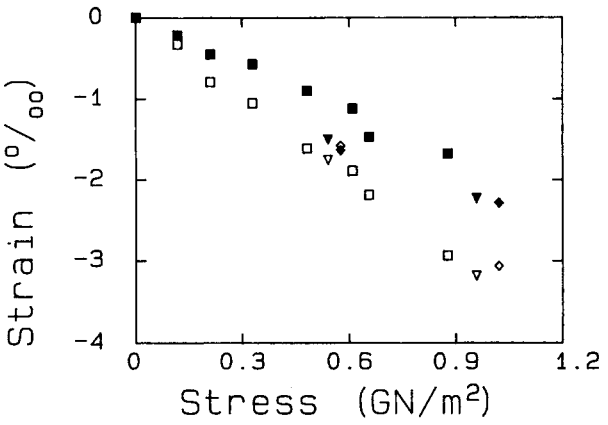

Figure 1. Plot of lattice strain versus stress for a *single* filament of PPTA fiber. (□) Laboratory-made PPTA fiber in the a direction; (■) laboratory-made PPTA fiber in the b direction; (▽) Kevlar 49 fiber in the a direction; (▼) Kevlar 49 fiber in the b direction; (◇) Kevlar 29 fiber in the a direction; (◆) Kevlar 29 fiber in the b direction.

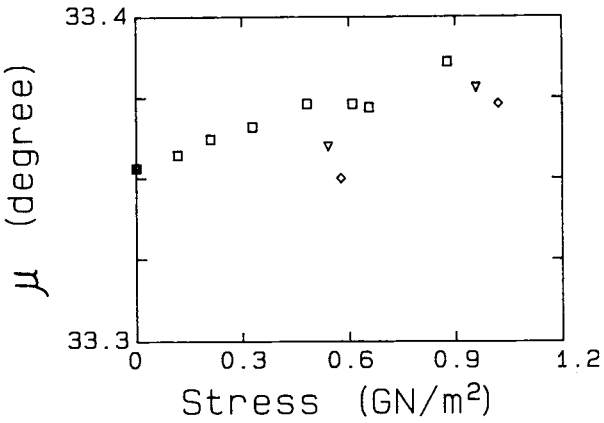

Figure 2. Plot of μ versus stress for (□) laboratory-made PPTA fiber; (▽) Kevlar-49 fiber; (◇) Kevlar-29 fiber.

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