

Deformation Behavior of Kevlar Fibers Studied by Raman Spectroscopy

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Synopsis

The tensile deformation of Kevlar fibers has been studied using Raman spectroscopy. The Raman bands shifted to lower wavenumbers and broadened with stress. The shift of the 1610 cm^{-1} Raman band per unit stress was about $-2.5\text{ cm}^{-1}/\text{GPa}$ in both Kevlar 29 and Kevlar 49. A simple one phase paracrystalline model is used to explain the observed shifts. The total increase in the width of the 1610 cm^{-1} Raman band was about 2.5 cm^{-1} and the increase in width was negligible till a stress of about 0.5 GPa.

INTRODUCTION

Raman Spectroscopy can be used to study the micromechanics of polymer fibers, due to the dependence of the frequencies of the vibrational modes of the crystal on the strain on the crystal.¹ Properties which depend on molecular vibrations, such as the peak positions of Raman spectra, generally alter with changes in unit cell dimensions caused by temperature or stress.²⁻⁴ The peak position may be used to determine the state of strain in the ordered regions of the fiber at constant temperature. Polydiacetylene crystals have been produced with a high degree of perfection and in these systems it has been possible to directly compare the molecular and macroscopic deformations using Raman spectroscopy.⁵ In the recent past, the effect of stress on the Raman band frequencies have been studied in a wide variety of polymers, like poly(*p*-phenylene terephthalamide), poly(*p*-phenylene benzobisthiazole), poly(ethylene terephthalate), polyethylene, and polypropylene.⁶⁻¹⁰

Polymeric chains containing many para substituted benzene rings or other rigid units can form nematic or polycrystalline structures with their chains straight and parallel, giving rise to high strength and modulus. The stiffness and strength of these fibers approach their theoretical values and are used as a reinforcing fiber in aerospace composites. This makes the mechanical properties of these materials of great scientific as well as practical interest. Poly(*p*-phenylene terephthalamide) (PPTA)^{11,12} and poly(*p*-phenylene benzobisthiazole) (BPZT)^{13,14} are examples of such fibers. We are concerned here with the relationship between molecular properties and mechanical properties in two types of poly(*p*-phenylene terephthalamide) fibers, commercially available from DuPont as Kevlar 29 and Kevlar 49.

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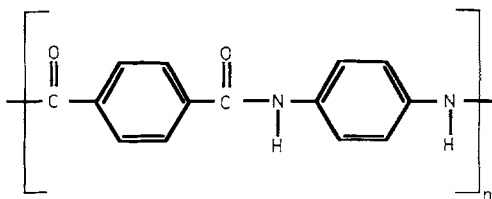


Fig. 1. Chemical structure of poly(*p*-phenylene terephthalamide).

Poly(*p*-phenylene terephthalamide) (Fig. 1) is a semirigid rod polymer with its molecular conformation in the crystalline region being fully extended all-*trans*.¹⁵ It has a monoclinic (pseudo orthorhombic) unit cell¹⁶ and a very high degree of crystallinity.¹⁷ Kevlar fiber is highly anisotropic, and partially ordered. The structure of the fiber is comparatively simple and the molecules are assumed to be straight, and the fiber is considered an assembly of rods. The fiber stiffness corresponds well with the degree of orientation of the anisotropic molecules. Wide angle X-ray scattering (WAXS) of Kevlar show sharp meridional reflections and no meridional reflections are observed in small angle X-ray scattering (SAXS), indicating low periodic electron density differences in the chain direction. High resolution transmission electron microscopy of fiber fragments has shown no evidence of chain folding or extensive chain disorder.^{18,19} Any disorder is due to chain termination or defects in sheet packing. Thus Kevlar can be considered to have an essentially extended chain conformation. The fiber can therefore be approximated by a bundle of parallel and identical chains, just like a simple uniaxial fiber composite, a sort of molecular composite. Kevlar fibers have poor regularity in the radial direction due to the microfibrillar structure of Kevlar fibers, and this gives rise to strong equatorial scattering in SAXS.¹⁷

The Raman spectrum of Kevlar fibers is affected by stress,⁶ allowing measurement of the local strain in the ordered regions of a single 13 μm diameter fiber. Van der Zwaag et al.²⁰ have measured the frequency shift in the Raman spectra of PPTA fibers of a range of moduli spun by Akzo Corp. due to an applied mechanical stress. In all-*trans* chains there is a linear relationship between the local stress in the molecular chain direction and the vibrational frequency corresponding to the polymer backbone. The line shape of the Raman band is then directly related to the stress distribution in the sample. Deconvolution of the line shape of zero applied stress would allow the exact stress distribution to be obtained. This distribution of stress in a fiber under load can

TABLE I
Properties of Kevlar Fibers

Property	Kevlar 29	Kevlar 49
Initial modulus (GPa)	62	114
Tensile strength (MPa)	2900	2900
Elongation (%)	3.8	2.4
Orientation angle (°)	16	10

be used to relate strength to molecular defects. In this paper we have studied the effect of tensile stress on the band position and band shape in the Raman spectra of Kevlar 29 and Kevlar 49.

EXPERIMENTAL

Two different fibers, Kevlar 29 and Kevlar 49 were used in this study. The properties of these fibers are given in Table I. The theoretical modulus of the PPTA chain is about 220 GPa and the shear modulus is approximately 2 GPa.

Raman spectra were recorded on a SPEX 1877 triplamate spectrometer, using a Coherent Nova 90-5 Ar⁺ laser. The experimental setup for micro-Raman experiment has been described in detail in a previous paper by the authors.⁸ The 488 nm emission line was used for excitation. Penn and Mialnovich²¹ found that Kevlar gets damaged when the laser power at the fiber exceeded 16 mW. So in all experiments the power of the laser at the specimen was kept below 15 mW. The collection time was low since Kevlar is an excellent scatterer. The spectra was averaged over 10 scans, each recorded for 5 s. Kevlar fibers were mounted using normal tabbing methods. These tabs were mounted in a small strain frame designed to fit on a microscope stage. Strain was applied in a stair case fashion. The spectrum was recorded after the stress stabilized to within ± 60 MPa. During this period the laser was not focused on the fiber to reduce any damage to the fiber due to long exposure. The Raman data were transferred to a CONVEX computer and the spectral region 1200–1700 cm^{-1} was selected for further analysis.

RESULTS AND ANALYSIS

The C—C stretching vibration in the phenyl ring gives rise to moderate to strong band in the 1200–1680 cm^{-1} region (Fig. 2).²¹⁻²³ A severe problem with Kevlar has been that, though it is the most suitable material mechanically, it

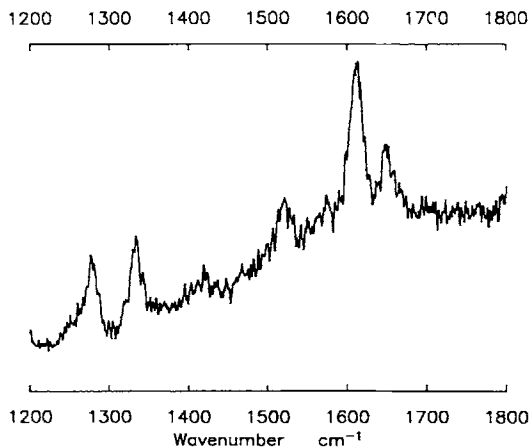


Fig. 2. Raman spectrum of Kevlar in the 1200–1800 cm^{-1} region.

has unusually broad Raman lines even under no load, and a large fluorescent background. The stress applied to the fiber in the chain direction manifests itself at the molecular level as changes in bond length and bond angle and is observed spectroscopically as a shift of the peak frequency and as an increase in the width of the band. The position of spectral peaks is easily measured, but the background makes small changes in linewidth very difficult to measure. Significant data manipulation is thus required to measure the linewidth changes.

Other techniques like Fourier transform Raman spectroscopy can be used to decrease the fluorescence. Figure 3 shows the Raman spectrum of Kevlar 49 and Kevlar 149 recorded using a Fourier transform Raman spectrometer in combination with a YAG laser.²⁴ Even though the fluorescence is considerably reduced, other experimental problems prohibited the use of this technique for stress Raman experiments. Some of them were large collection times, difficulty in focusing the beam on to a single fiber and damage of the fiber due to excessive heat produced on focussing.

In this study, we chose the peak at 1610 cm^{-1} , the ω_2 ring vibration since it was most sensitive to stress. The vibrations corresponding to the polymer backbone are not the only ones sensitive to stress. The peak at 1500 cm^{-1} corresponding to the N-H inplane bending also shifts with stress. Using spline fit, a baseline was drawn and the region $1550\text{--}1700\text{ cm}^{-1}$ of the background subtracted data set was fit to a sum of two gaussian functions using nonlinear least squared fitting routines. This was necessary as there was considerable overlap between the 1610 and 1649 cm^{-1} bands. When only the peak position was required, only the 1610 cm^{-1} band was fit to a Gaussian or a Gauss-Lorentz sum function as the accuracy of the peak position did not depend on the adjacent overlapping peak.

Determination of Pure Band Profile

The Raman spectrum can be considered to be a convolution of the true spectrum and the slit function (instrumental width). Since line shape is of particular interest here, deconvolution techniques were used to get the pure

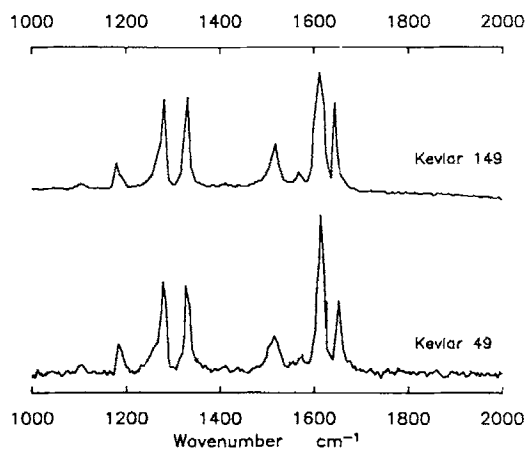


Fig. 3. Fourier transform Raman spectrum of Kevlar 49 and Kevlar 149.

profile.²⁵ The experimental profile $h(x)$ can be expressed in terms of the true profile $f(x)$ and the instrumental profile $g(x)$ as

$$h(x) = g(x) * f(x) \quad (1)$$

Here $*$ indicates the convolution operation. In order to deconvolute $g(x)$ from $h(x)$, we take the Fourier transform of both sides of eq. (1), divide, and take the inverse transform:

$$f(x) = \mathcal{F}^{-1} \left(\frac{\mathcal{F}\{h(x)\}}{\mathcal{F}\{g(x)\}} \right) \quad (2)$$

Routines using fast Fourier transform algorithms make this deconvolution procedure straightforward. In practice, resolution is limited by the finite number of data points. This truncates the useful range of the transform and is equivalent to a boxcar apodization, giving rise to large side lobes in the deconvoluted result. Various other apodization windows were used to reduce the sidelobes, but these also reduce the resolution of the peak. The choice of the apodization window made little difference as they had similar effects on the width of the deconvoluted peak. Figure 4 shows a series of Raman bands of Kevlar at different stress levels. The symbols represent the raw data and the solid line is the deconvoluted curve. There was no significant effect of deconvolution on the line shape of the Raman bands as the instrumental width is very narrow.

Deconvolution of this true band profile at zero applied stress would allow the exact stress distribution in the fiber to be obtained. The band shape critically depends on the form of the baseline chosen to subtract the background. But due to the low signal to noise ratio caused by fluorescence, it was very difficult to draw the baseline accurately and hence measurement of the stress distribution was not attempted.

Effect of Stress on the Raman Band Position

The change in the peak position of the 1610 cm^{-1} band with increase in stress is shown in Figure 5 for Kevlar 29 and Kevlar 49. The peak position corresponds to the most probable chain stress. The Raman peak shifts to lower frequencies as expected and the peak shift factor (frequency shift per unit stress), $d\tilde{\nu}/d\sigma$, is constant till fracture. The peak shift factor is $-2.44 \text{ cm}^{-1}/\text{GPa}$ for Kevlar 29 and $-2.15 \text{ cm}^{-1}/\text{GPa}$ for Kevlar 49 with an error of ± 0.5 .

Kevlar 29 and Kevlar 49 have different crystallite orientation and the effect of this misorientation on the peak shift factor can be explained if one assumes a one-phase paracrystalline model where the rigid rods are linked together by hydrogen bonds forming crystalline domains. The polymer is therefore an aggregate of anisotropic elastic units whose elastic properties are those of the highly orientated fiber. The polymer should be devoid of amorphous regions having different mechanical properties. The elastic properties depend on the orientation distribution of the crystallites. Assuming uniform stress throughout the aggregate, which is equivalent to a series model,²⁶⁻²⁸ one can express the average strain ϵ_{total} as

$$\epsilon_{\text{total}} = [s_{11}\overline{\sin^4\theta} + s_{33}\overline{\cos^4\theta} + (2s_{13} + s_{44})\overline{\sin^2\theta \cos^2\theta}] \sigma \quad (3)$$

where σ is the applied stress, θ is the angle the crystallite axis makes with the direction of the applied stress, and s_{11} , s_{33} , s_{13} , and s_{44} are the compliance constants. Substituting for $\overline{\cos^2\theta}$, we have

$$\epsilon_{\text{total}} = [s_{33}\overline{\cos^4\theta} + A\overline{\sin^4\theta} + B\overline{\sin^2\theta}] \sigma \quad (4)$$

where $A = s_{11} + 2s_{13} + s_{44}$ and $B = 2s_{13} + s_{44}$. For highly oriented fibers $\overline{\sin^4\theta} \rightarrow 0$. Therefore,

$$\epsilon_{\text{total}} = \frac{\sigma}{e_3} \overline{\cos^4\theta} + B\sigma \overline{\sin^2\theta} = \epsilon_{\text{stretch}} + \epsilon_{\text{rotation}} \quad (5)$$

where $e_3 = 1/s_{33}$ is the elastic modulus parallel to the crystallite axis.

The total strain is a combination of the stretching of the crystallites $\epsilon_{\text{stretch}}$, and a rotation of the crystallites towards the fiber axis, $\epsilon_{\text{rotation}}$, due to shear deformation. But only the strain due to stretching, $\epsilon_{\text{stretch}}$, of the crystallites gives rise to a shift in peak position. $d\tilde{\nu}/d\sigma$ is therefore dependent only on $\epsilon_{\text{stretch}}$ and is a function of the elastic modulus parallel to the crystallite axis and $\overline{\cos^4\theta}$. The crystallite misorientation in Kevlar 29 and Kevlar 49 is 16° and 10° , respectively. $\epsilon_{\text{stretch}}$ should therefore be $\sigma/200 \times \overline{\cos^4(16)} = \sigma/200 \times 0.85$ for Kevlar 29 and $\sigma/200 \times \overline{\cos^4(10)} = \sigma/200 \times 0.94$ for Kevlar 49, a difference of about 10%. In principle, a higher value of $\epsilon_{\text{stretch}}$ for the same applied stress in Kevlar 49 compared to Kevlar 29 should result in a larger peak shift factor for Kevlar 49, which is not observed. But a difference of only 10% in $\epsilon_{\text{stretch}}$ will not contribute to a large enough change in the value of $d\tilde{\nu}/d\sigma$ in Kevlar 29 and Kevlar 49 so as to discern it from the systematic error (scatter) in the measurements of the peak position of the Raman bands.

On the other hand, for the same applied stress, ϵ_{total} is very different for the two fibers. $d\tilde{\nu}/d\epsilon_{\text{total}}$ is strongly dependent on the misorientation angle. Plotting

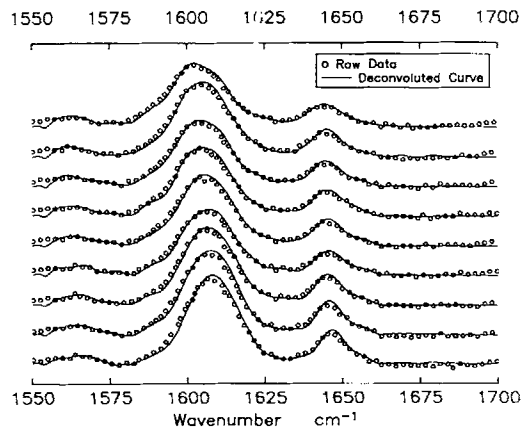


Fig. 4. True Raman band shape after deconvolution of the instrumental profile.

the peak position as a function of macroscopic strain S . van der Zwaag et al. in a recent paper²⁰ explain that both modulus and frequency shift per unit total strain, $d\tilde{\nu}/d\epsilon_{\text{total}}$, depend on orientation. They used PPTA fibers of a range of moduli spun by Akzo Laboratories. Misoriented regions rotate towards the fiber axis under tensile stress. This adds to the compliance but has no effect on the Raman spectrum. As the orientation improves, a larger portion of the applied stress deforms the chemical bonds, increasing $d\tilde{\nu}/d\epsilon_{\text{total}}$.

Effect of Stress on the Raman Band Width

Attempts have been made to understand the considerable widths of the Kevlar bands. The width of the vibrational peaks can be due to conformational distribution, lack of interchain order, or hydrogen bonding.^{29,30} Kim et al.²² attribute the large width of the Raman band to unresolved doublets from different structure and environment surrounding different sections of the polymer chain. They postulate that the Kevlar peak is actually a sum of the peaks of two model compounds $\text{N}-\text{H}-\text{Ph}-\text{H}-\text{N}$ and $\text{O}=\text{C}-\text{Ph}-\text{C}=\text{O}$. The chemical structure of poly(*p*-benzamide) (PBA) is very similar to Kevlar but has a different symmetry. The environment of the $\text{C}-\text{C}$ bond does not change periodically along the chain (Fig. 6). But the Raman spectrum of PBA also has very broad bands (Fig. 7). This implies that the large widths of the Raman bands in Kevlar is not due to the overlapping of two bands from different segments of the Kevlar chain. The broad band can still be a convolution of multiple bands which are not resolved or it can be due to hydrogen bonding.

The width of the 1610 cm^{-1} Raman band increased with loading. Even though there appears to be a low intensity tail at longer wavelengths, it is difficult to say if the band broadening is asymmetric due to the large fluorescence that swamps the Raman spectrum. The change in full width at half maximum (fwhm) of the 1610 cm^{-1} band with increase in applied stress is shown in

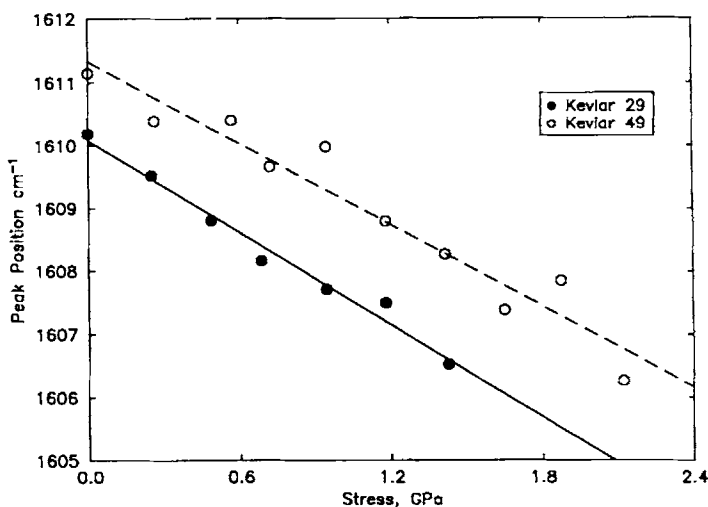


Fig. 5. Peak frequency of the $\text{C}-\text{C}$ stretching mode of Kevlar 29 and Kevlar 49 as a function of stress.

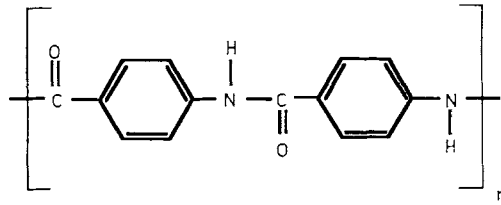


Fig. 6. Chemical structure of poly(*p*-benzamide).

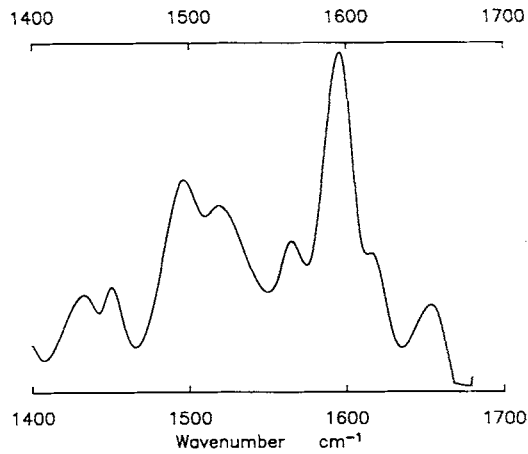


Fig. 7. Spline smoothed Raman spectrum of poly(*p*-benzamide) in the 1400–1700 cm^{-1} region.

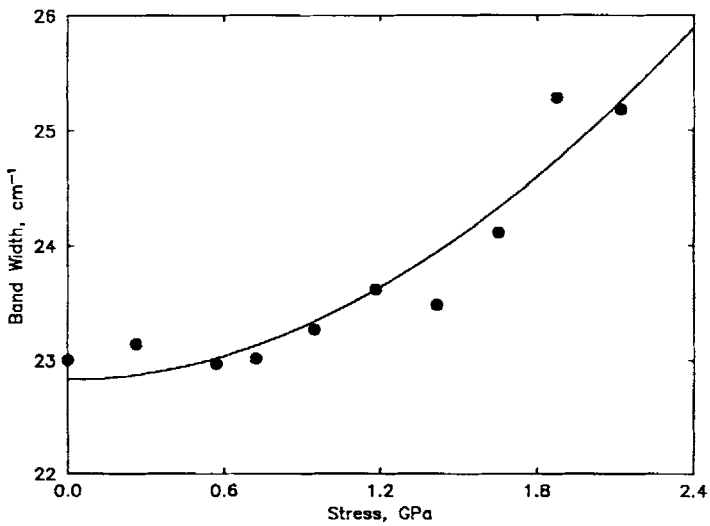


Fig. 8. Change in fwhm of the 1610 cm^{-1} band with stress in Kevlar 49.

Figure 8. The band broadening is due to uneven load distribution on the molecules within the fiber. The frequency shift in the Raman spectra of polymer fibers due to an applied stress depend on the sample morphology and chain orientation. A linear increase of width with stress is expected for a constant fiber modulus. The band broadening in polyethylene which is a semicrystalline polymer is asymmetric.⁸ In high strength polyethylene fibers the Raman band is distinctly bimodal at high applied stresses. It has a sharp peak and a broad tail at longer wavelengths. This can be explained by the sample morphology which has two load bearing phases, the crystalline phase, and the "disordered" phase⁸ primarily made up of taut tie molecules. The tail can be considered to be from the highly stressed tie segments and the peak from the crystalline phase.

There are no distinct disordered amorphous regions in Kevlar, unlike polyethylene. The structure of the fiber can be considered as an assembly of rods. The band broadening can therefore be attributed solely due to defects in the fiber or defects being created in the fiber under stress. One example of defects in the fiber is molecular ends due to the finite length of the rigid molecules. The molecule carries no load near its end, and neighboring molecules carry a higher load just as fibers next to a broken fiber do in a fiber reinforced composite. The load is transferred by the secondary bonds between molecules. In Kevlar these are hydrogen bonds. Since the Raman frequency is determined locally, the increase of line width relates directly to this stress redistribution.

If there are more defects in the fiber the stress redistribution due to load sharing should give rise to a greater increase in band width. To increase the number of defects in Kevlar, we reduced its molecular weight by exposing the fiber to ultraviolet light. This makes the fiber weaker.³¹ As expected, fibers exposed to ultraviolet light for a longer period of time had a greater broadening of the Raman band under load. Better data with reduced fluorescence are needed to quantitatively measure the increased broadening of the Raman band in weaker fibers.

The increase in fwhm is negligible till a stress of about 0.5 GPa. Also the total increase in the band width is only about 2.5 cm^{-1} . In comparison the total increase in the band width of the C—C asymmetrical stretch mode in polyethylene was about 6 cm^{-1} .⁸ One reason for the small increase in the band width at low stresses in Kevlar could be the large natural width of the 1610 cm^{-1} band. The total width of the band is the sum of the natural width and the width due to uneven stress distribution in the fiber. If their shapes can be approximated to gaussians, the resultant profile width will be the sum of the squares of their individual widths. As expected at low stresses, a small increase in the width due to uneven stress distribution would not lead to a measurable increase in the total width of the band.

SUMMARY

Raman spectroscopy is a useful technique in the study of the deformation behavior of high modulus fibers. There is a linear relationship between the Raman band shift and applied stress and this could be used in the study of the micromechanics of composites. Further work is in progress to decrease the

fluorescence in the Raman spectrum and to study the stress distribution in high performance fibers. This would help relate the mechanical properties to molecular defects in these fibers.

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References

1. A. I. Gubanov, *Polym. Mech.* **3**, 509, (1967).
2. R. P. Wool, R. S. Bretzlaff, B. Y. Li, C. H. Wang, and R. H. Boyd, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 1039 (1986).
3. Y. L. Lee, R. S. Bretzlaff, and R. P. Wool, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 681 (1984).
4. R. S. Bretzlaff and R. P. Wool, *J. Appl. Phys.*, **52**, 5964 (1981).
5. D. N. Batchelder and D. Bloor, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 569 (1979).
6. C. Galiotis, I. M. Robinson, R. J. Young, et al. *Polym. Commun.*, **26**, 354 (1985).
7. R. J. Day, I. M. Robinson, M. Zakikhani, and R. J. Young, *Polymer*, **28**, 1833 (1987).
8. Keshav Prasad and D. T. Grubb, *J. Polym. Sci. Polym. Phys. Ed.*, **27**, 381 (1989).
9. R. P. Wool and R. H. Boyd, *J. Appl. Phys.*, **51**, 5116 (1980).
10. L. J. Fina, D. I. Bower, and I. M. Ward, *Polymer*, **29**, 2146 (1988).
11. W. B. Black, in *MTP International Review of Science, Physical Chemistry Series Two, Macromolecular Science*, C. E. H. Bawn, Ed., Butterworth, London, 1975, Chap. 2, p. 88.
12. A. Ciferri and I. M. Ward, Eds., *Ultra-High Modulus Polymers*, Applied Science, London, 1979.
13. J. F. Wolfe, B. H. Loo, and F. E. Arnold, *Macromolecules*, **14**, 915 (1981).
14. E. W. Choe and S. N. Kim, *Macromolecules*, **14**, 920 (1981).
15. K. Tashiro, M. Kobayashi, and H. Tadakaro, *Macromolecules*, **10**(2), (March 1977).
16. M. G. Northolt, *Eur. Polym. J.*, **10**, 799 (1974).
17. M. Panar, P. Avakian, R. C. Blume, K. H. Gardner, T. D. Gierke, and H. H. Yang, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 1955 (1983).
18. M. G. Dobb, D. J. Johnson, and B. P. Saville, *J. Polym. Sci. Polym. Symp.* **58**, 237 (1977).
19. M. G. Dobb, D. J. Johnson, and B. P. Saville, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 2201 (1977).
20. S. van der Zwaag, M. G. Northolt, R. J. Young, I. M. Robinson, C. Galiotis, and D. N. Batchelder, *Polym. Commun.*, **28**, 276 (1987).
21. L. Penn and F. Mialnovich, *Polymer*, **20**, 31 (1979).
22. P. K. Kim, Y. Y. Xu, C. Chang, and S. L. Hsu, *Polymer*, **27**, 1547 (1986).
23. D. Y. Shen, S. E. Molis, and S. L. Hsu, *Polym. Eng. Sci.*, **23**(10), 543 (1983).
24. The Fourier Transform Raman Spectra of Kevlar were kindly recorded by J. Rabolt, IBM Almaden Research Center.
25. Klug and Alexander, *X-Ray Diffraction Procedures*, Wiley-Interscience, New York, 1974.
26. I. M. Ward, *Mechanical Properties of Solid Polymers*, 2nd ed., Wiley, New York, 1983.
27. M. G. Northolt and J. J. Aartsen, *Polym. Sci. Polym. Symp.*, **58**, 283 (1977).
28. M. G. Northolt, *Polymer*, **21**, 1199 (1980).
29. H. W. Siesler, *Infrared and Raman Spectroscopy of Polymers*, Dekker, New York, 1980.
30. P. C. Painter, M. M. Coleman, and J. L. Koenig, *The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials*, Wiley-Interscience, New York, 1982.
31. Harper and McAlister, Abstract No. Y-DA-6527, U.S. Atomic Energy Commission, 1975.

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