Raman spectroscopy of Kevlar 49 fibre[*]

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The Raman spectrum of poly(*p*-phenylene terephthalate) fibre, Kevlar 49, is reported. Fibre which had been exposed to heat, stress and radiation indicated that within experimental error, no general change takes place in the chemical structure of the material as a whole. However the spectrum of a filament under stress shows that all bands in the spectrum become increasingly polarized with increased stress. The spectral characteristics of the stress fibre lead to a possible explanation of the polymer's response to deformation – opening of the angles in the amide linkage of the polymeric chain and improved alignment of crystallites along the fibre axis.

INTRODUCTION

In the past few years, extensive studies have been conducted into the mechanical behaviour of poly(*p*-phenylene terephthalamide) fibre, known coloquially as PPT or commercially as Kevlar 49[†]. We have used vibrational spectroscopy to gain insight into the fibre's behaviour on a molecular level. This kind of information supplements mechanical performance data, leading ultimately to accurate descriptive models.

The Raman spectrum of poly(*p*-phenylene terephthalamide) fibre has been obtained with laser light of 488.0 nm. Band assignments have been made with the aid of Raman spectra of model monomeric compounds and known structure–absorption correlations. Examination of polymeric fibre samples which had been exposed to heat, stress and radiation revealed no significant changes in the spectrum. This indicates that a large scale chemical degradation is not occurring, and therefore any change in mechanical properties as a result of these treatments must be explained by changes involving a small percentage of the material. However, when the fibre is examined spectrally while under stress, changes in the spectrum do occur. No measurable frequency shifts take place, but the depolarization ratios of the spectral bands decrease with increasing stress. Such information leads to a better understanding of the material response to deformation.

EXPERIMENTAL

The Raman spectra were obtained using a photon-counting Raman spectrometer[1]. Typically, the samples were illuminated with 488.0 nm laser light from a Spectra-Physics Model 165 argon-ion laser. The fibres were held taut in the sample holder shown in *Figure 1*. The scattered light was collected perpendicular to the fibre laser plane. When pressed pellets of powdered material were used, they were illuminated in a similar manner while mounted on a precision goniometer. All spectra were recorded on a ratemeter–chart recorder system. Band frequencies at maximum height could be determined to an accuracy of ± 2 cm^{-1}.

To assess the time-dependent and spurious effects of laser energy on the fibre, a single stationary filament was bathed in the beam, and spectra were run at time intervals. Also, after irradiation, the specimen was allowed to remain undisturbed with the beam turned off. The sample was then

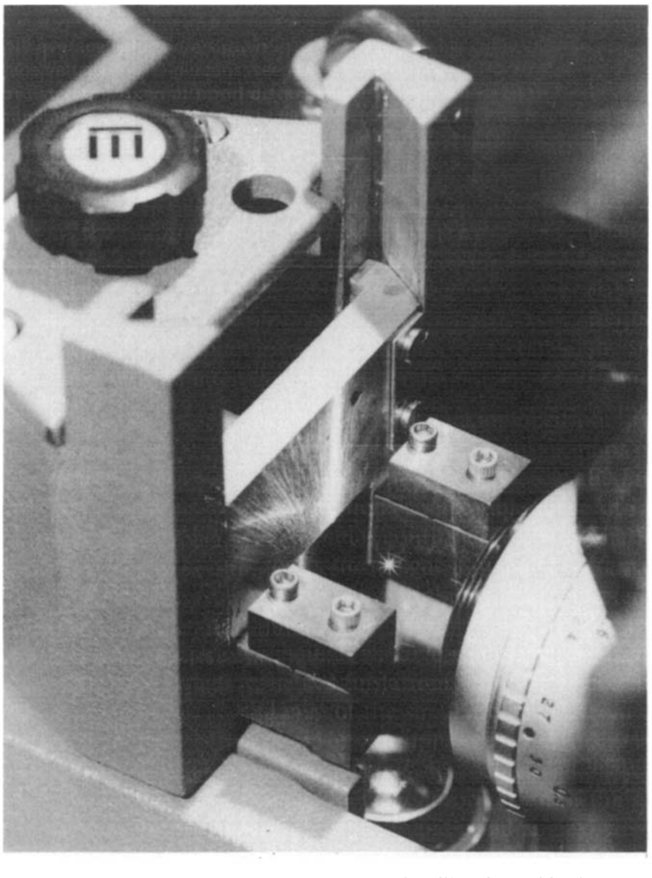

Figure 1 Single filament clamped in holder, illuminated by laser beam

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[†] Reference to a company or product name does not imply approval or recommendation by the University of California or the US Department of Energy to the exclusion of others that may be suitable.

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reilluminated to take a spectrum. This procedure was repeated with various beam-on and beam-off times. In addition, runs were made to determine the spectral differences from place to place on a filament and between filaments. We determined changes in spectral intensity by measuring band height at the peak.

For the spectra taken while the samples were under stress, we modified the sample holder. One of the end clamps for the filament was replaced by a pulley wheel. This enabled us to clamp the filament at one end and drape its free end over the wheel. Known weights then were tied to the filament's free end. Extreme care was taken not to prestress the filament while attaching the weights.

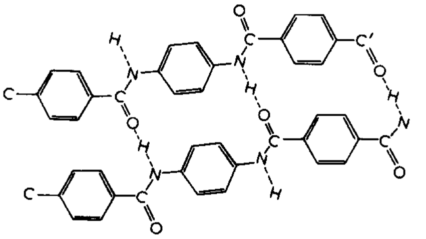


Figure 2 Structure of poly(*p*-phenylene terephthalamide)

RESULTS AND DISCUSSIONS

The polymer PPT can be pictured as phenyl groups linked together by amide bridges. It is known from crystallographic studies of the fibre[2,3] that the *para*-substituents of each phenyl ring are in the *trans* configuration and that the substituents are not quite coplanar with the phenyl groups (*Figure 2*). This lack of coplanarity would reduce somewhat those resonance effects that encompass phenyl and amide groups. Crystallographic studies also reveal that the fibre is highly crystalline and does not have regularly occurring amorphous regions, as do many polymers. The polymer is believed to be a collection of crystallites; characteristic dimensions have been identified in both fibre axis direction (longitudinal) and the lateral directions. Ballou[4] found 100 Å and 40 to 100 Å for longitudinal and lateral directions respectively. Northolt[5] found 700 Å and 50 Å for longitudinal and lateral directions (Differences are probably due to processing differences between the laboratories).

An assessment of the interaction of the laser beam with

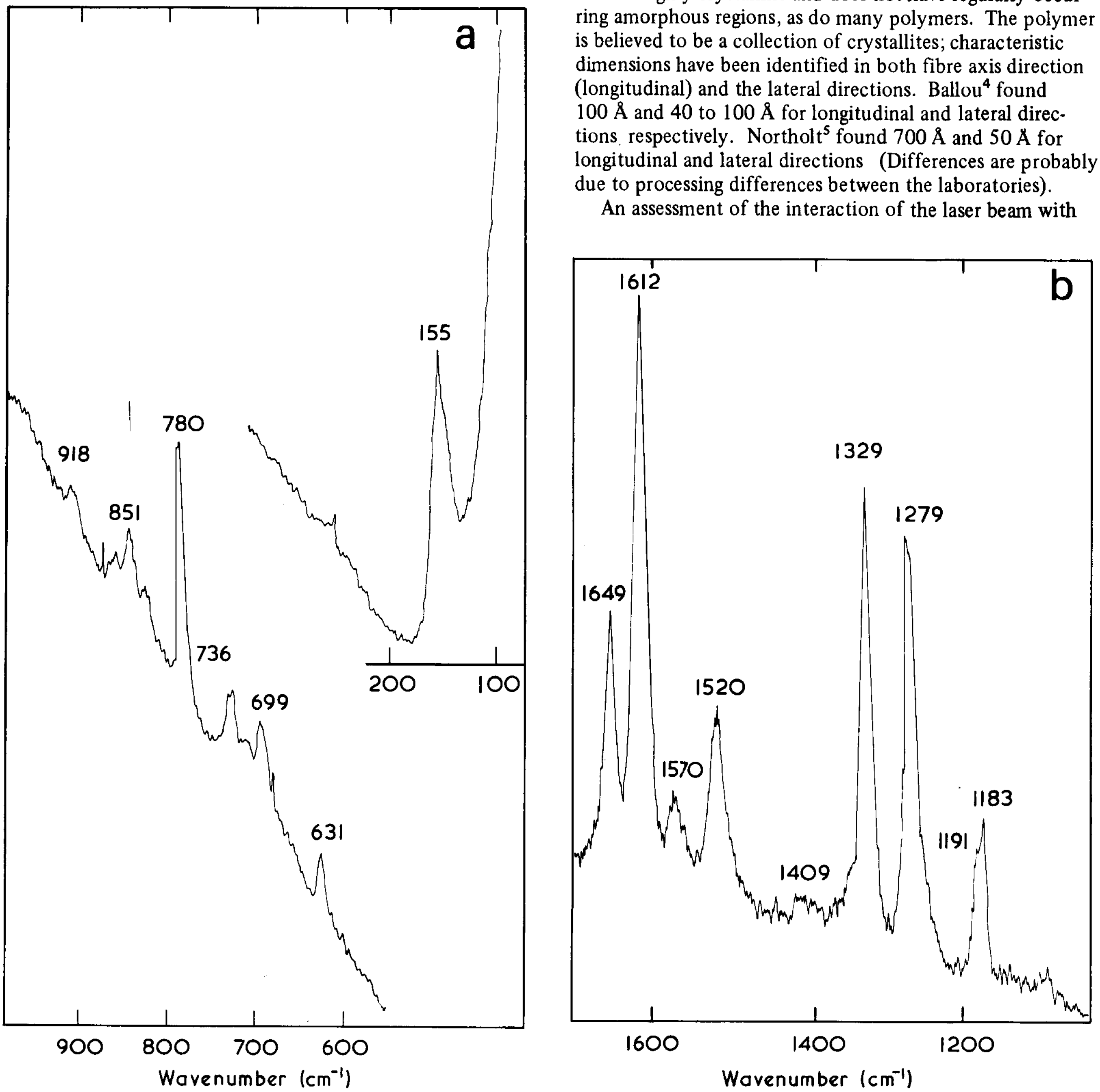


Figure 3 (a) Raman spectrum of Kevlar 49 fibre, single filament, 100–1000 cm^{-1}; (b) Raman spectrum of Kevlar 49 fibre, single filament, 1100–1700 cm^{-1}

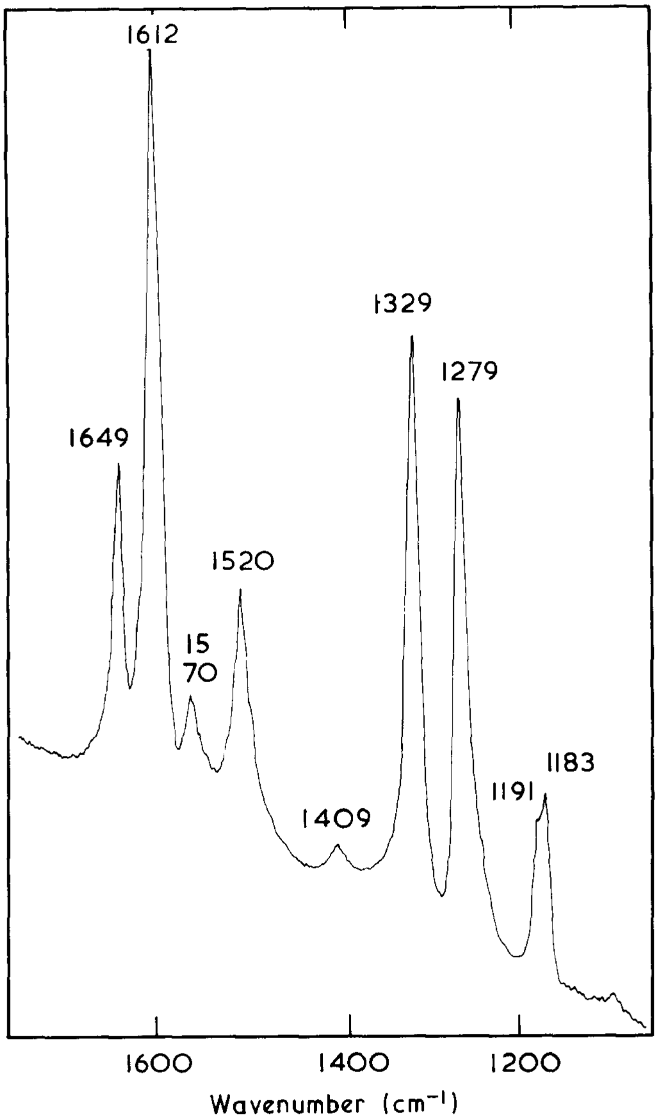


Figure 4 Partial Raman spectrum of Kevlar 49 fibre, multifilament bundle

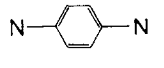
the fibre showed that if too high a beam power is deposited on the fibre, irreproducible spectra result. When a power level of not greater than 16 mW is used, spectral band amplitudes from the same location on a single filament are reproducible to within 1%. From place to place on a single filament, amplitudes were found to vary by 3%. The same variation was observed from filament to filament. In all cases, band peak locations are invariate to within ±2 cm^{-1}.

Figures 3 and *4* show spectra obtained from Kevlar fibre single filament and from the fibre bundle. *Table 1* lists the bands for the model compounds and for the fibre, giving band assignments, and pertinent references.

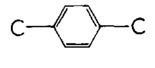
Most of the monomeric model compounds were selected to exemplify the features of the fibre's chemical structure. Two of the monomeric compounds were selected to determine the effect on the spectrum of polarity changes in the benzene ring substituent to enable better interpretation of all the spectra.

All of the spectra except that of the PPT fibre exhibit bands in the 800 to 860 cm^{-1} region, typical of 1,4-disubstituted benzene rings (C–H out-of-plane bending). Bands due to C–H in-plane bending are found in the 1000 to 1400 cm^{-1} region. All compounds exhibit moderate to strong bands in the 1100 to 1620 cm^{-1} region because of C–C stretch in the phenyl ring. The region 1620 to 2000 cm^{-1} contains few peaks in the Raman spectra, unlike infra-red spectra which exhibit many combinations and overtone bands of the phenyl ring. The few bands exhibited in this region by PPT fibre and the model compounds are assigned to substituents. Interestingly, for all compounds except the sodium salt of terephthalic acid, no bands were observed in the region above 1900 cm^{-1}. The –OH band in the sodium salt may be due to impurities. The Kevlar fibre was also examined with 514.5 nm laser light but still did not exhibit bands in the 2900–3100 cm^{-1} range where one would expect C–H and N–H stretching vibrations.

The most striking point about the Raman spectra of the compounds in *Table 1* is their notable differences. Only a few bands are common to all the materials – those at 1179 –1192 cm^{-1} due to ring and ring hydrogen vibration and those at 1615–1619 cm^{-1} also due to ring vibration. Clearly, band assignments cannot be made which separate the vibrational modes of the



or



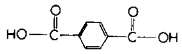
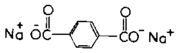
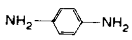
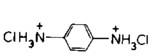
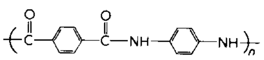
segments from the rest of the molecular moiety. To illustrate this point, compare the spectrum of terephthalic acid with the spectrum of its sodium salt, and compare the spectrum of of *p*-phenylene diamine with that of *p*-phenylene diamine dihydrochloride. The comprehensive changes in the spectrum with any modification of substituent group undoubtedly result from resonance effects which stabilize the entire substituted benzene residues, permitting internal vibrations of the phenyl ring to be affected by polarization changes in the substituents.

Depolarization ratio measurements of pressed pellets of the crystalline model compounds yielded almost no amplitude change in the bands from one polarization of the scattered light to another. This is because in the pressed pellet of monomer, with its randomly oriented crystals, the input radiation is scrambled by the pellet itself. On the other hand, all of the Kevlar bands exhibited a depolarization ratio ($I_\perp/I_\parallel$) well below 0.75.

Spectral examination of fibre which had been exposed previously to radiation, heat and sustained mechanical stress showed no significant changes. The exposure conditions are given in *Table 2*. These exposure conditions were sufficient to cause performance changes in the material. The gamma dosage of 10^7 rad degrades tensile strength of the bare fibre by 50%[16]. For heat, we found that every 10°C of temperature above room temperature shortens the lifetime to failure of Kevlar/epoxy strands by a factor of approximately 2. For stress, every additional 7% of the failure load that is applied decreases the lifetime to failure by a factor of 10^{17}. The fact that no significant changes occur in the spectrum indicates that whatever changes take place in the material (we have to assume some changes occur to cause mechanical property degradation) do not have manifestations exceeding the normal 3% amplitude variation and the ±2 cm^{-1} band centre variation found in repeated measurements of the same sample. This is consistent with the view that changes in a small percentage of a chain-extended polymer can be critical from a mechanical point of view.

The spectra taken of single filaments under stress revealed two major features. First, no measurable frequency shift occurs as a result of stressing the filament; and second, the depolarization ratios ($I_\perp/I_\parallel$) of all major bands decrease as stress is increased.

Table 1 Peaks and assignments for Raman spectra

 Terephthalic acid	 Sodium salts of terephthalic acid	 *p*-Phenylene diamine	 *p*-Phenylene diamine di HC1	 Kevlar 49	Comments and references
273 m	259 w				
287 vw	291 vs				
	331 vw				
356 m			362 m		ω_6 symmetric ring (6)
		370 m			
			385 w		
		436 w	435 w		C_ϕ-N deformation (7); ω_6 symmetric ring vib. calc. by (8)
		476 w	474 w		C_ϕ-N deformation (7)
637 s	634 w		641 s	632 w	Ring vibration (9)
		652 m			C_ϕ-H deformation (7)
676 vw					
	694 vw	699 vw		698 vw	
	715 vw				ω_{22} ring vibration (6)
				734 vw	
		792 vw		789 vw	
805 vw-sh					800- 860 cm^{-1} C_ϕ-H out-of-place band for 1,4 disubstituted arom. rings (10)
818 vw-sh					
	824 w				
837 vs	841 w, sh		830 s		
854 vw-sh		851 vs			Coupled vibration between aromatic ring and C_ϕ-N (7); ω_5 ring breathing including 1,4 substituents (6)
	869 m		863 sl		
		934 vw			
			958 vw		
985 vw					
1024 vw					
					ω_{21} C_ϕ-H bending calc. by (8)
		1061 vw	1093 w		
			1113 w	1104 vw	
1127 s					
	1138 m	1145 w	1151 w		
					ω_4 ring and ring H's, calc. (6)
1184	1185 w	1179 w	1190 s	1187 m	ω_4 ring and ring H's assigned by (6)(8) in pNA
				1192 m	
			1217 vs		
		1268 s			
				1279 s	ω_3 quinoid form ring observed (6) C=0 stretch of acid group (11,12)
1292 s					
1324 w					
			1338 w	1331 s^a	
1413 vw	1410 w, sl	1404 m		1409 vw^a	
					ω_3 calc. by (8), symm. ring puckering with C_ϕ H bending (9)
1454 w		1457 m			
			1492 vw		
1509 vw					ω_{19} ring vib. (6)
			1501 w	1518 v-m^a	
	1535 vw	1530 w			
	1559 vw		1567 w		
1579 vw					
				1570 w^a	Amide II (13, 8, 14, 10)
1619 sh	1618 vs	1618 m	1615 m	1615 vs^a	ω_2 ring vibration, common to all (11 15 13 6 8 12)
1635 s					
					C=O vib. of carbox. acids (11,15,13)
1648			1644 w-m	1649 n^a	For Kevlar, Amide I C=O stretch
	1660 vw				
	3078 vw				
	3096 m				

^{a}Also in IR

w = weak, vw = very weak, m = medium, s = strong, sh = sharp, sl = shoulder

Table 2 Exposures given to polymer fibre prior to Raman spectroscopy

Heat and stress (108 days)	Radiation (rad gamma)
40°C, no stress	10^7
60°C, no stress	10^8
80°C, no stress	10^9
60°C, 40%[a] stress	
80°C, 40% stress	
40°C, 60% stress	
60°C, 60% stress	

[a] i.e. 40% of the ultimate or failure stress

Microscopic examination of the fibres shows that they contain fibrils, indicating that stress probably is not borne uniformly by the polymer chains passing through the cross-section of the fibre. The spectroscopic effect of uneven stress would be a broadening of the vibrational band or the formation of a shoulder, not a clear-cut band shift. However, neither shoulder formation, broadening, nor band shift was observed in the Raman spectrum as stress was increased.

Band shifts as a function of stress have been reported in the polymer literature[18–21]. The fact that no measurable frequency shifts of the bands occur in the aramid fibre indicates that no or minimal stretching and bending of the chemical bonds in the polymer takes place. The elongation to failure of a dry fibre bundle is 1.9% as reported by Northolt and van Aartsen[5]. The more relevant quantity is the elongation to failure of a single filament, which has been measured to be about 2%[22]. Northolt and van Aartsen studied the effect of step increases of stress of a fibre bundle by X-ray crystallography. Because they were interested in only the first part of the stress–strain curve, the modulus, they reported measurements only to stress levels 25% of bundle fialure stress. They found that the unit cell does increase in length along the *c*-dimension, the polymer chain direction and the approximate fibre axis direction. The unit cell elongation was found to increase linearly with stress on the bundle to a value of 0.7% at 25% of the ultimate bundle stress.

Although no further data are available, it is possible that the unit cell may continue to elongate beyond 0.7% before final failure of the fibre bundle occurs. We made Raman spectral measurements at stress increments up to 90% of failure and saw no signs of shift in band position, broadening, or shoulder formation. It is difficult to explain the unit cell elongation in the absence of frequency shifts. However, the angles between bonds in the amide bridges between phenyls do not need to bend very much to permit a unit cell elongation of about 0.7%. Such a small change in bond angles might not change the bending constants enough to cause measurable Raman frequency shifts with our instrumentation. This is the most plausible explanation to reconcile apparently conflicting observations.

The observed change in depolarization ratio with stress is tabulated in *Table 3*. The change in amplitude of the major bands was well above the 1% variation in amplitude reproducibility. The observed decrease in polarization ratios can be explained by improved crystallite orientation. As mentioned before, the crystallites in the aramid fibre are oriented on the average along the fibre axis, but there is some distribution. As stress is increased, the crystallites, under the pull of the tie molecules between crystallites, align more perfectly along the *c*-axis, the distribution of crystallite orientations narrows. As this happens, the fibre behaves more like a single crystal and scrambles the polarized input radiation less. The more uniform alignment of the crystallites with respect to the beam changes the amplitude of the scattered light into each polarization. In support of this hypothesis, we cite the results of Northolt and van Aartsen again[5]. They found that the meridional arcs of the diffraction pattern of stressed fibre were intensified. They interpreted this as more perfect crystallite alignment with respect to the fibre axis.

The distribution of orientation of crystallites with respect to the fibre axis may also explain the 3% variation spectral intensity from place to place on a strand: a slightly different average crystallite orientation from one small area of the fibre to the next. This would result in different amplitudes when the laser beam is moved.

Another interesting feature of the effects of stress on amplitudes was observed in parallel polarization measurements of the amide II 1570 cm^{-1} band. As stress was increased, this band increased in intensity relative to a ring band at 1279 cm^{-1}. Such a relative intensity increase was not noticed in other bands (see *Figure 4*).

So far we have not discussed the often-propounded response to polymer deformation–chain scission. Chain scission indeed may occur in addition to unit cell elongation and the crystallite alignment. Some preliminary electron spin resonance work by deVries and Lloyd[23] provided evidence of free radicals which increased with stress. Any new end-groups that may be formed in the chain scission process are either totally Raman inactive or are not numerous enough to appear in the Raman spectrum.

Table 3 Depolarization ratios as a function of load on filament

Band (cm^{-1})	1 *g*	2 *g*	3 *g*	4 *g*	4-1/2 *g*
1279	0.32*	0.31	0.29	0.28	0.27
1328	0.35	0.34	0.29	0.29	0.30
1611	0.34	0.33	0.32	0.31	0.28
1650	0.34	0.31	0.31	0.26	0.27

* Variation of depolarization ratio as a result of scatter in amplitude reproducibility is about 3%

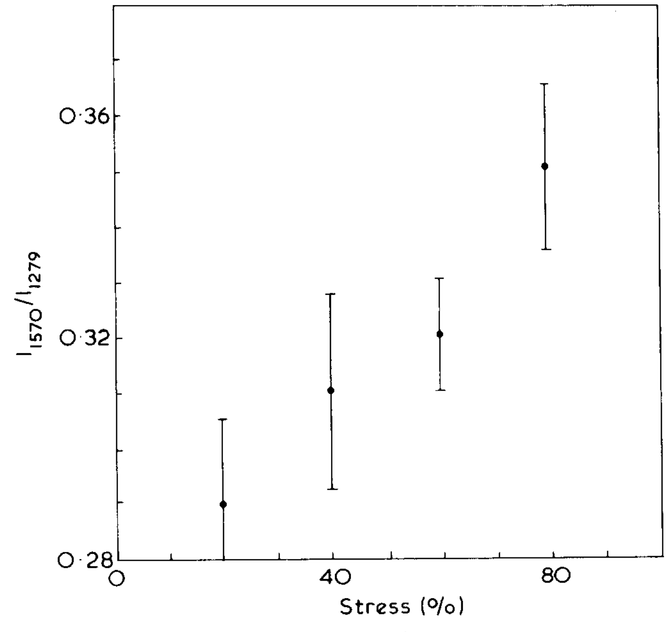


Figure 5 Intensity of band at 1570 cm^{-1} with respect to band at 1279 cm^{-1} *versus* load on filament

CONCLUSIONS

The Raman spectrum of the aramid fibre Kevlar 49 has been obtained and the bands have been assigned where possible to structural groups of the polymer molecule. Both amide bridges and phenyl groups are represented in the spectrum. Spectra taken after heat, stress, or radiation treatments reveal no chemical changes. Spectra taken while the fibre filament is under stress show no frequency shifts, but do show amplitude and depolarization ratio changes. We interpret these results to mean that no major bond stretching and bending occurs during elongation. The measured unit cell elongation may be achieved by a very slight opening of the amide bond angles. Simultaneously, there is an improvement in the crystallite alignment along the fibre axis.

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