

# Determination of the accessibility of N–H groups of Kevlar 49 fibres by photoacoustic FTi.r. spectroscopy

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Fourier transform infra-red (FTi.r.) photoacoustic spectroscopy in combination with deuterium exchange was used to determine the accessibility of the N–H groups of Kevlar 49 fibres. The spectra were corrected for the dependence of the photoacoustic signal on the frequency and the integrated intensities of the N–H and N–D stretching bands were used to calculate the fraction of accessible N–H groups. Exposure of the deuterated fibres to saturated water vapour showed a residual N–D stretching absorption, in agreement with the improved molecular packing expected after heat-treatment at high temperature.

(Keywords: infra-red spectroscopy; Kevlar 49; molecular packing)

## INTRODUCTION

Direct isotope exchange in combination with infra-red spectroscopy is a powerful tool for obtaining information on the accessibility of polymers containing NH and OH groups<sup>1,2</sup>. A complete or partial replacement of hydrogen by deuterium<sup>3</sup> can also assist in the assignment of hydrogen frequencies, since the frequency shifts by isotope substitution can be predicted from the nature of the vibrations and the atoms involved<sup>4,5</sup>.

In this study we used the fact that the NH groups in non-crystalline regions can undergo deuterium exchange on exposure to D<sub>2</sub>O vapour, in order to extract information on the accessibility of Kevlar 49 fibres. A new approach has been followed for performing the isotope substitution. In particular, we utilized the flexibility of the photoacoustic spectroscopy in order to assure minimum exposure of the deuterated sample to atmospheric humidity. We also calculated the fraction of accessible NH groups and showed the improvement of molecular packing of the fibres upon heat-treatment.

## EXPERIMENTAL

As-received Kevlar-49R fibres (DuPont) were first dried for 10 days at 120°C in vacuum and then they were exposed to saturated D<sub>2</sub>O/He atmosphere in a glove bag for 48 h at room temperature. Finally they were heated at 150°C under purging with helium for 2 h so that all the absorbed D<sub>2</sub>O is removed from the fibres. The FTi.r. spectra have been obtained using a Digilab photoacoustic detector accessory consisting of a sample cube and a microphone assembly. The sample cube, incorporating two valves, was carefully inserted in the glove bag. The sample was then loaded and the valves were closed to avoid exposure of the sample to moisture. Finally the sample cube was connected to the microphone assembly in the sample compartment under good purge. Care has also been taken to ensure sufficient purge of the gas line before connecting it to the gas input tube. The fibres were

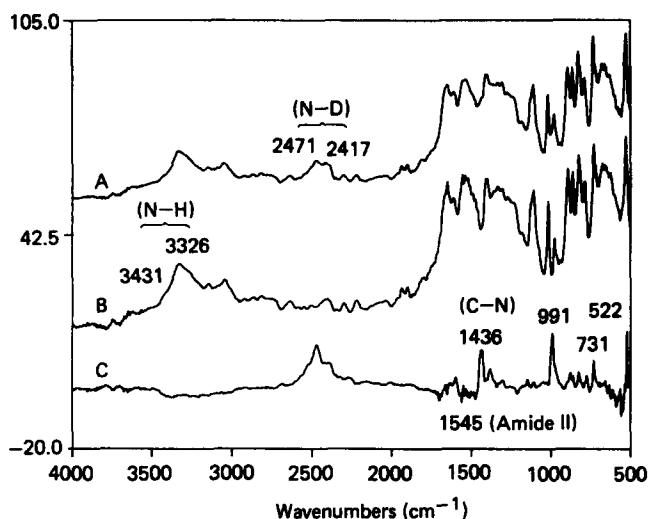
cut in pieces 5 mm long and sixteen samples of 6 mg each were prepared under the same conditions in order to determine the standard deviation of our measurements. Also a sample of dried fibres was heat-treated at the same conditions. Finally the same deuterated samples were exposed to saturated H<sub>2</sub>O/He atmosphere in a glove bag for 5 days and then dried at 120°C in vacuum for 14 d.

A Digilab photoacoustic attachment was used together with a Digilab FTS-20E spectrometer purged with nitrogen gas. One hundred scans recorded at a resolution 8 cm<sup>-1</sup> and moving mirror velocity 0.15 cm s<sup>-1</sup> were averaged to improve the signal-to-noise ratio. The frequencies were calibrated to an accuracy better than 0.01 cm<sup>-1</sup> with an internal He–Ne laser. All spectra were ratioed against carbon black powder (Fisher Scientific Co.). The sample was placed in a 5 mm deep sample cup and purged inside the cell with high purity (99.995% min) helium gas (Airco) for 10 min before scanning at a gas pressure of about 0.2 psi. The photoacoustic cell was stabilized at the temperature of the sample compartment for approximately one hour prior to the first use.

A model compound, di-benzanilide, was exposed to D<sub>2</sub>O vapour in the melted state and after recrystallizing KBr pellets were prepared. One hundred scans were recorded at a resolution 4 cm<sup>-1</sup> with a Digilab FTS-14 spectrometer purged with dry air. The digital subtraction and integrated intensity measurements are run on a VAX-11/780 computer interfaced with the dedicated minicomputer serving the spectrometers.

## RESULTS AND DISCUSSION

The spectrum of the heat-treated fibres with helium as a coupling gas is plotted in *Figure 1* (spectrum B) and the corresponding spectrum of the deuterated sample in spectrum A. A strong doublet can be seen in the spectrum of the deuterated sample at 2471 and 2417 cm<sup>-1</sup>. A similar study of polyamide-6,6 film<sup>6</sup> has shown that the direct H–D isotope exchange of the NH groups results in



**Figure 1** PA spectra with coupling gas helium of Kevlar 49 fibres in the region 4000–500  $\text{cm}^{-1}$ : A. exposed to  $\text{D}_2\text{O}$  vapour for 48 h and heated at  $120^\circ\text{C}$  under flowing helium for 2 h, B. heat-treated at  $120^\circ\text{C}$  under flowing helium for 2 h and C. difference  $(A - B) \times 2$

the partial replacement of the N–H by the N–D stretching vibration which gives rise to a doublet at 2465 and  $2410\text{ cm}^{-1}$ . The exact assignment of this vibration is somewhat complicated by Fermi resonance<sup>7</sup>. Thus, the observed doublet in the spectrum of deuterated Kevlar is due to the N–D stretching vibration.

The difference spectrum C in Figure 1 shows a broad negative band in the region of the NH stretching modes together with two positive N–D stretching modes at 2471 and  $2417\text{ cm}^{-1}$ , a positive C–N stretching mode at  $1436\text{ cm}^{-1}$  and a positive N–D deformation band at  $991\text{ cm}^{-1}$ . Also two positive bands can be seen at 731 and  $522\text{ cm}^{-1}$ , due to incomplete subtraction of the Amide IV and VI absorptions caused by frequency shifts of these modes. Similar spectroscopic features have been reported<sup>7</sup> for polyamide-6,6. The amide I band at  $1660\text{ cm}^{-1}$  is mainly attributed to the C=O stretching vibration and so it is unaffected by the deuteration. The amide II ( $1545$  and  $1530\text{ cm}^{-1}$ ) and amide III ( $1253$  and  $1237\text{ cm}^{-1}$ ) bands are coupled modes of the symmetric OCN stretching and the NH deformation vibrations. On substitution of hydrogen by deuterium, the coupling of these vibrations is weakened and both bands are partially replaced by the unperturbed C–N stretching mode at  $1436\text{ cm}^{-1}$  and the N–D deformation band at  $991\text{ cm}^{-1}$ . The corresponding bands for polyamide-6,6<sup>7</sup> are at  $1465$  and  $970\text{ cm}^{-1}$ . The band at  $970\text{ cm}^{-1}$  band is observed only for polymer samples with high NH accessibilities<sup>8</sup>. So the strong intensity of the peak at  $991\text{ cm}^{-1}$  for Kevlar indicates a large fraction of accessible N–H groups.

The broad negative absorption in the NH stretching region of the difference spectrum (spectrum C of Figure 1) includes the free N–H stretching mode ( $3431\text{ cm}^{-1}$ )<sup>9</sup>, the region of overtone and combination bands of the characteristic amide vibrations (e.g.  $3293$  and  $3192\text{ cm}^{-1}$ ) and the absorptions at  $3150$  and  $3090\text{ cm}^{-1}$  that have been assigned to *cis* and *cis-and-trans* N–H stretching modes<sup>10</sup>. This indicates that the amide groups which are not intermolecularly hydrogen bonded and amides in the *cis* conformation are accessible to exchange by deuterium. This is expected since these structures represent defects and cannot be incorporated in crystals without causing distortion and paracrystallinity.

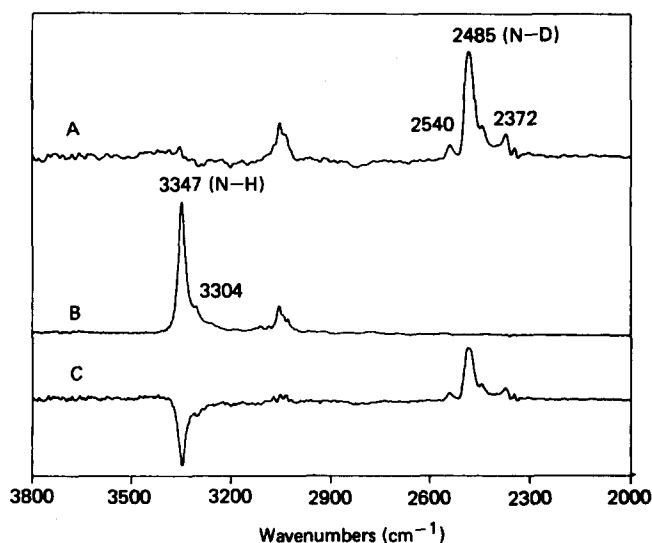
Negative absorption is also expected in the region of the combination and overtone bands of the amide peaks, since the amide II and III peaks are greatly affected when the amide hydrogen is substituted by deuterium. We do not exclude the possibility of amine end-groups that are also available for isotope exchange since these groups represent defects in the crystal structure. Their N–H stretching vibrations are expected in the same frequency region. The same difference spectrum does not show very strong negative Amide II bands, possibly because of optical saturation at these frequencies.

The fraction of the N–H groups accessible to exchange by deuterium can be calculated from the integrated absorbance of the N–H and N–D stretching bands,  $A_{\text{NH}}$  and  $A_{\text{ND}}$ , of the spectra of the deuterated samples by using the relationship<sup>11</sup>:

$$\frac{A_{\text{ND}}}{A_{\text{NH}}} = \frac{\beta_{\text{ND}}}{\beta_{\text{NH}}} \times \frac{C_{\text{ND}}}{C_{\text{NH}}} = \frac{\beta_{\text{ND}}}{\beta_{\text{NH}}} \times \frac{1 - C_{\text{NH}}}{C_{\text{NH}}} \quad (1)$$

where  $\beta_{\text{ND}}$  and  $\beta_{\text{NH}}$  are the absorption coefficients of the NH and ND bands. An assumption usually made for the use of this equation is that the specific absorptivities of the NH and ND bands are equal. In order to obtain the exact ratio of absorptivities, we deuterated a model compound, di-benzanilide ( $\text{Ph-NH-CO-Ph}$ ). Difference spectroscopy was used to obtain spectra corresponding to pure deuterated and protonated compounds which are shown in Figures 2 and 3. The NH stretching band at  $3347\text{ cm}^{-1}$ , the overtone of the Amide I band at  $3304\text{ cm}^{-1}$  and possibly other overtone and combination bands in the protonated compound, after deuteration they have been replaced by the bands at  $2540$ ,  $2485$ ,  $2443$  and  $2372\text{ cm}^{-1}$ . The spectrum of the deuterated compound (spectrum A of Figure 3) also shows a partial replacement of the Amide II ( $1536\text{ cm}^{-1}$ ) band by the unperturbed C–N stretching mode at  $1411\text{ cm}^{-1}$ . The ratio of the absorption coefficients was calculated from the integrated intensities of the positive ND stretching and the negative NH stretching bands of the difference spectrum (trace C of Figure 2):

$$\beta_{\text{ND}}/\beta_{\text{NH}} = A_{\text{ND}}/A_{\text{NH}} = 0.9882 \quad (2)$$



**Figure 2** Transmission spectra of di-benzanilide in the region 3800–2000  $\text{cm}^{-1}$ : A. pure deuterated compound, B. pure protonated compound, and C. difference  $(A - B)$

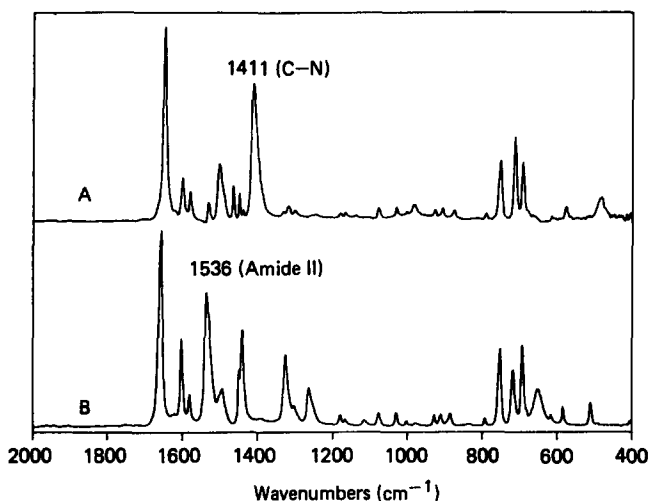


Figure 3 Transmission spectra of di-benzanilide in the region 2000-400 cm<sup>-1</sup>: A. pure deuterated and B. pure protonated compound

Hence the specific absorptivities of the NH and ND stretching modes are identical within the experimental error.

The intensities of the NH and ND stretching bands in the photoacoustic spectra depend on the depth of penetration at the corresponding frequencies, which is a function of the thermal and optical properties of the sample. Rosencwaig<sup>12</sup> has classified samples in four categories depending on the relative values of the thermal diffusion length,  $\mu$ , optical absorption length,  $l_p$ , and the sample thickness,  $l$ : optically opaque or transparent and thermally thick or thin. Most polymers have thermal diffusivity,  $\alpha$ , of approximately  $9.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ .<sup>13</sup> The thermal diffusion length is a function of the modulation frequency,  $f_v$ :

$$\mu = (\alpha/\pi f_v)^{0.5} = (\alpha/2\pi Vv)^{0.5} \quad (3)$$

where  $V$  is the moving mirror velocity. For  $V = 0.15 \text{ cm s}^{-1}$  used in this study, and for  $\alpha = 9.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ ,  $\mu$  varies from  $5 \times 10^{-4}$  to  $1.4 \times 10^{-3} \text{ cm}$  at 4000 and 500 cm<sup>-1</sup> respectively. This value is much smaller than 1 and so Kevlar can be considered a thermally thick material (simplified cases 1c, 2b or 2c of Rosencwaig's theory<sup>12</sup>). However, only photoacoustically opaque samples, such as carbon black, belong to case 2b. For both cases 1c and 2c only the light absorbed within the first thermal diffusion length of the sample contributes to the photoacoustic signal. Thus, the thermal diffusion length is a direct measure of the depth of penetration ( $DP$ ). For a certain moving mirror speed:

$$\frac{(DP)_{v_1}}{(DP)_{v_2}} = \frac{(\mu)_{v_1}}{(\mu)_{v_2}} = \left(\frac{v_2}{v_1}\right)^{0.5} \quad (4)$$

where  $(DP)_{v_1}$  and  $(DP)_{v_2}$  are the depths of penetration at frequencies  $v_1$  and  $v_2$  respectively. Figure 4 shows the change of the thermal diffusion length with frequency. So the spectra have to be corrected for the change of depth of penetration before calculating the integrated intensities to be used in equation (1). The intensity of the photoacoustic signal normalized to the signal at a given frequency  $v_{\text{standard}}$  is:

$$(I_{v_i})_{\text{normalized}} = \left(\frac{v_{\text{standard}}}{v_i}\right)^{0.5} I_{v_i} \quad (5)$$

This data manipulation was performed for all the collected spectra by a program written using a VAX-11/780 computer. Figure 5 shows the corrected and uncorrected spectra of a deuterated sample. The integrated intensities of the NH and ND stretching bands of the deuterated spectra were calculated after the depth of penetration correction for the regions 3468-3105 cm<sup>-1</sup> and 2541-2357 cm<sup>-1</sup> respectively. Finally, the fraction of the inaccessible NH groups for Kevlar 49 fibres was calculated:  $C_{\text{NH}} = 0.698 \pm 0.04$ . This means that only 70% of the N-H groups are inaccessible for exchange by deuterium. If we had first calculated the integrated intensities and then corrected them by using the position of the maxima for the NH and ND stretching bands (3326 and 2471 cm<sup>-1</sup>) we would have obtained:  $C_{\text{NH}} = 0.631 \pm 0.05$ , which is 6.7% off the correct value.

Figure 6 shows the PAS spectrum with helium as the coupling gas of the deuterated sample after exposure to water for the region 4000 to 2000 cm<sup>-1</sup> (spectrum B), in comparison to the spectrum of the deuterated sample (spectrum A). Their difference, spectrum C, shows again the existence of a broad negative N-H stretching band and a positive N-D stretching band. The spectrum of the

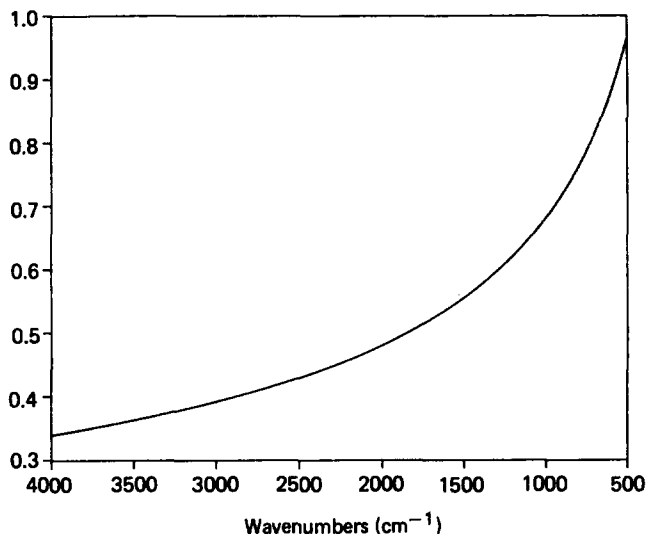


Figure 4 Change of the thermal diffusion length with frequency

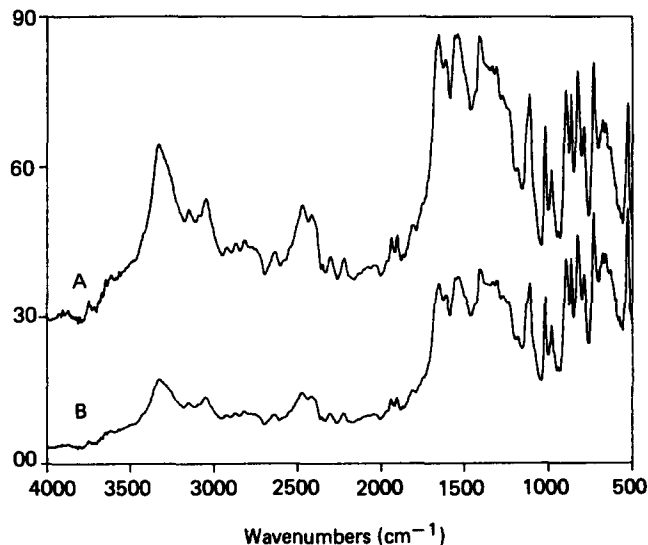


Figure 5 Correction of PA spectra for the change of the depth of penetration: A. corrected spectrum and B. uncorrected spectrum of a deuterated sample

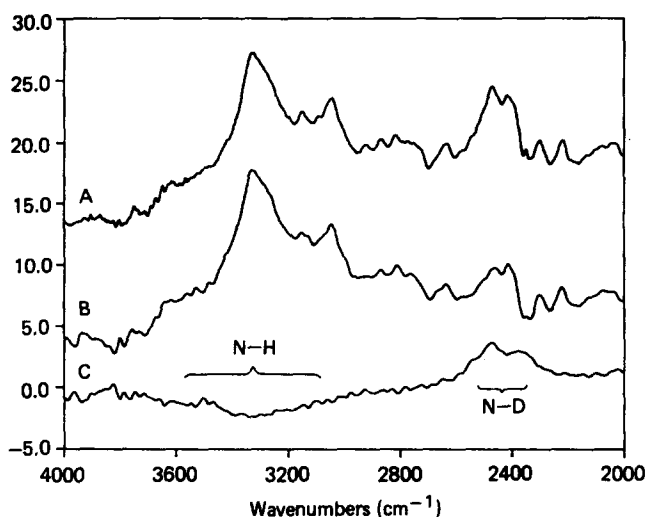


Figure 6 PA spectra with coupling gas helium of Kevlar 49 fibres: A. exposed to D<sub>2</sub>O vapour for 48 h and heated at 120°C under flowing helium for 2 h, B. same sample after exposure to H<sub>2</sub>O vapour for 5 d and dried at 120°C in vacuum for 14 d and C. difference (A - B)

H<sub>2</sub>O-exchanged sample shows a residual N-D stretching absorption, which indicates that the heat treatment of the sample after deuteration has caused annealing and recrystallization and so part of the N-D groups are permanently trapped in the crystals and are not accessible for exchange with hydrogen. The helium spectrum of the same sample is compared to the one of the heat-treated sample, in Figure 7. Their difference is given at trace C and shows a positive C-N stretching (1436 cm<sup>-1</sup>) a positive N-D deformation band (991 cm<sup>-1</sup>) and two negative peaks at the region of the Amide II bands. Again the intensity of the Amide II peaks is smaller than expected, possibly due to optical saturation at this frequency range. The fraction of the inaccessible N-H groups after heat-treatment was calculated from the spectra of the water-exchanged samples in the same way as for the deuterated samples:

$$C_{\text{NH}} = 0.869 \pm 0.02$$

The fraction of the permanently trapped N-D groups in the crystallites is:

$$X_{\text{trapped N-D's}} = \frac{1 - (C_{\text{NH}})_{\text{H}_2\text{O-exchanged}}}{1 - (C_{\text{NH}})_{\text{deuterated}}} = 0.433 \quad (6)$$

So approximately 43% of the originally accessible N-H groups have become unaccessible after heating the sample at 150°C for 2 h under purging with helium. This represents 13% of the original overall number of N-H groups of the material. So heat treatment of the Kevlar fibres results to an improvement of the molecular packing, in agreement to an increase in the crystallite size measured from electron micrographs<sup>14</sup>.

In a previous ATR study of deuterated Kevlar 29<sup>15</sup> the accessibility in per cent of NH proton has been calculated to be 10-15%. However, the poor contact of the fibres with the ATR crystal did not allow accurate measurements. Kevlar 29 or fibre B is 67.6% crystalline, as calculated by wide-angle X-ray diffraction<sup>16</sup>. Using the same technique<sup>16</sup> a crystallinity of 76% was calculated for Kevlar 49. According to our calculations, 70% of the N-H groups of the Kevlar 49 fibres belong to highly ordered

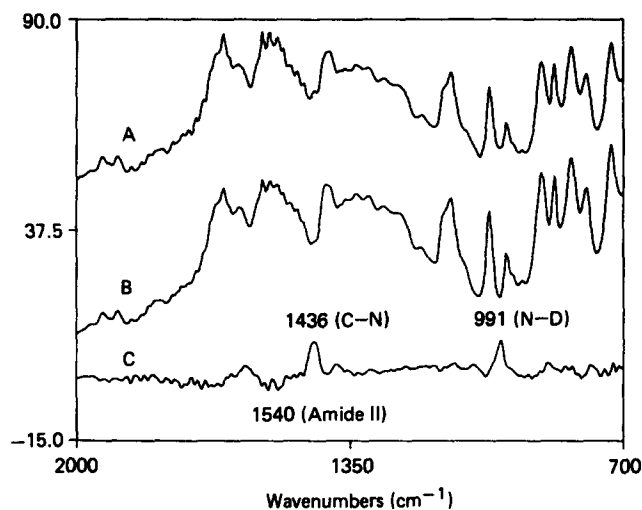


Figure 7 PA spectra with coupling gas helium of Kevlar 49 fibres: A. deuterated for 48 h and heat-treated under flowing helium for 2 h, and subsequently exposed to H<sub>2</sub>O vapour for 5 d and dried at 120°C in vacuum for 14 d, B. sample heated at 120°C under flowing helium for 2 h and C. difference, (A - B) × 2

inaccessible material. FTi.r. provides information on the molecular level, while X-ray diffraction can detect statistical deviations of the lattice spacings from the values corresponding to a perfect crystal. So it is expected that our value for the fraction of perfectly ordered inaccessible material is smaller than the crystallinity value calculated from X-ray studies. Our results show that the order in Kevlar 49 fibre is paracrystalline since the defects are accessible for exchange. Heat-treatment of the fibres heals some of these defects making for a more perfect order of paracrystallinity.

## CONCLUSIONS

Using photoacoustic FTi.r. spectroscopy it is possible to perform accurate accessibility measurements. For thermally thick materials the spectra can be corrected for the dependence of the depth of penetration on the frequency. It was calculated that 70% of the N-H groups of Kevlar 49 fibres belong to highly ordered inaccessible material. We also showed that heat treatment at 150°C for 2 h results to a 43% decrease of the originally accessible material, due to an improvement of the molecular packing.

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