

# Infrared spectroscopic studies of a nematic liquid crystalline poly(ester amide) in the solid phase

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Infrared spectroscopy has been used to study the hydrogen bonding conditions in a nematic liquid crystalline poly(ester amide). The results showed that the material formed interchain hydrogen bonding as a result of the inclusion of amide groups in the polymer chains. The hydrogen bonding was found to be stable in the temperature range studied (up to 150°C). However, the studies suggested that the hydrogen bond strength was weaker than in polyamide and did not appear to affect the mechanical properties of the material significantly. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid crystalline poly(ester amide); hydrogen bonding; infrared spectroscopy)

## INTRODUCTION

The importance of thermotropic liquid crystalline polymers (LCP) as high performance materials has led to the development of various commercial products and applications in recent years. Main-chain thermotropic liquid crystalline polymers, e.g. liquid crystalline polyesters, are one of the most important commercial LCPs. They have rigid backbones and can be processed to form fibres and films of high stiffness and strength. The development of thermotropic liquid crystalline poly(ester amide) materials was stimulated by the question of whether the introduction of hydrogen bonding, which may enhance the interchain interactions, might result in some useful property improvements<sup>1</sup>.

The work presented in this report is to study hydrogen bonding in a liquid crystalline poly(ester amide) by infrared spectroscopy. The material studied here is referred to as HNATA, a random copolymer of hydroxy-naphthoic acid, terephthalic acid and amino-phenol which contains both ester and amide linkages. For comparison, we have also studied a similar polymer with all ester linkages which we refer to as HNATH (produced from hydroxy-naphthoic acid, terephthalic acid and hydroquinone). The compositions of these materials are summarized in *Table 1*. The amide content of HNATA is close to the maximum that can be tolerated for melt processibility<sup>1</sup>.

## EXPERIMENTAL

### *Sample details*

The samples studied in this work were supplied by the Hoechst-Celanese Research Company, New Jersey, USA. The specimens provided were highly uniaxially

oriented thin films, about 5 mm wide. The HNATA film was 20 µm thick and HNATH film was 10 µm thick.

### *Rotating adjustable temperature controlled extensometer (RATCE)*

A sample holder in which the sample can be heated and stressed was designed so that the sample temperature, its orientation with respect to the i.r. beam, and the sample stress could be varied independently. The apparatus, called a rotating adjustable temperature controlled extensometer (RATCE), is shown in *Figure 1*. It sat on guide rails, which normally positioned a standard specimen holder in a Perkin-Elmer double beam i.r. spectrometer. The temperature was controlled by a three term controller which determined the current drawn by two Minco thermofoil heaters fixed in the environmental chamber. A copper-constantan thermocouple positioned in the chamber just outside the i.r. beam near the sample registered the temperature. As the heaters were small and of relatively low power, the chamber was insulated with a mica/polyurethane composite to minimize heat loss. Two compression springs, pushing against the upper specimen clamp which was free to move on linear bearings, determined the load on the sample.

### *Experimental procedure*

The tape sample about 7 cm long was clamped in the extensometer and cycled with a tensile stress of 100 MPa at 150°C (the maximum temperature studied) for a few minutes to eliminate plastic deformation before obtaining any spectra. The spectra were recorded on a Perkin-Elmer 580B ratio recording spectrometer at the temperature and the stress required. The chopper function of the spectrometer eliminated all the thermal radiation of the extensometer. A dry nitrogen purge was used during the runs to minimize the effects of water vapour and CO<sub>2</sub>. The data were digitized and stored on a

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floppy disk by a PE3600 data station and transferred to a mainframe computer for analysis.

Detailed studies were made in the region from 3550 to 3510  $\text{cm}^{-1}$ , in which the N–H stretching band is located. The data points were taken at 1  $\text{cm}^{-1}$  interval, sampled sixteen times and averaged. Data were accumulated and averaged from five such collections leading to a total noise reduction factor of 9.

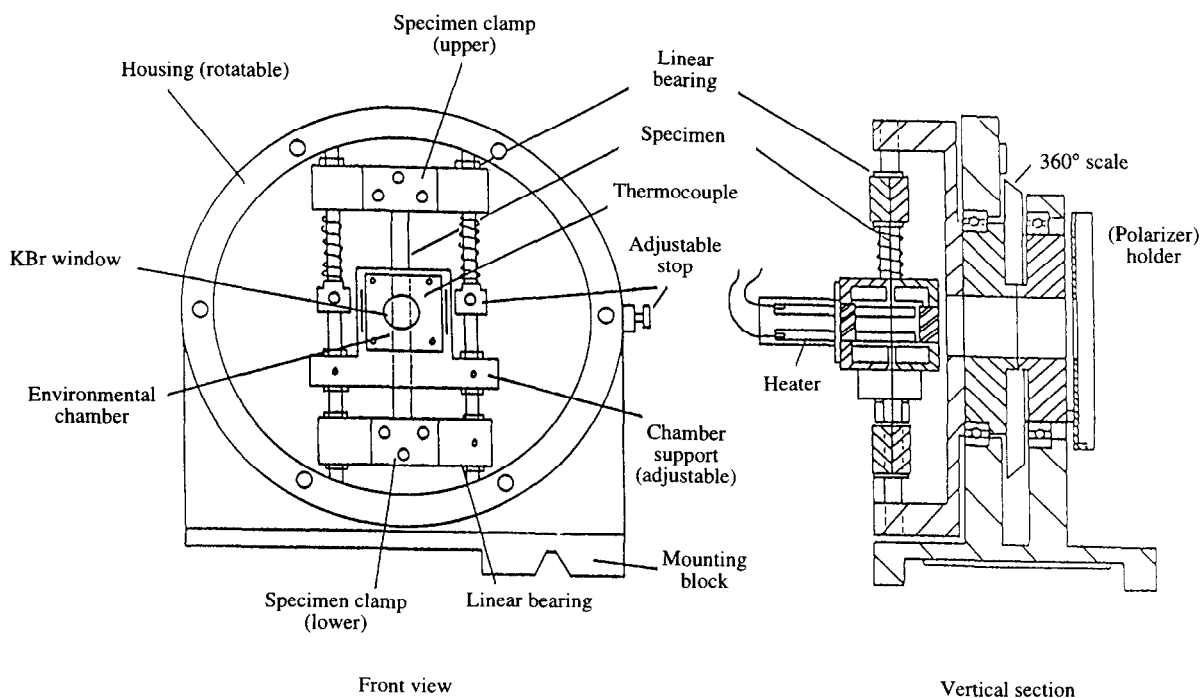
**RESULTS**

The hydrogen bonding studies on HNATA were focused on its N–H stretching band. *Figure 2* shows the i.r. spectra of HNATA and HNATH from 2600 to 3600  $\text{cm}^{-1}$ ,

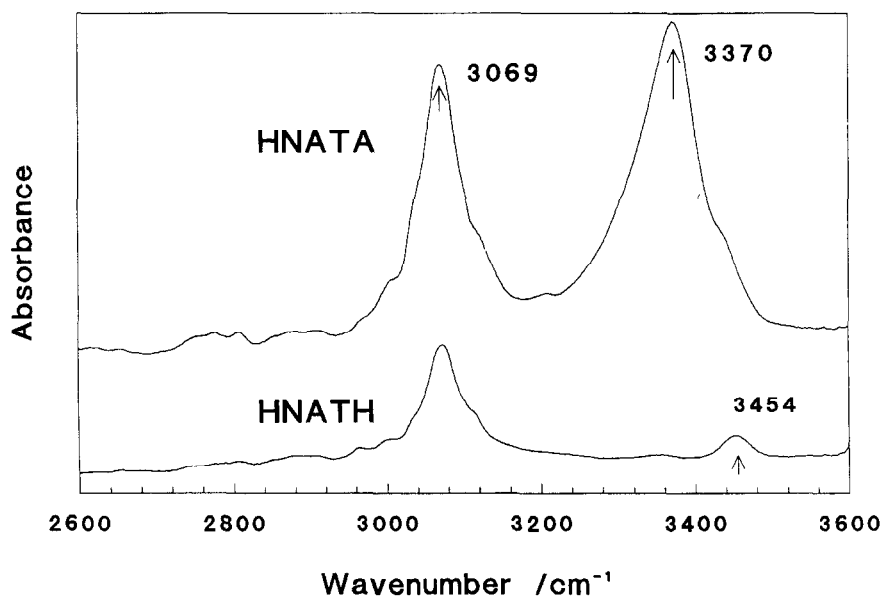
the region in which the N–H stretching band was expected to be found<sup>2-4</sup>. (Note that this is not an absolute comparison of the absorbances of HNATA and HNATH since the samples were of different thickness.)

**Table 1** The composition of the liquid crystalline copolymers studied. HNA: hydroxy-naphthoic acid, TA: terephthalic acid, AM: aminophenol and HQ: hydroquinone

Material	Mole percentage composition (%)			
	HNA	TA	AM	HQ
HNATA	60	20	20	
HNATH	60	20		20



**Figure 1** The rotating adjustable temperature controlled extensometer (RATCE)



**Figure 2** Infrared spectra of HNATA and HNATH in the range of 2600–3600  $\text{cm}^{-1}$  taken at room temperature

The common absorption band in the spectra of both materials at  $ca\ 3069\text{ cm}^{-1}$  is a C–H stretching vibration<sup>6</sup>. The broad peak centred at  $ca.\ 3370\text{ cm}^{-1}$  in HNATA is the expected N–H stretching vibration and the small band at  $ca.\ 3454\text{ cm}^{-1}$  in HNATH is the first overtone of the ester C=O stretching vibration. The appearance of this overtone in HNATH suggests its existence in HNATA at a similar frequency somewhere within the broad N–H band.

Figure 3 shows the effect of temperature on the infrared spectrum in the N–H vibration region of HNATA. The two spectra were taken at temperatures of  $22^\circ\text{C}$  and  $150^\circ\text{C}$ , respectively. As the temperature increases, it is seen that the shoulder at the high frequency end becomes

broader and the tail at the low frequency end reduces.

Figure 4 shows two spectra in the same frequency range taken at  $150^\circ\text{C}$  under different values of stress. One spectrum was taken with the sample under a very small tensile stress (about 10 MPa) to keep it straight. The other is under a tensile stress of about 70 MPa. The two spectra overlap within the noise level indicating that the N–H band is not highly sensitive to stress even at such high temperatures.

The changes observed in the spectral bands with temperature and stress were reversible. Spectra have been taken of several samples and every sample was measured twice. No obvious difference was observed between different individual samples.

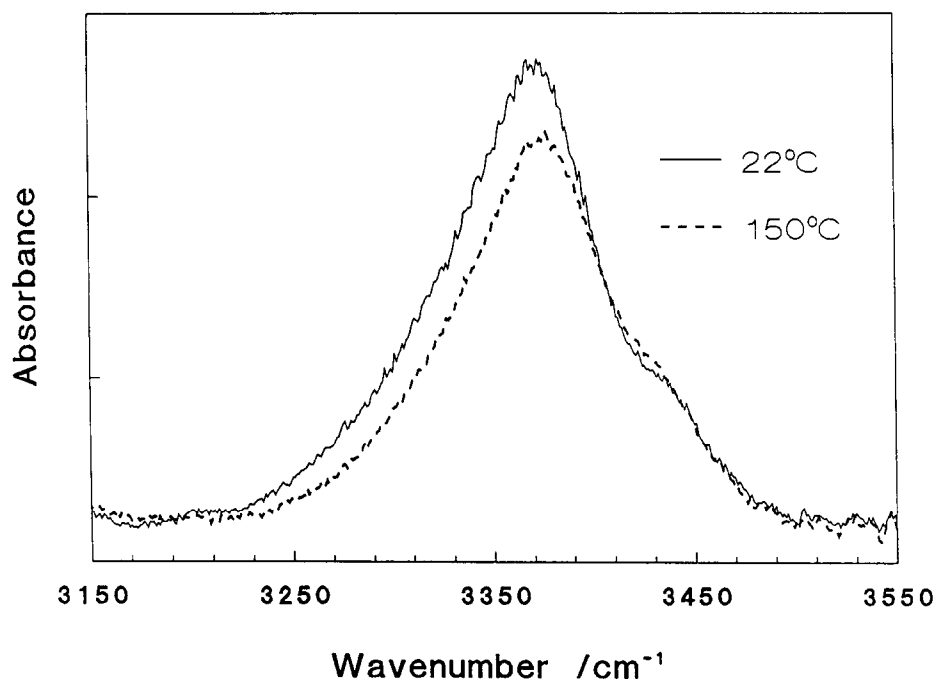


Figure 3 The effect of temperature on the N–H stretching vibration band of HNATA

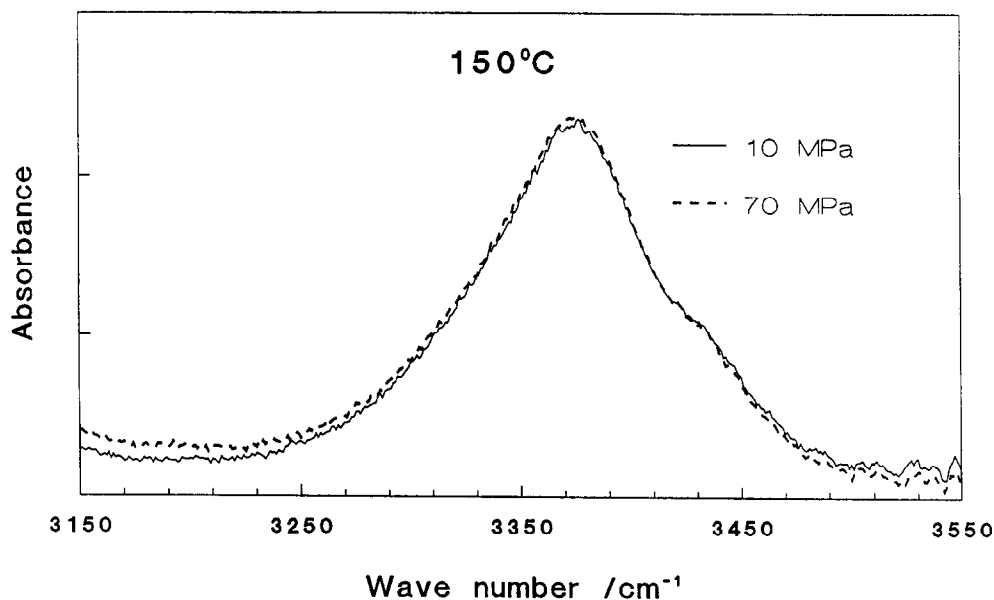


Figure 4 The effect of stress on the N–H stretching vibration band of HNATA

## ANALYSIS

Visual inspection of the N–H stretching band region for HNATA indicates that this band is broad, with a shoulder on the high frequency side and an asymmetrical tail on the low frequency side. It consists of the superposition of individual component bands. Quantitative analysis of the spectrum relies on the decomposition of the spectrum into its component bands. Any change in the bands with changing of physical conditions can then be monitored.

Generally, polymers with amide linkages in the main chain, such as HNATA, possess higher than normal levels of interchain interaction due to hydrogen bonding between the chains. Hydrogen bonding in these materials involves the interaction between the proton donating amide group,  $R_1-N-H$ , and proton acceptor,  $O-R_2$ , and is represented symbolically as:



The donor N is highly electronegative with a relatively small atomic radius whilst the acceptor O has a lone-pair of electrons.

There have been extensive studies on the effect of hydrogen bonding on the N–H stretching band<sup>7–10</sup>. In general, the N–H stretching vibration shifts to lower frequencies if the N–H group is hydrogen bonded due to the weakening of the force constant. The bonded absorption band is also much broader than the non-hydrogen bonded band due to a distribution of H-bond strengths.

The spectrum of HNATA clearly demonstrates a shoulder at the high frequency end in the N–H stretching area. In the case of polyamides, a shoulder in the high frequency end of their N–H stretching vibration absorbance has been normally assigned to the 'free' N–H vibration<sup>11</sup>. It is tempting to follow this assignment and assign the shoulder in HNATA spectrum as the 'free' N–H vibration. However, we have clearly seen the first overtone of the ester C=O stretching vibration at *ca.* 3454  $cm^{-1}$  in HNATH. HNATA, with about 80% ester

linkages, also has a very strong ester C=O stretching vibration at *ca.* 1733  $cm^{-1}$  and its first overtone is expected at *ca.* 3440  $cm^{-1}$  which is in the region normally assigned to the free N–H. We cannot, therefore, simply treat this shoulder in HNATA as a 'free' N–H band and neglect the existence of the ester C=O overtone. Our conclusion is that this shoulder is a mixture of 'free' hydrogen bonded N–H stretching band and the first overtone of the ester C=O stretching band.

Figure 5 shows the effect of temperature on the ester C=O overtone in HNATH. No difference can be observed which is expected as the C=O group is double bonded. The N–H band in HNATA, however, is expected to change with temperature since the N–H group is single bonded<sup>4</sup>. We therefore neglect any change of the first overtone of the ester C=O stretching band with temperature and all the spectral changes in the shoulder area of the N–H band in HNATA are assumed to be related to the change in the 'free' N–H species.

The asymmetrical tail of the N–H band on the low frequency side suggests that there is a distribution of peaks. Generally speaking, vibrational absorption curves are expected to be symmetric<sup>12</sup>. Asymmetric absorption curves can be considered to be composed of two or more absorptions which are symmetric. This further complicates our analysis.

Figure 6 shows a typical composite profile of the N–H stretching band of the HNATA material with its 4th and 2nd derivatives. It can be seen that two peaks located at about 3440  $cm^{-1}$  and 3375  $cm^{-1}$ , respectively, are clearly revealed by the derivative method. However, differentiation can neither confirm nor deny the existence of a peak at about 3330  $cm^{-1}$ . It is also unlikely that the C=O first overtone and the 'free' N–H band mixed in the shoulder could be deconvoluted by this peak-narrowing technique.

We then used curve fitting procedures to fit the N–H band for various spectra taken at different temperatures and stresses. It was found that a four peak fitting showed no improvement over a three peak one but a three peak

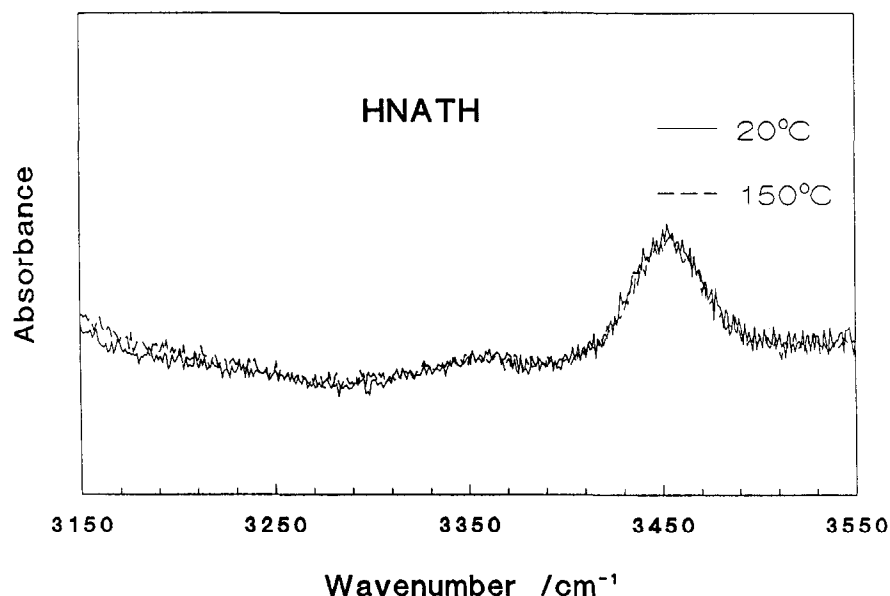


Figure 5 Temperature effect on the first overtone of ester C=O stretching vibration band of HNATH. No effect can be observed

fit was significantly better than two peaks. Three peaks were the minimum number required for a satisfactory fitting. It turned out that the small bump centred at *ca.*  $3437\text{ cm}^{-1}$  is fitted by one peak (peak 1) and the rest is fitted by two peaks (peaks 2 and 3). Due to their highly overlapping character, the free N–H band and the C=O first overtone are all included in peak 1 (see *Figures 7a* and *b*).

Precise assignment of peaks 2 and 3 seems very difficult. Coleman and his co-workers<sup>13</sup> have reported that for simple polyurethane, the first overtone of the amide I vibration, corresponding to a fundamental at  $1704\text{ cm}^{-1}$ , found to be at *ca.*  $3386\text{ cm}^{-1}$  is mixed with the bonded N–H stretching band at *ca.*  $3321\text{ cm}^{-1}$ . This kind of assignment, however, is unlikely to be applicable to HNATA for two reasons. Firstly, since the amide I of HNATA is at *ca.*  $1628\text{ cm}^{-1}$ , its first overtone is expected to be at a frequency of less than  $3260\text{ cm}^{-1}$ . This is at the low frequency end of the broad N–H peak and neither of the fitted peaks (*ca.*  $3376\text{ cm}^{-1}$  and  $3330\text{ cm}^{-1}$ ) can match it. Secondly, the amide I band of HNATA is a much weaker vibration than the ester C=O stretching band. Its overtone should also be weaker in contrast with the medium intensity of peaks 2 and 3. We therefore treat both peaks 2 and 3 as the contribution of bonded N–H stretching. Peaks 2 and 3 are artefacts of the curve fitting. They do not necessarily correspond to definite physical 'bands' but are a useful tool to describe and compare variations in the observed profile with temperature and stress.

The N–H stretching vibration band shape has been described as basically following a Gaussian shape for various polymers<sup>7,8,10</sup> whereas the i.r. spectra of solids are generally regarded as following a Lorentzian form<sup>14</sup>. We have used various mixed Gaussian/Lorentzian shapes to fit the profile. Examination of the goodness-of-fit (the sum of the squares of the deviation) for various fits indicated that 60% Gaussian + 40% Lorentzian line shape gave the best fits. This was found to be true for

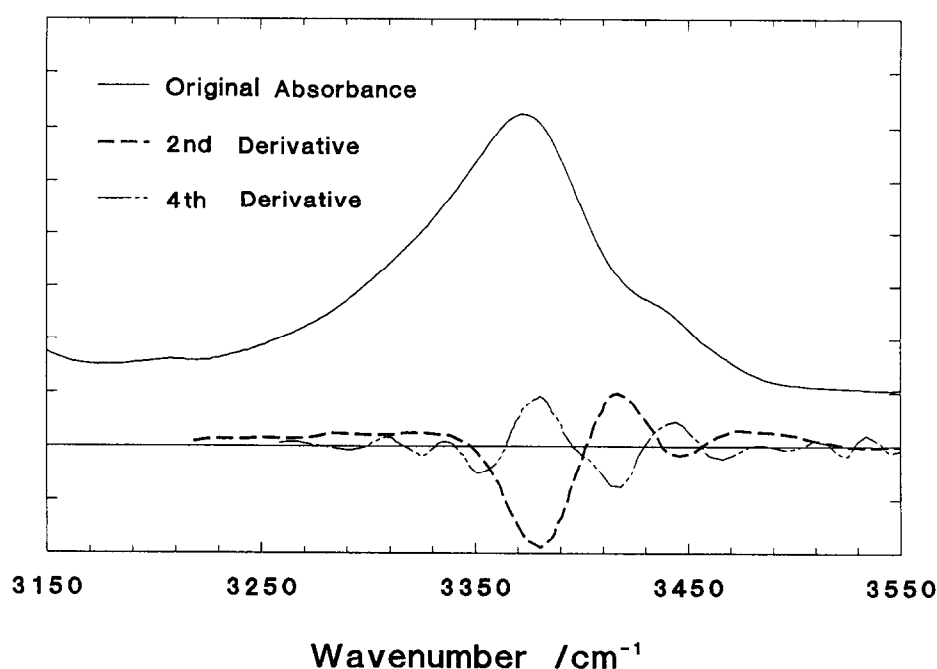
spectra taken at various temperatures and/or stretching conditions. The best fit to the experimental data was achieved by varying the line centre wavenumber,  $\nu_0$ , width at half-height,  $W_{1/2}$ , and absorption intensity,  $A$ , of three bands. The baseline was chosen to be  $A = a_0 + a_1\nu$  and the parameters  $a_0$  and  $a_1$  allowed to vary.

*Table 2* shows the curve fitting results for the N–H band in HNATA. Peak 1 is a mixture of the C=O first overtone and the 'free' N–H stretching band, and peaks 2 and 3 are both associated with hydrogen bonded N–H species. It is seen from the fitted numbers that the area of peak 1 increases slightly with temperature. The area of peak 3 for the bonded N–H part decreases by a factor of 2 whereas peak 2 is essentially constant. Curve fitting did not pick up any differences between the spectra of the unstressed and of the stressed samples at the temperatures studied.

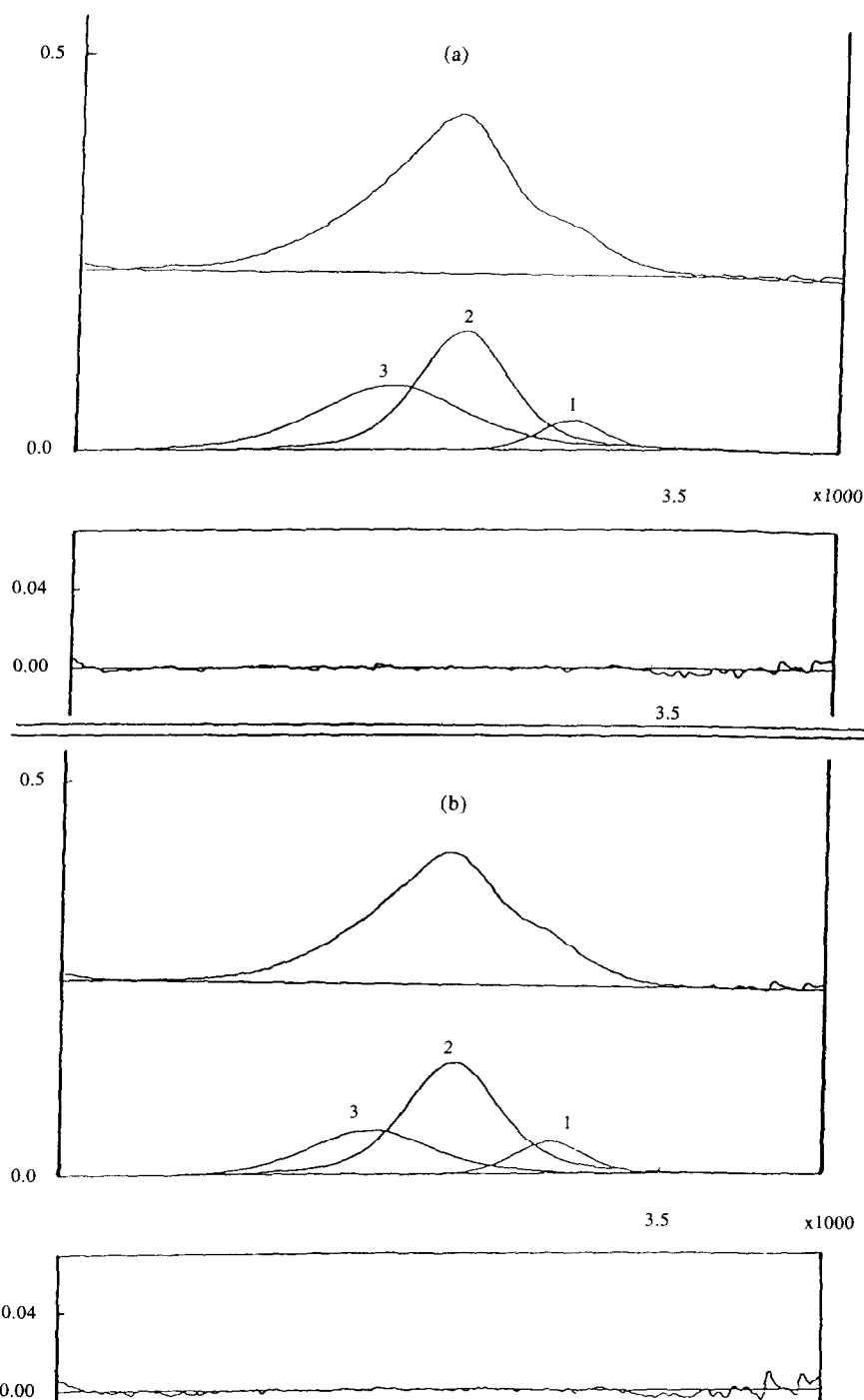
*Table 3* shows the curve fitting results for the ester C=O first overtone of the HNATH material at several temperatures. There is no obvious difference between

**Table 2** Curve fitting results of the N–H stretching band measured at various temperatures and stress conditions.  $\nu_0$ , peak position in wavenumber  $\text{cm}^{-1}$ ;  $W_{1/2}$ , half width in  $\text{cm}^{-1}$ ;  $A$ , integrated absorbance. The numbers in brackets are the standard deviation at the last significant number

Temp. (°C)	20	20	80	150	150
Load (MPa)	10	115	10	10	62
<b>Peak 1</b>					
$\nu_0$	3437.7(5)	3437.3(6)	3436.4(7)	3435.5(9)	3434.5(8)
$W_{1/2}$	44(1)	42(1)	45(1)	48(2)	47(1)
$A$	2.1(1)	2.1(1)	2.2(1)	2.4(1)	2.4(1)
<b>Peak 2</b>					
$\nu_0$	3376.0(4)	3376.0(5)	3377.7(5)	3378.7(5)	3378.8(5)
$W_{1/2}$	61(1)	62(1)	61(2)	64(2)	63(2)
$A$	11.5(6)	11.8(7)	11.4(7)	11.5(5)	11.4(5)
<b>Peak 3</b>					
$\nu_0$	3334(3)	3331(4)	3334(3)	3330(3)	3331(3)
$W_{1/2}$	99(3)	94(3)	92(3)	80(3)	80(3)
$A$	10.3(7)	10.4(7)	8.7(7)	5.6(5)	5.7(5)



**Figure 6** The N–H stretching vibration band and its 4th and 2nd derivatives



**Figure 7** Typical curve fitting of N-H stretching vibration band: (a) the spectrum taken at 22°C; and (b) the spectrum taken at 150°C. The bottom graph underneath the fitted bands shows the difference between the raw data and the fitted data

spectra taken at different temperatures in the peak position and half width. The C=O overtone band is essentially not affected by temperature.

**DISCUSSION**

*Hydrogen bonding in HNATA*

The above analysis shows that the N-H stretching band in HNATA is divided into a 'free' part and a hydrogen bonded part. The relative intensities of their absorbances provides information about interchain hydrogen bonding in the material.

The area of any absorbance peak is given by

$$A = \int \log\left(\frac{I}{I_0}\right) d\nu = \epsilon cl \tag{1}$$

where  $A$  is the integrated absorbance,  $\log(I/I_0)$  is the absorbance at frequency  $\nu$  in wavenumber,  $\epsilon$  is the integrated extinction coefficient,  $c$  the concentration of absorbing groups and  $l$  the path length through the sample. For HNATA, the integrated absorbance of the 'free' N-H stretching band can then be written as

$$A_f = \epsilon_f c_f l \tag{2}$$

and that of the bonded N–H stretching absorption band as

$$A_b = \varepsilon_b c_b l \quad (3)$$

where the subscripts f and b refer to free and bonded groups, respectively. The path length  $l$  in this case is the film thickness. The total area of the combined N–H stretching peak, which is a function of temperature, is

$$A = A_f + A_b = (\varepsilon_f c_f + \varepsilon_b c_b) l \quad (4)$$

The concentration of the free and hydrogen bonded functional groups is related to the total concentration of the groups by

$$c_0 = c_f + c_b \quad (5)$$

Combining equations (2)–(5), the proportion of bonded N–H species,  $X_b$ , can be expressed as

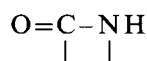
$$X_b = \frac{c_b}{c_0} = \frac{1}{1 + \frac{\varepsilon_b A_f}{\varepsilon_f A_b}} \quad (6)$$

where  $A_f$  and  $A_b$  can be obtained from the curve fitting. The determination of the extinction coefficients  $\varepsilon_b$  and  $\varepsilon_f$ , however, is rather complicated. Recent results reported by Coleman, Painter and co-workers<sup>13,15</sup> have demonstrated that the extinction coefficient,  $\varepsilon_b$ , for various hydrogen bonded species in polyamide and polyurethane, decreases with increasing temperature due to the fact that the strength of the hydrogen bonds decreases. They have proposed a simple model in which the extinction coefficient of the bonded species is related to the peak position. As the bonded absorption peak shifts to higher frequency with increasing temperature the  $\varepsilon_b$  value decreases. Massive frequency shifts of the bonded N–H stretching band with temperature have been reported for their materials. For example, the bonded N–H band shifts by 22 cm<sup>-1</sup> for amorphous polyamides (from 30°C to 210°C)<sup>15</sup>, and 20 cm<sup>-1</sup> for polyurethane (from 30°C to 145°C)<sup>13</sup>. A knowledge of the extinction coefficient as a function of temperature is therefore required for these materials in order to accurately quantify the concentration of relevant species.

Fortunately, there was no obvious peak shift in the deconvoluted HNATA bands as temperature changes (see Table 2). Similar results are also found for a rodlike polyamide<sup>18</sup>. Therefore, the average hydrogen bonding strength and the extinction coefficients,  $\varepsilon_b$  and  $\varepsilon_f$  for HNATA can be treated as constant in our case. A value of

$$\varepsilon_b/\varepsilon_f = 3.46 \quad (7)$$

is used in the following calculations. This value is experimentally determined from compounds containing the



group for the N–H stretching band<sup>10</sup>. It is worth noting that since the extinction coefficient of the free N–H group is only about one-third of that for the hydrogen bonded N–H groups, when some bonded N–H groups become free with increased temperature, the increase in the free N–H infrared absorption band is expected to be much smaller than the decrease in the bonded N–H

absorption band. This results in a reduction in the total N–H absorption area as has been observed in Figure 3.

We have assigned peak 1 in Table 2 to a mixture of the absorption of 'free' N–H species and that of the C=O overtone. To obtain  $A_f$ , the integrated absorption area of 'free' N–H species, the contribution of the ester C=O overtone should be subtracted from peak 1. The absorption area of the ester C=O overtone of the HNATA sample was determined from that of the HNATH sample in Table 3 after a correction for the different sample thickness and absorbing group concentration. We also assumed that the change of the C=O overtone band in HNATA with temperature is negligible as in the case of HNATH (see Figure 5). The sum of the areas of peaks 2 and 3 in Table 2 is used as the bonded N–H absorption area,  $A_b$ .

The extent of hydrogen bonding for three temperatures are estimated based on equations (6) and (7), where  $X_b$  is the percentage of the bonded N–H concentration in all N–H species. The results, given in Table 4, show that the N–H groups in HNATA are highly hydrogen bonded. With increasing temperature, some hydrogen bonds break, resulting in a slightly lower  $X_b$  value. However, the data suggest that even at 150°C, well above its glass transition temperature, most of the N–H species are still hydrogen bonded. This result is in line with studies of several other thermotropic liquid crystalline poly(ester amide) materials<sup>17</sup>.

For some conventional polymers, e.g. polyamides<sup>8,13</sup>, significant changes can be observed in the intensity, wavenumber position and shape of the N–H stretching absorption band as a consequence of the changes in the hydrogen bonding state, e.g. with increasing temperature, the intensity of the free N–H band increases at the cost of the bonded N–H band, the peak maximum of the bonded N–H band is shifted towards larger wavenumbers, and the half width of the bonded N–H band increases considerably. The intensity change is indicative of the shift in equilibrium concentration of the hydrogen bonded and free N–H groups, whereas the change in the peak position and the half width of the bonded N–H band are the result of a general weakening of the

**Table 3** Curve fitting results of C=O first overtone of HNATH sample.  $\nu_0$ , peak position in wavenumber cm<sup>-1</sup>;  $W_{1/2}$ , half width in cm<sup>-1</sup>;  $A$ , integrated absorbance. The numbers in brackets are the standard deviation at the last significant number

Temp. (°C)	22	80	150
$\nu_0$	3453.6(6)	3453.8(5)	3454.1(6)
$W_{1/2}$	39(2)	39(1)	40(2)
$A$	0.98(4)	0.98(5)	0.95(4)

**Table 4** Estimation of hydrogen bonding extent at different temperatures in HNATA material from the 'free' and bonded N–H species measured by infrared spectroscopy.  $A_f$ , infrared absorbance of the 'free' N–H species, and  $A_b$ , infrared absorbance of the hydrogen bonded N–H species. Numbers in brackets are the standard deviations

Temp. (°C)	$A_f$ (= $A_1 - A_{\text{overtone}}$ )	$A_b$ (= $A_2 + A_3$ )	$X_b$ (in the range of)
20	0.14 (0.10)	21.8 (1.3)	99%–96%
80	0.24 (0.10)	20.1 (1.4)	97%–94%
150	0.50 (0.10)	17.1 (1.0)	93%–88%

hydrogen bonds and a broader distribution of their energies<sup>4</sup>. However, comparing our results with the published data we have found that for HNATA the hydrogen bonding state changes with temperature far less than for the polyamides<sup>8,13</sup>. The hydrogen bonding in HNATA is rather stable.

#### *The material moduli and hydrogen bonding*

The elucidation of the role played by hydrogen bonding on the structure and properties of polymeric solids has been the subject of numerous investigations. As far as the mechanical properties are concerned, the contributions from hydrogen bonding are still open to question. Some researchers stress its importance in determining mechanical properties<sup>18</sup>, others conclude that too much emphasis has been placed on its role<sup>19</sup>. Our various mechanical measurements on HNATA<sup>20</sup> have shown that its shear and tensile moduli are little different from those of HNATH, a material with similar composition but with all ester linkages and no hydrogen bonding between chains.

The i.r. studies on HNATA show that the interchain interactions due to hydrogen bonding occur. However, two further factors need to be considered. Firstly, its hydrogen bonding strength seems lower than that in polyamide or polyurethane materials. The difference in the stretching frequencies between the hydrogen bonded N–H group and the 'free' N–H group is generally accepted as a measure of the hydrogen bond strength and is an important factor in discussing material properties<sup>2</sup>. A larger frequency difference,  $\Delta\nu$ , means a stronger hydrogen bond strength and a shorter bond length. We see that  $\Delta\nu$  for HNATA is less than  $103\text{ cm}^{-1}$  (taking the frequency difference between peak 1 and peak 3).  $\Delta\nu$  values for some well-known polymeric materials, such as nylon 6,6<sup>21</sup>, polyurethane<sup>13</sup>, Kevlar<sup>11</sup> and amorphous rod-like polyamides<sup>10</sup> are all greater than  $120\text{ cm}^{-1}$ . A polymer blend of polybenzimidazole/polyimide even showed a  $270\text{ cm}^{-1}$  frequency difference between its bonded and free N–H stretching vibration<sup>22</sup>. Secondly, the number of amide linkages in HNATA is less than 20% (the rest being ester linkages) and consequently the number of interchain bonds is small. On the other hand, it has been proposed that hydrogen bonding is not involved in explaining the modulus improvement<sup>23</sup>. Instead, the mechanical properties appear to be governed by solid state morphology rather than by secondary bonding. Much work still needs to be done to clarify the situation.

## CONCLUSIONS

Infrared studies of the N–H stretching vibrations suggest that HNATA is hydrogen bonded at all temperatures. Based on our previous mechanical measurements, however, we conclude that the interchain hydrogen bonding arising from the inclusion of the limited amide groups have not enhanced the tensile and shear moduli to any significant extent.

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