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Hydrogen Bonding in Polymers: Infrared Temperature Studies of an Amorphous Polyamide

Daniel J. Skrovanek, Stephen E. Howe, Paul C. Painter, and Michael M. Coleman*

Polymer Science Program, Department of Materials Science, The Pennsylvania State University, University Park, Pennsylvania 16802. Received December 21, 1984

ABSTRACT: Fourier transform infrared temperature studies of an amorphous polyamide are presented. The results strongly suggest that prior interpretations of the changes occurring in the N-H stretching region of the spectra of polyamides and polyurethanes with temperature were greatly oversimplified. In essence, these spectral changes were interpreted to be solely due to hydrogen-bonded N-H groups transforming to "free" N-H groups. Subsequent use of these data to obtain thermodynamic parameters associated with hydrogen bond dissociation must now be considered erroneous. The primary factor not taken into account concerns the very strong dependence of the absorption coefficient with hydrogen bond strength. With increasing temperature, the average strength of the hydrogen bonds decreases, which is observed in the infrared spectrum by a shift to higher frequency. Concurrently, the absorption coefficient decreases, leading to a reduction in the absolute intensity of the hydrogen-bonded N-H band. In this study we present experimental results in the N-H stretching and amide I, II, and V regions of the infrared spectrum of an amorphous polyamide. In addition, we present a model, justified by theoretical considerations, which we believe advances our understanding of the strong dependence of absorption coefficient with the strength of the hydrogen bonds. The ramifications of this work to hydrogen-bonded polymers are discussed.

Introduction

Over the past several years, we have been concerned with the application of Fourier transform infrared (FT-IR) spectroscopy to the characterization of polymer mixtures. Information concerning the nature, strength, and number of intermolecular interactions occurring between the polymeric components of such mixtures as a function of temperature has been gained. The thrust of this work, summarized in a recent review,¹ has been to relate these measurements to the phase behavior of polymer blends. Patterson and Robard² consider the phase behavior to be governed by two competing factors: a free volume contribution to the equation of state which is unfavorable to mixing and an interactional contribution which is potentially favorable to mixing. In our studies we have placed emphasis on the "interactional" component and it is intuitively clear that there has to be a corresponding balance between strength of intermolecular interactions among the different components of the blend and the forces of self-association. Because of these factors, we have paid particular attention to systems in which strong intermolecular interactions occur, characteristically those involving hydrogen bonds. This has led us to consider the infrared methods that have previously been used to determine thermodynamic parameters. For example, in a recent publication,³ we presented the results of an FT-IR temperature study of poly(4-vinylphenol) blends containing poly(vinyl acetate) and three ethylene-vinyl acetate copolymers. From a quantitative measure of the fraction of hydrogen-bonded carbonyl groups as a function of temperature, we obtained an estimation of the enthalpy of the intermolecular interaction from a van't Hoff plot. There were many assumptions inherent in this calculation, but the estimated value of ΔH was in pleasing agreement with

previously published values for low molecular weight analogues. This result is probably fortuitous because we now believe that there are major problems associated with methods previously used to determine such parameters from spectroscopic data.

Extensive research on hydrogen bonding in polyamides and polyurethanes has been performed by numerous authors.⁴⁻¹⁴ Trifan and Terenzi⁴ concluded that at room temperature there is essentially 100% hydrogen bonding in linear, aliphatic homopolyamides, as measured by the absence of bands in the infrared spectra above 3300 cm⁻¹. However, in structurally irregular copolymers and in linear homopolyamides at elevated temperatures, an absorption at 3448 cm⁻¹ was observed and assigned to "free" N-H groups. Bessler and Bier⁶ measured the "free" and bonded N-H peak heights of various polyamides as they change with temperature. Analysis was complicated, however, by the overlap and inherent broadness of the infrared bands, especially at elevated temperatures.

A quantitative study of hydrogen bond dissociation in polyamides was performed by Schroeder and Cooper.¹³ In an elegant procedure which avoids curve resolving, these authors reasoned that if one has a knowledge of the absorption coefficients corresponding to the "free" and bonded N-H stretching modes, then it is only necessary to measure the total area of the N-H stretching region to obtain the required data. In other words, when the temperature is raised, the change in total area reflects the difference in absorption coefficients as the bonded N-H groups transform to "free" N-H groups. Two assumptions were necessary: that the absorption coefficients did not vary significantly with temperature and that the degree of hydrogen bonding was known at some reference temperature. The data obtained were used, via an equilibrium

scheme and a van't Hoff plot, to gain an estimation of the thermodynamic parameters associated with hydrogen bond formation. Values of ΔH were reported in the range 8–12 kcal mol⁻¹, depending upon the polyamide. A similar procedure was very recently used by Garcia and Starkweather¹⁴ in their studies of nylon 6,6 and analogous model compounds. For this polymer the authors obtained a value of 14 kcal mol⁻¹ for ΔH , while for the model compounds values of 7–8.5 kcal mol⁻¹ were reported. These authors also reported, from an extrapolation of their data above the melting point of the polyamide, that there was a retention of 26% of the hydrogen bonds at 270 °C.

The infrared studies of Senich and MacKnight¹² performed on polyurethanes should also be mentioned. These authors attempted to circumvent the problems of curve resolving by employing a spectral subtraction technique to accentuate the changes occurring with temperature. The subtractions were not "clean", however, and there were problems involving derivative-type residuals resulting from band shifting and broadening, which complicate the interpretation. A value of 6.9 kcal mol⁻¹ for the enthalpy of dissociation was reported.

These results are disturbing in that studies of low molecular weight amides using a variety of techniques¹⁵ suggest values of ΔH ranging from 3.5 to 6.5 kcal mol⁻¹. There appears to be no good reason for such a discrepancy between the results reported for low molecular weight amides and their polymeric analogues. Indeed, the discrepancy has been ignored or given short shrift in most discussions.

As discussed briefly in a recent note,¹⁶ we believe we have discovered a serious error in the previous interpretation of the infrared spectral features observed in the N–H stretching region. This has led to an overestimation of the fraction of "free" N–H groups and, in turn, the estimation of the enthalpy of hydrogen bond formation. Further elaboration will be presented in the text and the thrust of this paper is concerned with the interpretation of the infrared spectra, obtained as a function of temperature, of an amorphous polyamide.

Experimental Section

The amorphous polyamide used in this study was obtained from E. I. du Pont de Nemours and Co. The polymer was synthesized from hexamethylenediamine and a mixture of the isomers of phthalic acid. The random placement of the latter isomers in the polymer chain prevents crystallization. Thermal analysis reveals a glass transition temperature of 135 °C and there is no evidence of a crystalline melting point.

The sample for infrared analysis was prepared by casting a film onto a potassium bromide (KBr) window from a 1% (w/v) solution in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) obtained from Fisher Scientific Co. After evaporation of the majority of the solvent at room temperature the sample was placed under vacuum in an oven at 100 °C to remove residual solvent and water. The sample was then immediately sandwiched between KBr windows and transferred to a temperature cell contained in the infrared spectrometer.

Exchange of the amide proton with deuterium was effected by stirring the film in a sealed, nitrogen-purged, container of deuterium oxide at room temperature for a period of 1 week. The film was immediately transferred to the spectrometer and the spectrum recorded. Subtraction of the spectrum of deuterium oxide yielded the spectrum of the essentially pure N-deuterated amorphous polyamide.

Infrared spectra were acquired on a Digilab FTS-15E Fourier transform infrared spectrometer at a resolution of 2 cm⁻¹. A minimum of 64 scans were signal averaged and the spectra stored on a magnetic disk system. The frequency scale is internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm⁻¹. The film used in this study was sufficiently thin to be within an absorbance range where the Beer–Lambert law is

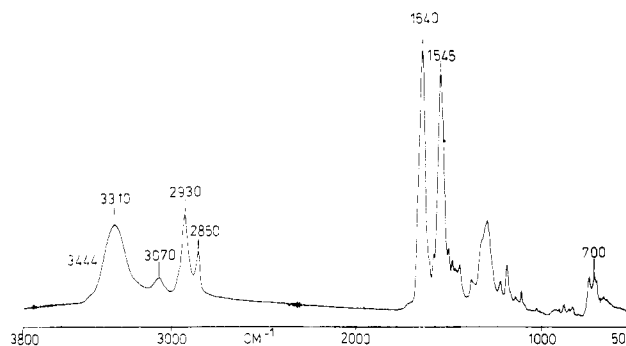


Figure 1. FT-IR spectrum of the amorphous polyamide recorded at room temperature in the range 500–3800 cm⁻¹.

Table I

freq, cm ⁻¹	approx descrip
3444	"free" N–H stretch
3310 (br)	hydrogen-bonded N–H stretch
3070	aromatic C–H stretch
2930	asymmetric CH ₂ stretch
2850	symmetric CH ₂ stretch
1640	amide I mode
1545	amide II mode
~1290	amide III mode
700	amide V mode

obeyed.¹⁷ Spectra recorded at elevated temperatures were obtained with a Micristar heat controller, which has a reported accuracy of ± 0.1 °C.

Results and Discussion

Infrared Spectrum of Amorphous Polyamide.

General Overview. At first glance, it may seem somewhat unusual that we should choose for these studies an inherently complex amorphous polyamide; but it must be emphasized that this was a deliberate choice. In the first place, truly amorphous polyamides are rare and we did not wish to have the added complication of crystallinity. Secondly, as we will see below, the infrared spectrum of the amorphous polyamide is remarkably straightforward and easy to interpret. The majority of the infrared bands of direct interest, those involving vibrations of the amide group, are well separated and reasonably free from underlying absorptions.

Figure 1 shows the infrared spectrum recorded at room temperature, in the range 500–3800 cm⁻¹, of the amorphous polyamide sample cast from HFIP. In common with other strongly self-associated amorphous polymers containing aromatic rings, such as atactic poly(vinylphenol),³ phenoxo,¹⁸ etc., the infrared spectrum is characterized by relatively sharp bands attributed to the predominantly conformationally insensitive modes of the aromatic rings and relatively broad bands attributed to conformationally sensitive backbone modes together with hydrogen-bonded amide modes. For the purposes of this study, we will be primarily concerned with the vibrational modes involving the amide group. The major infrared bands of interest may be summarized as shown in Table I.

For expository convenience, we will separately describe the results obtained in three major spectral regions and then turn our attention to the description of a model which we believe advances our understanding of the spectral features observed as a function of temperature. Finally, we will discuss the ramifications of the theoretical and experimental results on the interpretation of infrared temperature studies of hydrogen-bonded polymers in general.

N–H Stretching Region. The N–H stretching region of polyamides spans a range of about 3100–3500 cm⁻¹. At room temperature (Figure 1), the amorphous polyamide

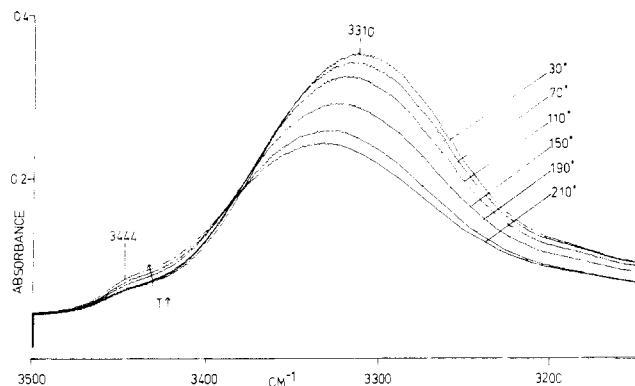


Figure 2. FT-IR spectra in the N-H stretching region of the amorphous polyamide recorded as a function of decreasing temperature in the range 3150–3500 cm^{-1} .

exhibits two infrared bands at 3444 (weak shoulder) and 3310 cm^{-1} (very broad), which are assigned to “free” and hydrogen-bonded N-H stretching modes, respectively. The N-H stretching vibration may be considered to be an isolated mode and normal coordinate calculations^{19,20} of polyamides and polypeptides indicate that the potential energy distribution is essentially composed solely of this stretching motion. Accordingly, it is not a conformationally sensitive mode. Instead, the broadness of the hydrogen-bonded N-H band reflects, in large part, a distribution of hydrogen-bonded N-H groups of varying strengths dictated by distance and geometry. It is readily envisaged that in an amorphous polyamide, hydrogen bonds will be formed between complementary N-H and C=O moieties and given the “spaghetti-like” nature of random chain molecules, there will be a distribution of distances and geometries of these hydrogen bonds.

Figure 2 shows the effect of temperature on the spectrum of the amorphous polyamide in the N-H stretching region. There are a number of points that are worthy of mention concerning how we obtained these results. The amorphous polyamide sample was cast from HFIP onto a KBr window. Residual solvent and water absorption are always problems of concern in studies such as these. Care was taken to minimize these problems by first evaporating the majority of the solvent under vacuum at 100 °C. The sample was then heated to 210 °C in the spectrometer and spectra were recorded as a function of decreasing temperature. No evidence of residual solvent was found in the infrared spectrum and it was determined that consistent results were obtained upon cycling up and down in temperature. In addition, the total area of the bands in the N-H stretching region at any given temperature did not vary by more than 1%. Finally, it must be emphasized that the spectra are displayed on an absolute absorbance scale. In other words, they are not arbitrarily scale expanded.

The results displayed in Figure 2 are intriguing and immediately indicate problems with the previous interpretations of this region of the spectrum of polyamides. With increasing temperature, the peak maximum of the hydrogen-bonded N-H band shifts to higher frequency (3310 to 3332 cm^{-1} from 30 to 210 °C), and there is a large decrease in area (approximately 35%). Concomitantly, there is an *apparent* increase in the absorbance of the “free” N-H band, albeit marginally. Previously workers^{8,12–14} have made the implicit assumption that with increasing temperature the reduction in area of the hydrogen-bonded N-H band and the increase in area of the “free” N-H band solely reflect the transformation of a fraction of hydrogen-bonded N-H groups to “free” groups.

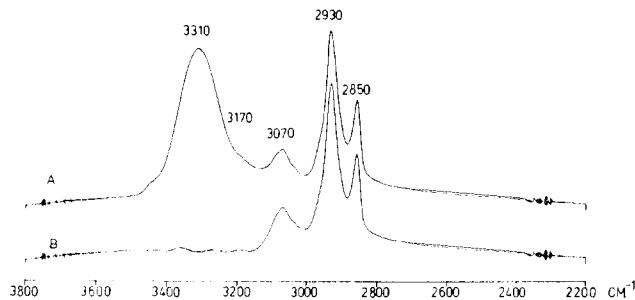


Figure 3. FT-IR spectra of the amorphous polyamide recorded at 210 °C in the range 2200–3800 cm^{-1} : (A) absorbance spectrum; (B) curve-fitted spectrum subtracted from absorbance spectrum.

The change in total area is thus explained on the basis of the difference in the *average* absorption coefficients for the “free” and hydrogen-bonded N-H stretching vibrations. Intuitively, if one examines the results displayed in Figure 2, it is apparent that the above explanation is highly unlikely. The difference between the absorptivity coefficients of the “free” and hydrogen-bonded N-H modes, experimentally found in low molecular weight analogues to be in the ratio of 1:3.2,⁸ would have to be inordinately large to explain the change in areas of these bands with increasing temperature. Furthermore, as we will see below, the increase in absorbance at 3444 cm^{-1} with increasing temperature is primarily due to increasing overlap with the hydrogen-bonded N-H band as it shifts to higher frequency.

We are fully aware of the inherent problems involved in curve resolving. Without a priori knowledge of the band shape, position, width, and number of the component curves comprising the complex band envelope, as well as the problem of drawing a base line, the results obtained from curve resolving are always open to debate.²¹ Nevertheless, using a set of reasonable and consistent assumptions, we have resolved the N-H stretching region into three components, all of which can be justified from the literature. Two of the curves correspond to the “free” and hydrogen-bonded N-H stretching modes and the third is attributed to the amide B mode. The latter band has been assigned to the first overtone of the amide II mode, which is enhanced by Fermi resonance,²⁰ although there is some debate concerning the precise origin of this band.²² In any event, upon careful examination of the N-H stretching region, one can discern by eye a contribution to the envelope at approximately 3180 cm^{-1} . A flat base line was chosen from 3550 to 2500 cm^{-1} where there are no underlying bands (see Figure 1). Using a curve fitting procedure which has been previously described,²³ we resolved the N-H stretching region into the three components. The identical procedure was employed for all the spectra recorded at the different temperatures. Although the band shape was not initially fixed, the least-squares program produced a best fit with Gaussian band shapes. Given the inherent broadness of the bands, this result is not unexpected. The “goodness of fit” can be seen in Figure 3, which shows the original spectrum obtained at 210 °C (denoted A) and the same spectrum after subtraction of the three components. The residual is well within experimental error. Similar results were obtained at the other temperatures. The “free” N-H stretching band was found to have a frequency ($3446 \pm 1 \text{ cm}^{-1}$) and width at half-height that were essentially constant with temperature. In contrast, the frequency of the hydrogen-bonded N-H band increased systematically from 3310 to 3332 cm^{-1} on going from 30 to 210 °C. The width at half-height, however, was remarkably constant at $130 \pm$

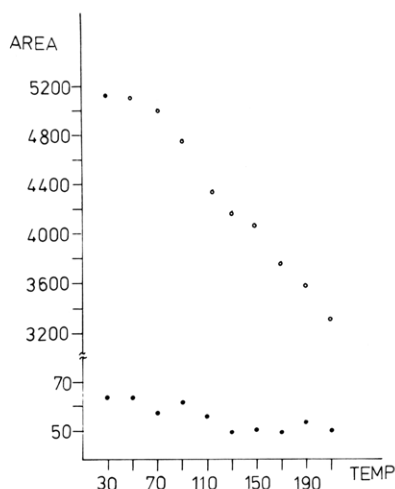


Figure 4. Plot of area in arbitrary units of the N-H stretching bands vs. temperature: top (O) bonded; (●) "free".

2 cm^{-1} , a result that will be of importance to our subsequent modeling.

Figure 4 shows a plot of the respective areas of the "free" and hydrogen-bonded bands obtained from the curve fitting procedure. It is immediately striking that, within experimental error, the area ascribed to the "free" N-H stretching band remains essentially constant. (The results, if anything, suggest a slight decrease in area with temperature and it is tempting to attribute this to a slight corresponding decrease in absorptivity coefficient with temperature.) Conversely, the area of the hydrogen-bonded N-H stretching band drops dramatically with temperature. These results strongly suggest that the previous interpretation of infrared temperature studies of polyamides and polyurethanes is too simplistic. We will return to these results later in the text.

Amide I and II Regions. Unlike the essentially isolated N-H stretching vibration, the amide I and II modes are more complex vibrations. The amide I mode may be considered to be comprised of contributions from the C=O stretching, the C-N stretching, and the C-C-N deformation vibrations. In poly(glycine I), for example, normal coordinate calculations reveal that the potential energy distribution is comprised of 77% C=O stretch, 14% C-N stretch, and 12% C-C-N deformation.²⁰ This mode is conformationally sensitive and the frequency of this band has been extensively used to differentiate between the different conformations found in polypeptides and proteins.²⁴ The amide II band is a mixed mode containing contributions from the N-H in-plane bending, the C-N stretching, and the C-C stretching vibrations. Again, for poly(glycine I) as an example, the potential energy of the amide II band is distributed as 43% N-H in-plane bend, 26% C-N stretch, 18% C α -C stretch, and 11% N-C α stretch.²⁰ Thus it is also a conformationally sensitive mode.

In the amorphous polyamide employed for these studies, the amide I and II modes occur at 1640 and 1545 cm^{-1} , respectively, for the sample recorded at 30 $^{\circ}\text{C}$ (Figure 1). These two modes are the most intense bands in the spectrum. Figure 5 shows the region from 1480 to 1800 cm^{-1} for the amorphous polyamide sample recorded as a function of temperature. It again must be emphasized that the spectra are displayed on an absolute absorbance scale. For the sake of clarity, we will first discuss the results obtained in the amide I region and then turn our attention to the amide II band.

As mentioned above, the amide I band is a mixed mode containing a large contribution from the C=O stretching

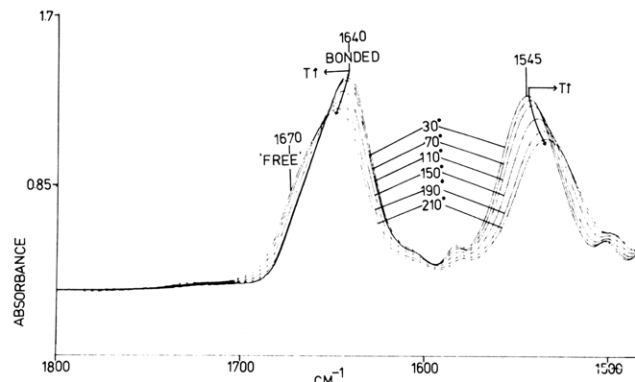


Figure 5. FT-IR spectra of the amorphous polyamide in the amide I and II regions recorded as a function of decreasing temperatures in the range 1480–1800 cm^{-1} .

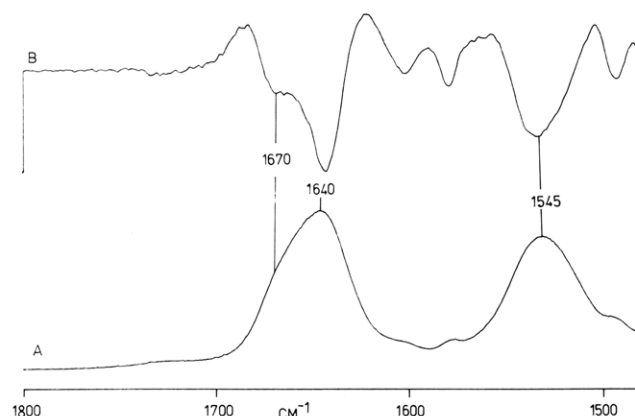


Figure 6. FT-IR spectra of the amorphous polyamide in the amide I and II regions recorded at 210 $^{\circ}\text{C}$ in the range 1480–1800 cm^{-1} : (A) absorbance spectrum; (B) second-derivative spectrum.

vibration. Deuterium-exchange experiments yield a relatively small shift to lower frequency (20 cm^{-1}), consistent with the calculated potential energy distribution of the amide I mode.²⁰ As the temperature is increased, the amide I band appears to shift to higher frequency (1640 to 1646 cm^{-1} from 30 to 210 $^{\circ}\text{C}$), decreases in intensity and there is increasing evidence of a shoulder at about 1670 cm^{-1} . A second-derivative plot, shown in Figure 6, plainly reveals two bands at 1640 and 1670 cm^{-1} for the sample recorded at 210 $^{\circ}\text{C}$. Similar results are obtained from the second-derivative plots at the other temperatures. Given that we have already shown the N-H stretching region is comprised of two major contributions, namely "free" and hydrogen-bonded N-H groups, we would expect to observe a corresponding effect in the amide I mode, that is, infrared bands attributed to "free" and hydrogen-bonded carbonyl groups. In addition, we would also expect a one-to-one correspondence between the fraction of "free" N-H and carbonyl groups as a function of temperature, because there is the same number of N-H and carbonyl moieties associated with the amide group present in the amorphous polyamide.

Curve fitting of the amide I band into two components was performed by using a similar procedure described for the N-H stretching region. A flat base line was drawn from 1800 to 900 cm^{-1} (see Figure 1). This time, a Gaussian band shape was assumed (rather than determined by the iterative procedure), and the amide I region was resolved into two bands. Neither the frequency nor the breadth of the bands was fixed. The results, as indicated by the standard deviation from the least-squares program, exceeded our expectations. The hydrogen-bonded amide I mode shifted in a consistent manner from 1642 to 1647

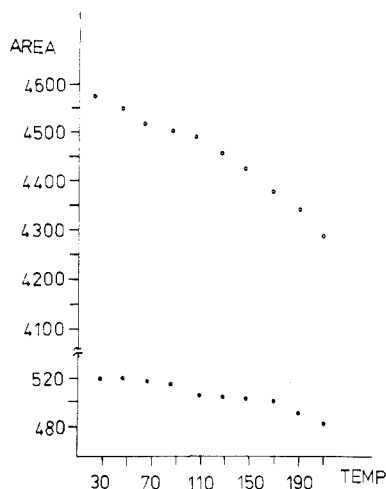


Figure 7. Plot of the area in arbitrary units of the amide I band vs. temperature: top (○) bonded; (●) "free".

cm^{-1} as the temperature increased from 30 to 210 °C. The width at half-height remained essentially constant at $37 \pm 2 \text{ cm}^{-1}$. The "free" amide I band shifted in frequency from 1668 to 1672 cm^{-1} over the same temperature range and its width at half-height also remained essentially constant at $21.2 \pm 0.3 \text{ cm}^{-1}$. A plot of the respective areas of the "free" and hydrogen-bonded amide I bands is shown in Figure 7. The striking similarity of these results and those obtained for the N-H stretching region is obvious and extremely satisfying. The one-to-one correspondence between the fraction of "free" N-H and carbonyl groups as a function temperature is important to our subsequent arguments. Although the area of the hydrogen-bonded amide I band decreases markedly with temperature, it is important to emphasize that this does not mean that the fraction of hydrogen-bonded carbonyl groups has necessarily decreased significantly. Elaboration of this point will occur later in the text.

The amide II band seen at 1545 cm^{-1} in the spectrum recorded at 30 °C is a mixed mode containing a major contribution from the N-H in-plane deformation vibration. This is substantiated by a deuterium-exchange experiment where the amide II band of the amorphous polyamide shifts from 1545 to 1440 cm^{-1} . With increasing temperature, the amide II band is observed to shift to lower frequency and there is also a decrease in the area of the band (Figure 5). There is no evidence of a separation into "free" and hydrogen-bonded contributions. The second-derivative plots (see Figure 6) do not suggest the presence of two bands. Weak bands observed in both the spectra and the second-derivative plot (Figure 6) around 1580 and 1498 cm^{-1} are presumably aromatic ring modes.²⁵ The shift to lower frequency of the amide II band with temperature is consistent with a decrease in the average hydrogen bond strength. The reduction in intensity of the amide II band is more complex and we will defer further discussion of this point until we have described our proposed model later in the text.

Amide III and V Regions. We will not discuss the amide III region in much detail. The amide III mode is highly mixed and is complicated by coupling to backbone and aromatic ring modes. Suffice it to say that there are shifts in frequency and variations in intensity of several infrared bands in the 1150–1350- cm^{-1} region of the infrared spectrum of the amorphous polyamide as a function of temperature. Of some passing interest is a relatively weak band at 1175 cm^{-1} which shows very similar trends to those to be discussed for the amide V band below.

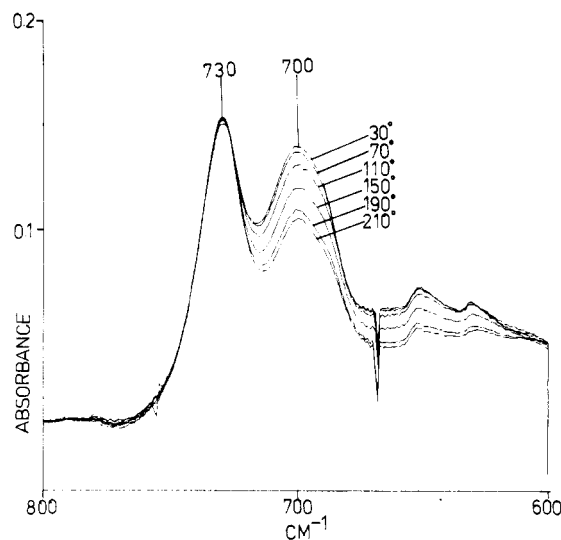


Figure 8. FT-IR spectra of the amorphous polyamide in the amide V region recorded as a function of decreasing temperature in the range 600–800 cm^{-1} .

The amide V band is also a highly mixed mode containing a significant contribution from the N-H out-of-plane deformation. In poly(glycine I), where the amide V mode occurs at 720 cm^{-1} , the potential energy distribution is distributed as 75% C-N torsion, 24% N-H out-of-plane bend, 13% H...O stretch, and 13% N-H...O in-plane bend.²⁰ In our amorphous polyamide, the amide V band occurs at 700 cm^{-1} , an assignment that has been confirmed from the deuterium-exchange experiment. Upon deuterium exchange the 700- cm^{-1} band is essentially eliminated and shifts to below 500 cm^{-1} .

Figure 8 shows the amide V region of the spectrum as a function of temperature. It can be seen that the amide V mode decreases in intensity with increasing temperature. There does not appear to be any shift in the frequency of this mode with temperature, however. It is pleasing to observe that the 730- cm^{-1} band does not shift or change in intensity with temperature. Although we do not know the precise form of this mode, it is most likely an aromatic ring out-of-plane hydrogen bending vibration; the fact that this mode does not change with temperature over the range studied increases our confidence that the intensity changes we do observe for modes attributed to the amide group are indeed real. The reduction of intensity of the amide V band with increasing temperature is significant. Zerbi and co-workers²⁶ have demonstrated that the absolute intensity of the out-of-plane bending mode of X-H groups (X = C, N, O) is related to the effective equilibrium charge of the hydrogen atom, which in turn is related to the dipole moment. Once again we will return to this subject later.

A Model

In the forthcoming discussion we will be emphasizing a model proposed to explain the results observed in the N-H stretching region of the spectrum of the amorphous polyamide as a function of temperature. The model, however, must also explain the results obtained in the other regions of the spectrum. As the N-H stretching vibration is essentially an isolated mode, the spectral observations are easier to interpret compared to the mixed amide I, II, III, and V modes.

Before we embark on the description of our model, it is perhaps worthwhile to reiterate the major facets of the problem that we need to explain. First, our results suggest that there is no significant increase in the concentration of "free" N-H groups in the amorphous polyamide sample

as the temperature is varied from 30 to 210 °C. Second, the hydrogen-bonded N-H band is observed to shift to higher frequency and to markedly decrease in intensity with increasing temperature over the same range. If there is no significant increase in the concentration of the "free" N-H groups, how are we to explain this marked decrease in the area of the hydrogen-bonded band?

We will start by making the assumption that at a given temperature, T_1 , there is a Gaussian distribution of hydrogen-bonded N-H groups of varying strengths centered about a mean position, ν_1 , which corresponds to the average strength of the intermolecular interaction. Intuitively, this appears to be a reasonable assumption. One can readily envisage that at any given moment there will be N-H groups at varying distances and geometries from complementary carbonyl groups. If there are a large number of such groups in a particular sample, we would expect the distribution to be Gaussian. At some elevated temperature, T_2 , the average strength of the hydrogen-bonded N-H groups will diminish as the volume of the polymer and the average intermolecular distance between chains increases. We will assume that the distribution of the strengths of the hydrogen-bonded N-H groups is of identical form with that occurring at T_1 , the only difference being the mean position, ν_2 , which reflects the reduction of the average strength of the hydrogen bonds present at T_2 .

If the broad hydrogen-bonded N-H band observed in the experimental spectrum reflected only the normalized weight fraction distribution of hydrogen-bonded species, then we would anticipate identical curves of the same area centered at different frequencies corresponding to the particular temperature. This is not what is observed and we will assume that the reduction in area observed experimentally upon increasing the temperature from T_1 to T_2 is solely due to a variation of absorption coefficient with the hydrogen bond strength and hence frequency, $a(\nu)$. This naturally assumes that the concentration of "free" N-H groups does not change significantly with temperature, a result we obtained experimentally in this study (see Figure 3).

The intensity of the hydrogen-bonded N-H band at T_1 may thus be described by a function of the form

$$I_1(\nu) = a(\nu) \frac{1}{\sigma(2\pi)^{1/2}} \exp \left[-\frac{1}{2} \left(\frac{\nu - \nu_1}{\sigma} \right)^2 \right] \quad (1)$$

This equation is made up of two contributions, namely a term that accounts for the variation of absorption coefficient with frequency and a term that describes the Gaussian distribution of species present. Similarly, at T_2

$$I_2(\nu) = a(\nu) \frac{1}{\sigma(2\pi)^{1/2}} \exp \left[-\frac{1}{2} \left(\frac{\nu - \nu_2}{\sigma} \right)^2 \right] \quad (2)$$

Dividing these two equations and taking the natural logarithm of both sides yield

$$\ln \frac{I_1(\nu)}{I_2(\nu)} = -\frac{1}{2} \left(\frac{\nu - \nu_1}{\sigma} \right)^2 + \frac{1}{2} \left(\frac{\nu - \nu_2}{\sigma} \right)^2 \quad (3)$$

Substitution of $\nu_2 = \nu_1 + \Delta\nu$, expanding, rearranging, and collecting terms allow the equation to be cast in the form

$$\ln \frac{I_1(\nu)}{I_2(\nu)} = -\frac{\Delta\nu}{\sigma^2} \nu + \frac{\Delta\nu}{\sigma^2} \left(\nu_1 + \frac{\Delta\nu}{2} \right) \quad (4)$$

This is a linear equation of the form $y = mx + b$. Thus a plot of the left-hand side of eq 4 vs. frequency, ν , should yield a straight line with a slope of $-(\Delta\nu/\sigma^2)$ and an intercept of $(\Delta\nu/\sigma^2)(\nu_1 + \Delta\nu/2)$. From this the unknown

parameters ν_1 and $\Delta\nu$ can be determined. The only other unknown parameter is the standard deviation, σ . We have previously stated that the width at half-height of the hydrogen-bonded N-H stretching band is remarkably constant, having values lying between $130 \pm 2 \text{ cm}^{-1}$ over the range 30–210 °C. From a table of the ordinates of a standard normal curve,²⁷ the standard deviation may be found by dividing the width at half-height by the corresponding number of standard deviations, in this case 2.34. Accordingly, we have assumed a width at half-height of 130 cm^{-1} , which yields a value of 55.6 for σ . It did not escape our attention that this assumption could lead to significant errors in the subsequent calculation of ν_1 and $\Delta\nu$. Changes in the value of σ , however, do not materially affect the overall form of the results and the arguments we wish to make. They only affect the absolute numbers.

Returning to eq 4, we may obtain the values of $I_1(\nu)$ and $I_2(\nu)$ from a pair of experimental spectra recorded at two different temperatures T_1 and T_2 and the values of the slope and intercept calculated from a least-squares regression. For example, using the spectral data obtained at 30 and 210 °C, we calculated $\Delta\nu$ to be 22.7 cm^{-1} and ν_1 equals 3367 cm^{-1} with a correlation coefficient of better than 0.99. This implies that the peak maximum representing the average position of the distribution of the strengths of the hydrogen-bonded N-H groups at 30 °C is at 3367 cm^{-1} . The experimentally observed peak maximum is seen at 3310 cm^{-1} . This, in turn, implies that the experimentally observed peak maximum occurs at a lower frequency than that of the "true" peak maximum representing the distribution of the strengths of the hydrogen bonds, because it has been multiplied by a function describing the variation of absorptivity coefficient with frequency. (Incidentally, if the above hypothesis is correct, it advances our understanding of why it has not been possible to generally scale the frequency difference between "free" and hydrogen-bonded N-H or O-H bands with the enthalpy of dissociation. In other words, the observed frequency of the hydrogen-bonded band may be markedly affected by the $a(\nu)$ function, which, in turn, could be strongly dependent upon the chemistry involved.)

The average value of ν_1 was obtained from the spectral data recorded at the different temperatures with respect to the reference spectrum recorded at 30 °C. To our delight, an average value for ν_1 of $3367 \pm 3 \text{ cm}^{-1}$ was determined. (Naturally, the values of $\Delta\nu$ varied but were entirely consistent with the experimental observations). One can now substitute back into eq 1 to obtain the absorptivity coefficient as a function of frequency. The results of this calculation are displayed graphically in Figure 9. A very strong dependence of the absorption coefficient with frequency is immediately apparent. In fact, the results indicate that the absorptivity coefficient effectively doubles over the 40-cm^{-1} range from 3320 to 3360 cm^{-1} .

Although the above model appears intuitively satisfying, we would be the first to admit that there are elements of a "circular argument" present. The reduction in area of the hydrogen-bonded N-H band with temperature has been assumed to be solely due to the change in absorption coefficient with frequency and we employed the experimental data to "back calculate" the $a(\nu)$ function. In fact, for the specific case of the amorphous polyamide presented here, where both the assumed theoretical distribution of hydrogen-bonded strengths and the experimentally observed hydrogen-bonded N-H band are Gaussian with the same standard deviations, it can be demonstrated mathematically that the $a(\nu)$ function is exponential in form. There is, however, no a priori assumption of the form of

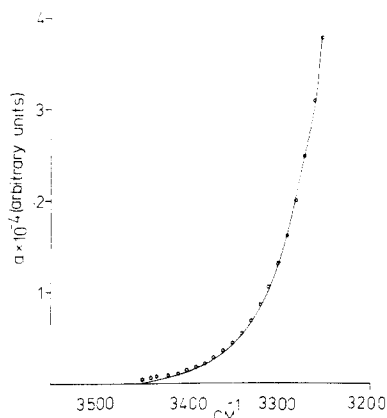


Figure 9. Plot of absorption coefficient in arbitrary units vs. frequency.

the $I(\nu)$ function in the model. At this stage, we would prefer to emphasize the very strong dependence of the absorption coefficient with hydrogen-bonding strength rather than the precise form of the $a(\nu)$ function.

Theoretical Considerations. The strong dependence of absorption coefficient with frequency may be rationalized theoretically. The intensity, I_i , of a given normal mode may be expressed in terms of the Beer-Lambert law:

$$I_i = a_i bc \quad (5)$$

where a_i is the absorption coefficient, b the path length, and c the concentration of the species. For our studies we do not know the absolute value of bc , but it is constant throughout the temperature studies.

From the theory of infrared intensities,^{28,34} I_i is the proportional the square of the dipole moment change with normal coordinate. For the purposes of this discussion it is only necessary to consider an isolated N-H bond:

$$I_i = C(\delta\mu/\delta Q)^2 \quad (6)$$

The dipole moment, μ , is related to the bond distance, r , and the effective charge, q , by

$$\mu = qr \quad (7)$$

Differentiation with respect to normal coordinate leads to

$$\frac{\delta\mu}{\delta Q} = q \frac{\delta r}{\delta Q} + r \frac{\delta q}{\delta Q} \quad (8)$$

A complete knowledge of the parameters in eq 8, that is r , q , $\delta q/\delta Q$, (the charge flux), and $\delta r/\delta Q$ (the change of r with normal coordinate), for hydrogen-bonded N-H groups of varying strengths would permit a calculation of $\delta\mu/\delta Q$. This in turn permits a calculation of absolute intensities from eq 6. Unfortunately, although there has been considerable progress made in the calculation of infrared intensities during the past decade,²⁹⁻³⁴ to our knowledge there have been no published data that we can use to calculate the intensity of hydrogen-bonded N-H groups of varying strengths from first principles (although Krimm and co-workers are working on this problem³⁵). Nevertheless, we can at least rationalize the dependence of absorption coefficient with increasing strength of the hydrogen bond. It is well established that the N-H bond length increases upon hydrogen bonding and the effective charge also changes with hydrogen bond strength.³⁶ Accordingly, changes in the parameters given in eq 8 would

lead to a change in $\delta\mu/\delta Q$. As intensity is proportional to the square of the dipole moment change with normal coordinate (eq 6) and also with absorptivity coefficient (eq 5), it is anticipated that the absorption coefficient should be a strong function of frequency.

Additional Comments. The above proposed model and the theoretical justification are based upon the results obtained in the N-H stretching region of the spectrum. As stated previously, we must also consider other regions of the spectrum to see if the changes observed with temperature are consistent with this model.

The results obtained in the amide I region appear to be entirely consistent. To reiterate, the fraction of "free" carbonyls does not appear to vary significantly with temperature (Figure 7). Furthermore, in common with the hydrogen-bonded N-H band, the hydrogen-bonded amide I band decreases in area and shifts to higher frequency with increasing temperature. However, both the area change and frequency shift with temperature are much less in the case of the amide I region. This is to be expected for several reasons. First, the small mass of the hydrogen atom in the N-H group results in relatively large displacements upon vibration compared to those occurring for the oxygen atom of the carbonyl group. Accordingly, one would expect to observe much greater frequency shifts and intensity variations with strength of hydrogen bonds for the N-H group. Secondly, the amide I mode is a mixed vibration and consequently one has to consider the other contributions to the potential energy distribution which may (or may not) be affected significantly by the strength of the hydrogen bonds. The main point to emphasize, however, is that the same trend is observed for both N-H stretching and amide I modes.

The amide II and V regions of the spectrum do not display features that can be ascribed to "free" and hydrogen-bonded N-H groups. In essence, the amide II band decreases in intensity and shifts to lower frequency with increasing temperature while the amide V band decreases in intensity but does not shift in frequency. As mentioned previously, both of these bands are highly mixed modes containing contributions from the in-plane and out-of-plane N-H vibrations, respectively. Concrete conclusions are difficult to make but it should be noted that Zerbi³⁴ has suggested that the reduction in intensity of these modes may be correlated with the decrease in hydrogen-bond strength.

Conclusions and Ramifications of This Work

There are a number of important conclusions that arise from the experimental observations and the theoretical considerations presented in this work.

(1) The changes occurring in the N-H stretching region of the infrared spectrum of polyamides and polyurethanes with temperature has been misinterpreted in the past. The strong dependence of absorption coefficient with the strength of the hydrogen bond has been generally ignored. With increasing temperature, the frequency of the N-H stretching band increases as the average strength of the hydrogen-bonded N-H groups diminishes. The large area decrease of the hydrogen-bonded N-H band with increasing temperature is primarily caused by the reduction in the absorptivity coefficient with frequency or average strength of the hydrogen-bonded groups. The concentration of "free" N-H groups does not increase significantly over a temperature range 30–210 °C. It must be emphasized, however, that we are not stating that there is no change in the concentration of the "free" N-H groups with temperature, only that we are unable to measure the change if it occurs. For example, if there were 10% "free"

N-H groups at 30 °C and there was a 10% increase in the concentration at 210 °C, we could not distinguish between 10% and 11%, given the experimental limitations.

(2) The fraction of "free" N-H groups, as measured from infrared temperature studies in the N-H stretching region, has been overestimated in the past. Accordingly, the subsequent calculations of the thermodynamic parameters must be viewed as being erroneous. This would explain the large discrepancy between the values of ΔH for polymers compared to their low molecular weight analogues.

(3) We have proposed a model to describe the large area change observed in the hydrogen-bonded N-H band as a function of temperature which is supported by theoretical considerations. This model is based upon a Gaussian distribution of hydrogen-bonded N-H groups of varying strengths and a function describing the variation of absorption coefficient with frequency or hydrogen bond strength. From the experimental spectral data we have been able to separate out the contribution attributed to the variation of absorption coefficient with frequency. It is found to be a strong function resembling a quadratic, which is precisely what we would anticipate from theoretical considerations.

(4) The amide I region of the infrared spectrum may also be interpreted in terms of "free" and hydrogen-bonded groups. Our results, obtained in the amide I region of the spectrum as a function of temperature, are in excellent agreement with those obtained in the N-H stretching region.

(5) Spectral observations in the amide II and V regions are consistent with a reduction of the strength of the hydrogen-bonded groups with temperature.

(6) Finally, it is generally believed that with increasing temperature of amorphous polyamides, including crystalline polyamides above their melting point, the fraction of "free" N-H groups also increases significantly. In fact, in a recent paper it is reported that in nylon 6,6 the fraction of hydrogen-bonded N-H groups is only 26% at 270 °C and 16% at 300 °C.¹⁴ The results of this study strongly suggest that we must revise these concepts, however simple and satisfying they may be. Our experimental observations show that the fraction of "free" N-H groups does not vary significantly over a temperature range between 30 and 210 °C. Rather, the predominant effect with increasing temperature is the reduction of the average strength of the hydrogen-bonded N-H groups.

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