Macromolecules **1986**, *19*, 699–705

(26) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1977; p 629.

(27) Graessley, W. *Polymer* **1980**, *21*, 258.

(28) Kajiura, H.; Oshiyana, Y.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1978**, *11*, 894.

(29) Isono, Y.; Fujimoto, T.; Kajiura, H.; Nagasawa, M. *Polym. J. (Tokyo)* **1980**, *12*, 363.

(30) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1002.

(31) Lange, N. A., Forker, G. M., Eds. "Lange's Handbook of Chemistry", 10th ed.; McGraw-Hill: New York, 1967; p 1403.

Hydrogen Bonding in Polymers. 2. Infrared Temperature Studies of Nylon 11

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

Polymer Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802.

Received July 30, 1985

ABSTRACT: Fourier transform infrared temperature studies of a semicrystalline polyamide, nylon 11, are presented. From previous studies of an amorphous nylon, we demonstrated that the absorptivity coefficient of the hydrogen bonded N–H stretching mode was a very strong function of the strength of the hydrogen bond. Accordingly, area changes in the N–H stretching envelope as a function of temperature were not solely the result of hydrogen bonded N–H groups transforming the "free" groups. This result is also applicable to semicrystalline nylons. As a result, significant errors exist in the previously reported thermodynamic parameters obtained from infrared studies. Emphasis has been placed in this study on the N–H stretching and amide I modes of nylon 11. The two regions yield different information. The hydrogen bonded N–H stretching frequency does not exhibit separable features attributable to ordered and disordered hydrogen bonded conformations but rather reflects the overall distribution of hydrogen bonded strengths. In contrast, the amide I mode is conformationally sensitive through dipole–dipole interactions, and separate bands can be identified that are assigned to ordered and disordered hydrogen bonded conformations. Finally, in both regions of the spectrum, bands attributable to "free" (non-hydrogen bonded) amide groups are discernable.

Introduction

In a recent paper[1] we reported the results of an infrared temperature study of an amorphous polyamide. There were several significant conclusions arising from this work. Changes occurring in the N–H stretching region of the spectrum with temperature had been misinterpreted in the past. The strong dependence of the absorption coefficient with the strength of the intermolecular hydrogen bond had not been fully appreciated. This led to an overestimation of the fraction of hydrogen bonded amide groups that transform to "free" groups upon increasing the temperature. Furthermore, subsequent estimations of thermodynamic parameters associated with hydrogn bond dissociation in polyamides and analogous materials were subject to unacceptable error. Our interpretation of the N–H stretching region of the spectrum of the amorphous nylon was supported by results obtained in the amide I, II, and V regions.

The above studies were performed deliberately on an amorphous polyamide to reduce the complexity due to crystallinity. However, most nylons are semicrystalline in the condensed phase at ambient temperatures. Furthermore, we considered it essential to establish whether the effects observed in the amorphous nylon also occur in the semicrystalline materials. Nylon 11 was chosen for this study because of its relatively low melting point, which reduces the problems of degradation at elevated temperatures.

Schroeder and Cooper[2] have previously employed infrared spectroscopy to study nylon 11 and a series of semicrystalline nylons. The main thrust of their paper concerned the use of infrared spectroscopy to obtain thermodynamic parameters associated with hydrogen bond dissociation. More recently, Garcia and Starkweather[3] used a comparable approach for nylon 6,6. In both cases estimations of the enthalpy of dissociation of hydrogen bonds appear high (8–12 and about 14 kcal mol^{-1} N–H, respectively). The question arises "are these values high because of a misinterpretation of the infrared spectral changes occurring with temperature?". Our primary concern in this paper is to reexamine the infrared spectrum of semicrystalline nylons.

Experimental Section

Poly(aminoundecanoic acid), or more commonly, nylon 11, was kindly supplied by the E.I. Du Pont de Nemours Co. The polymer exhibits a glass transition temperature of approximately 45 °C and a crystalline melting point of 196 °C, as determined by differential scanning calorimetry.

Samples for infrared analysis were prepared by casting films from a 1% (w/v) solution of the polymer in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) onto potassium bromide windows at room temperature. Following evaporation of the majority of the solvent, the samples were placed in a vacuum oven at 100 °C for 12 h to remove residual solvent and moisture and then immediately transferred to the temperature cell contained in the spectrometer.

Spectra were acquired on a Digilab Model FTS-15E Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal-averaged, and the spectra were stored on a magnetic disc 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 obeyed.[4] Spectra recorded at elevated temperatures were obtained with a Micristar heat controller. This device has a reported accuracy of ± 0.1 °C.

Thermal analysis was performed on a nylon 11 sample prepared under identical conditions with that used for the infrared studies. A Perkin-Elmer differential scanning calorimeter (DSC-2) coupled with a Perkin-Elmer computerized data station was employed.

0024-9297/86/2219-0699$01.50/0 © 1986 American Chemical Society

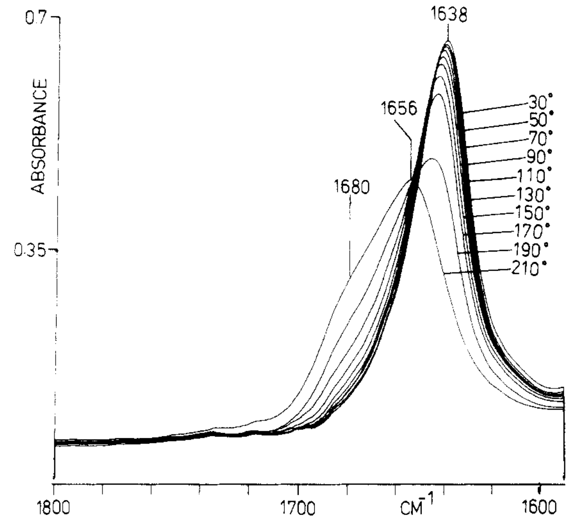

Figure 1. FTIR spectra of the amide I region of nylon 11 recorded from 30 to 210 °C in the range 1590–1800 cm^{-1}.

A heating rate of 20 K/min was used, with a sample size of approximately 10 mg. The reported glass transition temperature refers to the midpoint of the heat capacity change, while the melting point was taken as the peak maximum of the endotherm.

Results and Discussion

In common with our recently published infrared temperature study of a completely amorphous polyamide,[1] we will concentrate our attention on two major regions of the infrared spectrum of a semicrystalline polyamide, nylon 11. These are the N–H stretching region from 3100 to 3500 cm^{-1} and the amide I region from 1600 to 1700 cm^{-1}. For reasons that will become clear later, however, it is more convenient to reverse the order and discuss the amide I mode first.

Amide I Mode. The infrared spectra in the amide I region of nylon 11, recorded as a function of increasing temperature, are displayed in Figure 1. It is important to emphasize that the spectra have not been arbitrarily scale-expanded but are shown on an absolute absorbance scale. The amide I mode of nylon 11 at 30 °C is characterized by a relatively sharp band skewed to the high-frequency side and centered at about 1638 cm^{-1}. Upon a temperature increase in a stepwise fashion to 170 °C, the amide I mode shifts systematically to higher frequency and appears to decrease in absolute intensity. Concurrently, there is increasing evidence of spectral contributions at approximately 1650 and 1680 cm^{-1}. At 190 °C, before the semicrystalline nylon has completely melted, one can discern three contributions to the amide I mode. This is confirmed by second-derivative spectroscopy (see Figure 2). Increasing the temperature further to 210 °C, which is above the crystalline melting point of nylon 11, yields a spectrum in the amide I region that is very similar in form to that peviously published for a completely amorphous nylon.[1] Only two obvious components to the amide I mode are seen at about 1656 and 1680 cm^{-1}.

In marked contrast to the conformationally insensitive N–H stretching vibration, the amide I mode is sensitive to local order. However, this conformational sensitivity does not arise through mechanical coupling to the main chain but through differences in the pattern of hydrogen bonds that determine the relative arrangement of C=O groups and hence the degree of dipole–dipole interactions. More on this later. In the infrared spectrum of a semicrystalline nylon sample we might therefore anticipate distinct spectral features in the amide I region attributable to hydrogen bonded carbonyl groups in ordered ("crystalline") domains, in addition to those hydrogen bonded carbonyl groups associated with disordered (amorphous) conformations and non-hydrogen bonded (free) carbonyl groups. From the above description of the experimental results, it does appear that there are three distinct contributions to the amide I region of the semicrystalline nylon 11, and to extract additional information it is necessary to resolve the amide I mode into its constituents.

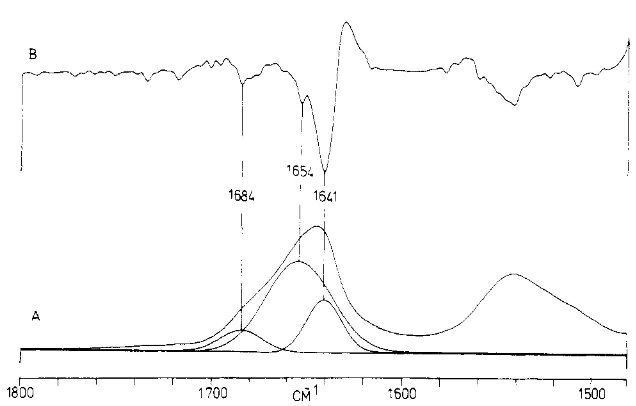

Figure 2. FTIR spectra of the amide I region of nylon 11 recorded at 190 °C in the range 1480–1800 °C: (A) absorbance spectrum; (B) second-derivative spectrum.

One is always reluctant to resort to curve fitting. Even if the procedure performed intelligently, there are skeptics (including the authors!) who will never be convinced. It is not an exaggeration to state that if one does not have prior knowledge of the band shape, the number, position and breadth of the bands, the position of the base line, etc., one can arrive at almost any desired solution. In fact, our first attempts at least-squares curve fitting the amide I region of nylon 11 to three bands yielded an excellent fit, but the results were physically meaningless. Because of this experience, we have taken a somewhat different but, in our view, more logical approach to the problem of curve fitting. Rather than permitting the computer to obtain a best fit by changing a multitude of variables, we have severely restricted the options by making a number of justifiable assumptions:

1. The amide I region of the semicrystalline nylon will be assumed to be composed of a maximum of three bands attributable to hydrogen bonded carbonyl groups in ordered domains, hydrogen bonded carbonyl groups in disordered conformations, and "free" carbonyl groups. Second-derivative spectroscopy indicates the presence of three bands in the transition zone before complete melting, and the trends observed in the spectra as a function of temperature are consistent with systematic changes in the intensity and position of three major contributions.

2. The frequency and breadth of the bands attributed to the disordered hydrogen bonded and "free" carbonyl groups and their dependence upon temperature will be assumed to follow the same trend as that observed for the analogous bands in the totally amorphous nylon.[1] In other words, as we know the frequency and the breadth of the disordered hydrogen bonded and "free" bands from the spectra recorded above the melting point of nylon 11, we can make a reasonable initial estimation of the frquency and breadth of these bands in the spectrum of the semicrystalline nylon at a lower temperature from the previous studies of the amorphous nylon. For example, in our previous study on the amorphous nylon, we determined that the relatively broad ($W_{1/2}$ = 37 ± 2 cm^{-1}) disordered hydrogen bonded amide I band shifted in frequency from 1640 to 1646 cm^{-1} upon raising the temperature from 30

Table I
Curve-Fitting Results of the Amide I Region of Nylon 11[a]

	hydrogen bonded										
	ordered			disordered			"free"				
temp, °C	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_o	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_d	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_f	A_t	A_o/A_t
30	1636	17	30.0	1645	34	55.0	1679	26	4.0	89.0	0.34
50	1637	18	30.2	1646	35	56.5	1680	28	4.9	91.6	0.33
70	1637	18	29.8	1646	35	57.5	1681	28	5.0	92.3	0.32
90	1638	18	29.9	1647	36	58.6	1682	27	5.4	93.9	0.32
110	1638	18	28.4	1647	38	60.6	1683	26	5.1	94.1	0.30
130	1639	18	26.7	1648	40	63.2	1684	25	5.0	94.9	0.28
150	1640	18	25.6	1649	41	64.8	1684	25	5.3	95.7	0.27
170	1641	18	23.2	1650	42	66.5	1684	25	5.8	95.5	0.24
180	1641	18	21.9	1651	42	66.4	1685	24	6.3	94.6	0.23
190	1641	21	19.8	1654	41	64.8	1684	26	9.6	94.2	0.21
200				1653	39	73.8	1684	26	17.1	90.9	
210				1653	38	72.7	1683	27	19.3	92.0	
220				1654	38	72.2	1683	27	19.8	92.0	

[a] A_o = area (arbitrary units) of band attributed to ordered domains, A_d = area (arbitrary units) of band attributed to amorphous conformations, A_f = area (arbitrary units) of band attributed to "free" carbonyl groups, and A_t = total area = $A_o + A_d + A_f$. $W_{1/2}$ = width at half-height of Gausian curve.

to 210 °C. Similarly, the relatively narrow ($W_{1/2} \approx 21$ cm^{-1}) "free" amide I band shifted in frequency from 1668 to 1672 cm^{-1} over the same temperature range. A similar temperature dependence for these two bands in the semicrystalline nylon was anticipated.

3. The frequency of the band attributed to the ordered hydrogen bonded amide I band is readily established from a second-derivative plot of the spectra obtained below 190 °C. From experience, we know that this band will be considerably narrower than the corresponding disordered amide I band. An initial estimation of the $W_{1/2}$ of 20 cm^{-1} (approximately half that of the disordered band) was employed.

4. The band shape was assumed to be Gaussian. Previous studies of the amorphous nylon indicated that the shape of the two bands in the amide I region were best approximated by Gaussian band shapes.[1] Furthermore, in the initial attempts at curve fitting the amide I region by allowing the computer to vary band shape, an esssentially pure Gaussian band shape was consistently determined by a least-squares fit.

5. A linear base line was assumed from 2000 to 850 cm^{-1}, where there are no significant underlying absorbances. Although the "correct" base line is rather subjective, the perils of a wrongly chosen base line cannot be overstated.

6. Curve fitting was limited to the spectral data available from between 1626 and 1700 cm^{-1}. This circumvents the problems of overlapping contributions in the wings of the amide I region.

In summary, each spectrum recorded at the different temperatures was resolved into three components (two above the crystalline melting point). The base line and the band shape (Gaussian) was fixed. Initial frequencies, band widths, and intensities were estimated according to the assumptions detailed above. A least-squares iterative procedure was then employed to obtain a best fit. Representative examples are shown in Figure 3. At 220 °C, above the crystalline melting point, only two bands are necessary to obtain a satisfactory fitting of the experimental data. This is entirely consistent with the results obtained previously for the amorphous nylon.[1] The disordered hydrogen bonded amide I band of nylon 11, which occurs at 1654 cm^{-1} at 220 °C, has a width at half-height almost identical with that of the amorphous nylon studied previously. The "free" band at 1684 cm^{-1} is significantly narrower than this but again consistent with the results obtained for the amorphous nylon. at 190 °C, in the transition region, three bands are necessary to satisfactorily fit the data. In addition to the two bands at approximately 1654 and 1684 cm^{-1}, a third at about 1641 cm^{-1} is required. This is pleasingly consistent with the second-derivative data (see Figure 2). At 30 °C, three bands are again necessary. However, the relative intensities have changed and there have been some subtle but important frequency shifts.

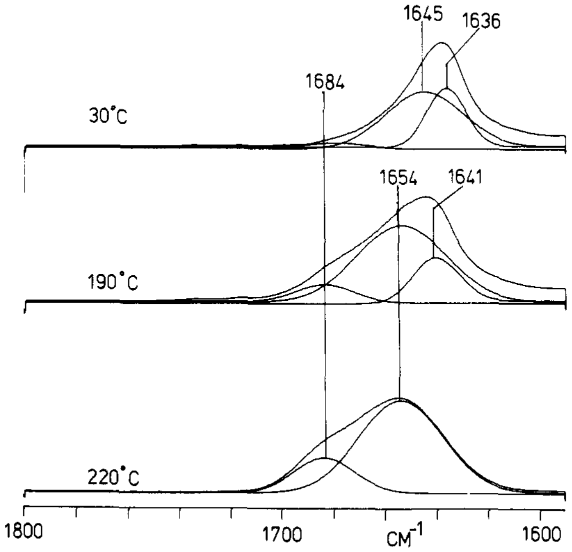

Figure 3. Least-squares curve fitting results of the amide I region of nylon 11 from 1590 to 1800 cm^{-1} at 30, 190, and 220 °C.

The detailed results of the curve fitting of the amide I region throughout the temperature range 30–220 °C are given in Table I. These results exceeded our expectations and increased our confidence in the curve-fitting procedure. The infrared band attributed to the ordered conformation is relatively narrow ($W_{1/2} \simeq 18$ cm^{-1}), is observed at 1636 cm^{-1}, and gradually shifts to 1641 cm^{-1} over the temperature range 30–190 °C. This is precisely the relative breadth and temperature dependence we expected. Above 190 °C, above the crystalline melting point of nylon 11, the computer rejects any contribution close to this frequency. The disordered hydrogen bonded amide I band starts at 1645 cm^{-1} at 30 °C and systematically shifts to 1654 cm^{-1} at 220 °C. It is about twice as broad as the band attributed to the ordered amide I mode and almost identical in breadth with the analogous band in the completely amorphous nylon.[1] The "free" band similarly shifts from 1679 to 1683 cm^{-1} over the same temperature range. This

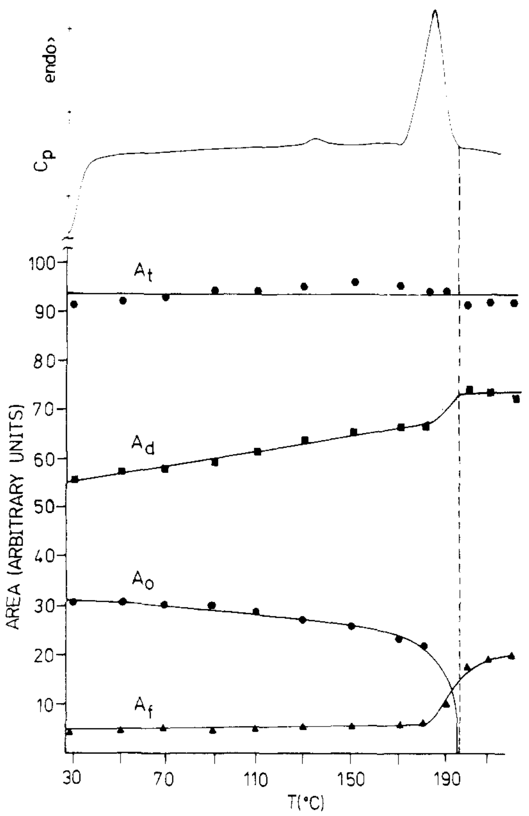

Figure 4. Plots of the areas of the "free" (A_f), ordered (A_o), and disordered (A_d) hydrogen bonded and total (A_t) carbonyl groups obtained from the amide I region as a function of temperature. Also included is a DSC thermogram of nylon 11.

band is inherently narrower than the disordered hydrogen bonded band, again an expected result. The areas of the bands contributing to the amide I mode are also given in Table I. It should be emphasized that as the curve-fitting results were obtained on the same sample in the infrared spectrometer, the areas represent a quantitative but relative measure of the amount of the different species at the various temperatures. There is, however, the question of the value of the absorption coefficients of the three different bands and, as we have emphasized previously,[1] how they change with the strength of the hydrogen bond. Unlike the N–H stretching region, however, the total area of the amide I region (A_t) does not vary appreciably with temperature (see Table I): approximately 7% over the entire temperature range 30–220 °C. Accordingly, for the purposes of this study we will assume that large errors will not be introduced by assuming that the absorptivity coefficients are the same and that there is not a strong dependence with the strength of the hydrogen bond.

A graph of the respective areas of the three components to the amide I band as a function of temperature is displayed in Figure 4. Also included is the total area of the amide I region and a thermogram of a nylon 11 sample prepared under the same conditions as that used for the infrared studies. The area of the ordered band (A_o) steadily decreases to about two-thirds of its original value over a range 30–190 °C, whereupon a discontinuity is observed as it vanishes at higher temperatures. This correlates beautifully with the thermogram of nylon 11, which exhibits a melting transition close to 200 °C. Although in the vast majority of cases infrared spectroscopy cannot readily be used to obtain an absolute measure of the degree of crystallinity, the ratio of the area of the ordered amide I band to the total area of the amide I envelope should correlate with crystallinity. From the DSC thermogram and with a value for $\Delta H_f°$ of 54 cal/g,[5] an estimation of 37–40% crystallinity was obtained. This value is similar to that obtained by Garcia and Starkweather[3] for nylon 6,6 prepared from HFIP using comparable experimental conditions. Our result of 34% for the fraction of ordered hydrogen bonded amide groups is therefore quite satisfying.

The area of the disordered hydrogen bonded amide I band, on the other hand, increases in a fashion that parallels the corresponding decrease in the ordered band between 30 and 190 °C. Thus, it appears perfectly reasonable to conclude that upon increasing the temperature to 190 °C, a reorganization of the semicrystalline nylon occurs that leads to a reduction in the overall degree of crystallinity of the sample and a corresponding increase in the amount of amorphous material. Above 190 °C, complete melting occurs and there is an obvious jump in the amount of amorphous material.

The character of the "free" amide I band with temperature is interesting. A slight and gradual increase in the concentration of the "free" groups is observed from 30 to 180 °C. (It should be noted that these results are subject to the greatest error, but the trend does appear real.) Above 180 °C, there is a significant increase in the amount of "free" groups, approximately fourfold at 220 °C. Again the jump occurs at the melting point where the material becomes completely amorphous. A rough estimate of the "free" (non-hydrogen bonded) carbonyl groups can be obtained by dividing A_f by the total area A_t. This would suggest that 4.5% and 22.5% of the amide carbonyl groups are not hydrogen bonded at temperatures of 30 and 220 °C, respectively.

N–H Stretching Mode. In our recent infrared temperature studies of a completely amorphous polyamide[1] we observed that the broad disordered hydrogen bonded N–H stretching band shifted to higher frequency (3310–3332 cm^{-1}), essentially remained at a constant breadth ($W_{1/2} = 130 \pm 2$ cm^{-1}), but decreased in area by approximately 35% as the temperature was raised from 30 to 210 °C. Additionally, it was demonstrated that the large reduction in area with temperature could not be explained solely by a transformation of disordered hydrogen bonded N–H groups to "free" (non-hydrogen bonded groups). Rather, we proposed that area reduction was primarily caused by a large reduction in the absorptivity coefficient as the *average* strength of the hydrogen bonds decreases with temperature. This conclusion calls into question the previous quantitative estimations of the concentration of "free" and hydrogen bonded N–H groups in polyamides and polyurethanes as a function of temperature, which were based upon changes in the total area of the N–H stretching envelope. Naturally, it follows that subsequent calculations of thermodynamic parameters associated with hydrogen bonding must also be questioned. Our previous studies were deliverately performed on an amorphous polyamide to eliminate the additional complexity of polymer crystallinity in the infrared spectrum. Most useful nylons are semicrystalline, however, and it was deemed important to verify that the same effects occur in these materials.

Figure 5 shows infrared spectra in the range 3150–3500 cm^{-1} of nylon 11 recorded as a function of increasing temperature. Again we must emphasize that the spectra are plotted on an absolute absorbance scale and consequently the changes in frequency, breadth, and relative area can be directly visualized. The spectrum at 30 °C is characterized by a relatively narrow band (but still very broad in comparison to other bands in the spectrum) centered

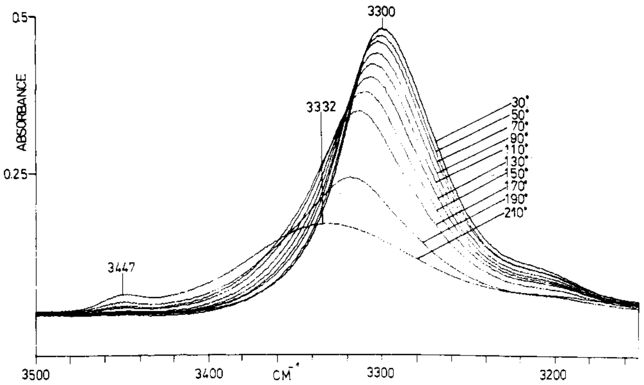

Figure 5. FTIR spectra of the N–H stretching region of nylon 11 recorded from 30 to 210 °C in the range 3150–3500 cm^{-1}.

Table II
Hydrogen Bonded N–H Stretching Mode of Nylon 11

temp, °C	freq, cm^{-1}	$W_{1/2}$, cm^{-1}	normalized area[a]
30	3299	52	1.000
50	3300	56	0.997
70	3302	56	0.991
90	3303	58	0.974
110	3305	60	0.959
130	3308	65	0.937
150	3310	71	0.900
170	3313	72	0.854
180	3315	74	
190	3318	84	0.744
200	3332	112	
210	3332	112	0.701
220	3332	112	

[a] Area at 30 °C = 1.00.

at 3300 cm^{-1}. A more fascinating observation, however, is that the band is to all extents and purposes symmetric. There is a small contribution from a two-phonon band at approximately 3220 cm^{-1}, which may be easily removed by curve fitting. This leaves the primary band, which may be approximated very well by a single Gaussian curve with a width at half-height of 52 cm^{-1}. This observation causes one to pause. If the nylon sample is semicrystalline, with a degree of crystallinity of about 35%, why does the hydrogen bonded N–H stretching mode not display obvious features attributable to ordered ("crystalline") and disordered (amorphous) hydrogen bonded N–H groups? In other words, there is no obvious evidence that the sample consists of two phases; that is, amorphous and crystalline contributions. We will return to this interesting subject later in the text.

Returning to Figure 5: as the temperature is increased from 30 to 170 °C the hydrogen bonded N–H stretching band shifts in frequency from 3299 to 3313 cm^{-1} and there is a steady increase in the breadth of the band (see Table II). The total area of the band also decreases with temperature but not as dramatically as it might appear at first glance from studying Figure 5. Some of the reduction in the peak height is compensated for by the increase in breadth. At 190 °C, in the transition zone before complete melting, a further shift to higher frequency and a greater increase in the breadth of the band is noted, together with a larger decrement in area. Above 190 °C, which is above the crystalline melting point, the band shifts to 3332 cm^{-1} and dramatically broadens, and there is a further reduction in area.

Figure 6 compares the temperature dependence of the normalized area of the hydrogen bonded N–H stretching band for nylon 11 and the completely amorphous polyamide studied previously.[1] In the amorphous nylon we

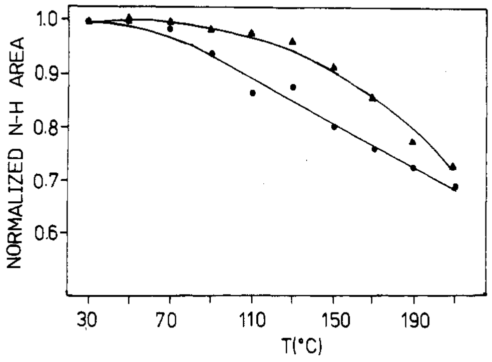

Figure 6. Plot of the normalized area of the hydrogen bonded N–H stretching band of (▲) nylon 11 and (●) amorphous nylon.

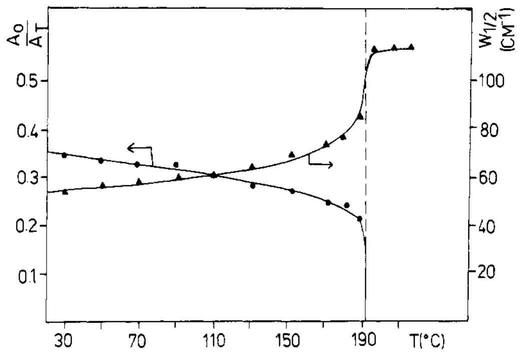

Figure 7. Comparison of the temperature dependence of the width at half-height of the hydrogen bonded N–H stretching band (▲) to the fraction of ordered hydrogen bonded carbonyl groups obtained from the amide I region (●) of nylon 11.

observed as steady decrease in the area with temperature (to approximately 65% of the original area over a temperature range 30–210 °C), which we attributed predominantly to a change in the absorption coefficient as the overall strength of the hydrogen bonds diminished. The situation in the case of the semicrystalline nylon 11 is more complicated. From 30 to 130 °C there is a small decrease in the overall area of the hydrogen bonded N–H band followed by much larger reductions as the temperature is increased to 210 °C. Significantly, at 210 °C, when the semicrystalline nylon has completely melted, the normalized area is approaching the value seen for the completely amorphous nylon. Before we attempt to explain the above behavior one further observation is relevant.

Figure 7 shows a plot of the width at half-height ($W_{1/2}$) of the hydrogens bonded N–H stretching band with temperature. As detailed in Table II, $W_{1/2}$ increases from 52 to 84 cm^{-1} in a nonlinear fashion as the temperature is raised from 30 to 190 °C. Above 190 °C, above the crystalline melting point, a sudden jump in $W_{1/2}$ occurs, after which the band appears to remain at a constant breadth (consistent with the results described for the completely amorphous polyamide[1]). Also shown in Figure 7 is a plot of the corresponding temperature dependence of the fraction of hydrogen bonded carbonyl groups in ordered domains, determined from the amide I region of the spectrum (see Table I). The two curves are mirror images of each other up to the crystalline melting point; an observation that we do not think is fortuitous. The implication of this result is that the breadth of the hydrogen bonded N–H stretching mode correlates directly with the degree of order in the nylon sample.

Intuitively, the above results can be rationalized rather easily; the theoretical spectroscopic justification, however, is not so straightforward and will be considered in depth later in the text. To reiterate, the hydrogen bonded N–H stretching mode of the semi crystalline nylon at 30 °C is symmetric, centered at 3300 cm^{-1}, and has a $W_{1/2}$ of 52 cm^{-1}. If this nylon was completely amorphous at this temperature, we would anticipate, based upon our previous study,[1] a band centered at about 3310 cm^{-1} with a $W_{1/2}$ of approximately 112 cm^{-1}. To a first approximation and ignoring the strong dependence of the absorption coefficient with the strength of the hydrogen bond which may distort the position of peak maximum, we see that the frequency of the hydrogen bonded N–H stretching mode reflects the *average* strength of the hydrogen bonded N–H groups. The breadth of the band, on the other hand, is mainly a reflection of the distribution of hydrogen bonded groups at different distances and geometries. In the semicrystalline state the density of the nylon sample is significantly greater than that of a truly amorphous sample of the same polymer at the same temperature. The average interchain distance is therefore smaller in the semicrystalline material, which results in an increase in the average strength of the hydrogen bonds. In addition, the distribution of the hydrogen bonded species would be expected to be narrower in the semicrystalline state because the amorphous regions are restrained by the surrounding crystalline regions and have a density higher than the corresponding totally mobile amorphous material. It is important to emphasize that unlike the C=O stretching region, where there is a dependence upon conformation that is a result of dipole–dipole interactions, we do not see separate N–H stretching modes characteristic of crystalline and amorphous (hydrogen bonded) phases. Instead, one band characteristic of the distribution of hydrogen bonds present is observed.

Within the temperature range 30–130 °C, increasing the temperature results in a small increase in frequency, a modest increase in the breadth, and a slight decrease in the area of the hydrogen bonded N–H stretching mode (see Table II). This is consistent with only a slight change in the overall degree of crystallinity and an increase in the average interchain distance due to thermal expansion. The area loss is presumably due primarily to absorption coefficient changes as the average strength of the hydrogen bonded groups diminishes somewhat. Between 130 °C and the melting point there are more pronounced frequency shifts, band broadenings, and area losses (see Table II). In this temperature region reorganization and annealing of the crystalline domains occur together with a decrease in the overall degree of molecular order. Finally, above the melting point there are no crystallites to restrain the amorphous material, the specific volume increases, permitting a greater average interchain distance between the hydrogen bonded species, and there is extensive mobility of the polymer chains. Thus we observe a very broad band centered at a significantly higher frequency, which is consistent with a decrease in the average strength of the hydrogen bonds and an increase in the breadth of the distribution. On top of this, the area of the band decreases because of a decrease in the absorptivity coefficient as the strength of the hydrogen bond diminishes and a portion of the hydrogen bonded groups are transformed to "free" groups.

Concomitant with the changes occurring to the hydrogen bonded N–H band over the temperature range 30–220 °C, there are small but significant increases in the "free" or non-hydrogen bonded N–H band observed at 3447 cm^{-1}. There are several points that should be discussed. At temperatures of 130 °C and below there is no evidence of any "free" N–H groups, or more precisely, if there are "free" N–H groups present the concentration is below the detection limit. From 130 to 210 °C, there is a steadily increasing contribution from the "free" N–H stretching band. As we pointed out in our previous paper, however, some of the apparent increase in the absorbance at 3447 cm^{-1} is caused by the increasing overlap of the broad hydrogen bonded N–H band as it shifts to higher frequency with temperature.[1] In any event, using the curve-fitting procedure described in this previous paper, we estimate that the "free" N–H stretching band at 3447 cm^{-1} contributes approximately 7% to the total area of the N–H region at 220 °C. The next question that must be addressed is "do these results jibe with those obtained in the amide I region?". It may be recalled (see Table I) that below 130 °C the concentration of "free" carbonyl groups was estimated to be about 5%, while at 220 °C the value was 21.5%. As a "rule of thumb" it has been established from low molecular weight model compound studies that the difference in the absorptivity coefficients of the "free" and hydrogen bonded N–H modes is about 1:3.2.[6] This is obviously oversimplified, as we emphasize in our previous paper.[1] Nevertheless, if we assume that there are no significant differences in the absorption coefficients of the bands in the amide I region and thus the results given in Table I represent a reasonable estimate of the concentration of "free" carbonyl groups, then as there is a one-to-one correspondence in the fraction of "free" carbonyl and N–H groups, it follows that less than 2% of the area in the N–H stretching region is equivalent to the 5% "free" carbonyl groups determined from the amide I region. This would indeed be difficult to detect. On the other hand, when 21.5% "free" carbonyl groups are present as estimated at 210 °C, this would translate to a contribution to the total area in the N–H stretching region of about 6–7%. This is precisely what we observe. Before we get too enthusiastic, however, it should be remembered that the absorption coefficient of the hydrogen bonded N–H stretching mode is changing significantly with the strength of the hydrogen bonds, which complicates a simple fractional area determination. In summary, given the inherent problems mentioned above, together with the limitations of detection and curve fitting, we do not believe the N–H stretching region of the infrared spectrum of polyamides can be utilized to obtain meaningful quantitative measurements of the concentration of "free" and hydrogen bonded N–H groups.

Theoretical Consideration. The above results directly affect how we think about the structure of nylons and amide group normal modes. Our conceptual model of a semicrystalline polymer involves a sharp distinction between ordered and amorphous phases. Thus, we would anticipate that in the N–H stretching region of the spectrum we would observe two characteristic sets of bands. The first would consist of a (relatively) sharp band characteristic of the ordered phase. Although dipole–dipole interactions apparently cause a splitting of the amide I mode, the N–H stretching band appears insensitive to such effects. The second set of bands would consist of a broad band characteristic of the distribution of hydrogen bonded states found in the amorphous phase at a given temperature in equilibrium with a much weaker but sharper band characteristic of free N–H groups. This is not what we observe. Instead, it is as if someone had resurrected the paracrystalline model, where the spectrum would reflect a single, partially ordered state with a corresponding single, broad distribution of hydrogen bond strengths. Such a model does not conform to our observations of the amide I mode, however, so there remains a dichotomy between the two regions that has to be explained.

A reasonable interpretation depends upon an understanding of the differing sensitivities of the two modes. Although linked to the amide carbonyl group by a hydrogen bond, the N–H stretching mode is more or less conformationally insensitive. Normal mode calculations indicate that the dispersion curve is flat[7] (little or no mechanical coupling) and there is no evidence for appreciable dipole–dipole interactions. It is extraordinarily sensitive to hydrogen bonding, however. Accordingly, if we could isolate samples in a particular hydogen bonded state, each would be characterized by a single band corresponding to a single, flat dispersion curve. Each mode, corresponding to a specific hydrogen bonded state, would still be broadened by, for example, anharmonic effects but would be considerably sharper than the overall spectra presented in this study. In a sample with a distribution of states we then observe the effect of summing the contributions of an enormous number of such close lying dispersion curves, with the intensity of each mode weighted by concentration and an absorption coefficient.[1]

The amide I vibration is also a highly localized mode[7] but is sensitive to conformation through dipole–dipole interactions. If we consider a particular hydrogen bonded state, for example, in highly ordered crystalline domains, the amide I mode is characterized by an unperturbed frequency ν_0. It must be emphasized that ν_0 is not the frequency of the amide I mode corresponding to the non-hydrogen bonded ("free") carbonyl group (ν_f). Actually, the frequency difference between ν_f and ν_0 is a measure of the strength of the hydrogen bond. The unperturbed frequency, ν_0, is now in turn perturbed by dipole–dipole interactions so that the frequencies of points on the dispersion curve, ν, are given by

$$\nu = \nu_0 + D \cos \phi$$

where ϕ is the phase angle between vibrations in coupled groups. Because amide groups are related by translational symmetry in nylon 11, only modes at the edge of the lattice band, corresponding to $\phi = 0$, should be observed. Note that this mode is shifted from the unperturbed hydrogen bonded frequency, ν_0, by an amount that depends upon the size of the interaction term, D. Unlike the N–H stretching region, the effect of disorder would be to then produce a frequency shift that depends upon the local arrangement of amide groups in the amorphous state as well as the distribution of hydrogen bonded strengths. If the carbonyl groups associated with the amorphous phase (hydrogen bonded and "free" non-hydrogen bonded groups) are surrounded by a random arrangement of their fellows, then the interaction term D would average out to zero. We would then see a broad band characteristic of the distribution of hydrogen bonded states present.

Accordingly, the effect of coupling in the amide I region is to produce spectroscopically distinguishable states that depend upon a dipole–dipole interaction term in addition to the effect of hydrogen bonding. Instead of a single broad band characteristic of a convolution of factors, we then observe a band characteristic of ordered hydrogen bonded domains that is frequency-shifted and separable from a band that is largely independent of dipole–dipole interactions and represents the distribution of hydrogen bonded states in the amorphous phase.

Conclusions

There are several conclusions arising from this work that deserve to be underscored.

(I) The strong dependence of the absorptivity coefficient with hydrogen bond strength, which was inferred to be the primary cause of the reduction in area of the hydrogen bonded N–H stretching mode with increasing temperature in the amorphous nylon,[1] is also present in the semicrystalline nylon 11. Consequently, the thermodynamic parameters previously reported[2,3,8–11] for the dissociation of hydrogen bonds in nylons and analogous strongly self-associated polymers using infrared analysis should be viewed with healthy skepticism.

(II) The amide I region of the spectrum of semicrystalline nylons, although a highly localized mode, is sensitive to confromation through dipole–dipole interactins. Accordingly, infrared bands attributed to ordered and disordered hydrogen bonded amide groups are readily discerned. In addition, a band ascribed to "free" (non-hydrogen bonded) amide groups is also well separated and resolved. Quantitative measurements of the areas of these respective bands correlate well with the results obtained from thermal analysis.

(III) the N–H stretching region of the spectrum of semicrystalline nylons is also a highly localized mode but, in marked contrast to the amide I mode, appears insensitive to conformation. Therefore, there is no differentiation between hydrogen bonded N–H groups in ordered or disordered conformations. However, the breadth of the hydrogen bonded N–H mode reflects the distribution of hydrogen bonded strengths in the nylon.

Acknowledgment. We thank Drs. H. W. Starkweather, Jr., B. A. Varnell, and B. Epstein of the E. I. du Pont de Nemours Co. for their help in this study. We would also like to thank Professors I. R. Harrison and J. P. Runt for many helpful discussions. Finally, the financial support of the National Science Foundation, Polymers Program, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is greatly appreciated.

Registry No. Nylon 11 (SRU), 25035-04-5; poly(11-aminoundecanoic acid) (homopolymer), 25587-80-8.

References and Notes

(1) Skrovanek, D. J.; Howe, S. E.; Painter, P. C.; Coleman M. M. *Macromolecules* **1985**, *18*, 1676.

(2) Schroeder, L. R.; Cooper, S. L. *J. Appl. Phys.* **1976**, *47*, 4310.

(3) Garcia, D.; Starkweather H. W.; Jr. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 537.

(4) Coleman, M. M.; Painter, P. C. *J. Macromol. Sci., Rev. Macromol. Chem.* **1978**, *C16*, 197.

(5) Wunderlich, B. "Macromolecular Physics"; Academic Press: New York, 1973; Vol. 1.

(6) MacKnight, W. J.; Yang, M. *J. Polym. Sci., Polym. Symp.* **1973**, *No. 42*, 817.

(7) See, for example: Painter, P. C., Coleman, M. M.; Koenig, J. L. "The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials"; John Wiley: New York, 1982.

(8) Sung, C. S. P.; Schneider, N. S. *Macromolecules* **1975**, *8* (1), 68.

(9) Senich, G. A.; MacKnight, W. J. *Macromolecules* **1980**, *13*, 106.

(10) Trifan, D. S.; Terenzi, J. F. *J. Polym. Sci.* **1958**, *28* (117), 443.

(11) Srichatrapimuk, K. W.; Cooper, S. L. *J. Macromol. Sci., Phys.* **1978**, *B15* (2), 267.