

A "Chain Fold Band" in the Infrared Spectra of Nylon 6

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Synopsis

An absorption band found at 974 cm^{-1} in the infrared spectra of "amorphous" nylon 6 films has been assigned to CH_2 wagging or twisting vibrations in molecular chain folds. Annealing amorphous films in air at increasing temperatures up to 150°C has been shown to induce a steady increase in the intensity of the absorption band at 974 cm^{-1} . Annealing at higher temperatures resulted in a sharp decrease in intensity up to an annealing temperature of 210°C . This sharp decrease coincided with a sharp increase in the long period determined by low-angle x-ray diffraction studies. Drawing amorphous films has been shown to induce a decrease in the intensity of the band at 974 cm^{-1} . Polarized infrared investigations of amorphous drawn films revealed that the band at 974 cm^{-1} was strongly perpendicular in character. Treatment of amorphous films in water induced no frequency change in the band at 974 cm^{-1} .

INTRODUCTION

Infrared absorption bands have previously been assigned to molecular chain folds in nylon 6.6,^{1,2} but no one has assigned similar bands in nylon 6. An absorption band near 974 cm^{-1} in the infrared spectra of nylon 6 has been variously assigned by other workers.³⁻⁶ However, using a recently developed technique for the preparation of thin "amorphous" films of thermoplastic polymers,⁷ previously undetected molecular rearrangements were observed in nylon 6.

Materials. Pellets of nylon 6 free from additives were obtained from Courtaulds Ltd. In order to carry out the investigation, these pellets were converted into amorphous films approximately $40\text{ }\mu\text{m}$ thick using the technique described in a previous paper.⁷

Instrumentation. Infrared spectra were recorded on a Grubb Parsons Spectromaster II Double Beam Spectrophotometer. In order to obtain polarized infrared radiation, a wire grid polarizer of aluminium on a thallium-iodobromide substrate was temporarily incorporated into the infrared spectrophotometer. Infrared derivative spectra were recorded by means of an electronic differentiator,^{8,9} which was coupled to the infrared spectrophotometer.

EXPERIMENTAL

All amorphous films were stored in a desiccator at room temperature prior to treatment or investigation. Sample films were treated in various ways.

Annealing

Infrared Studies. Amorphous films were annealed free from constraint in air up to a temperature of 210°C and then allowed to cool in air at room temperature. The infrared spectra of these films, together with the spectrum of an amorphous film, were recorded in the spectral region 1150–800 cm^{-1} (Fig. 1). In addition, graphs were plotted of absorption band intensity (absorbance) against annealing temperature for each sample film (Fig. 2).

The intensities of all absorption bands in this study have been measured by taking the difference between the intensities which correspond to a band maximum on the one hand and a band minimum or base line on the other.

Low Angle X-Ray Diffraction Studies. Low angle x-ray diffraction photographs were taken of some of the annealed samples, and from these

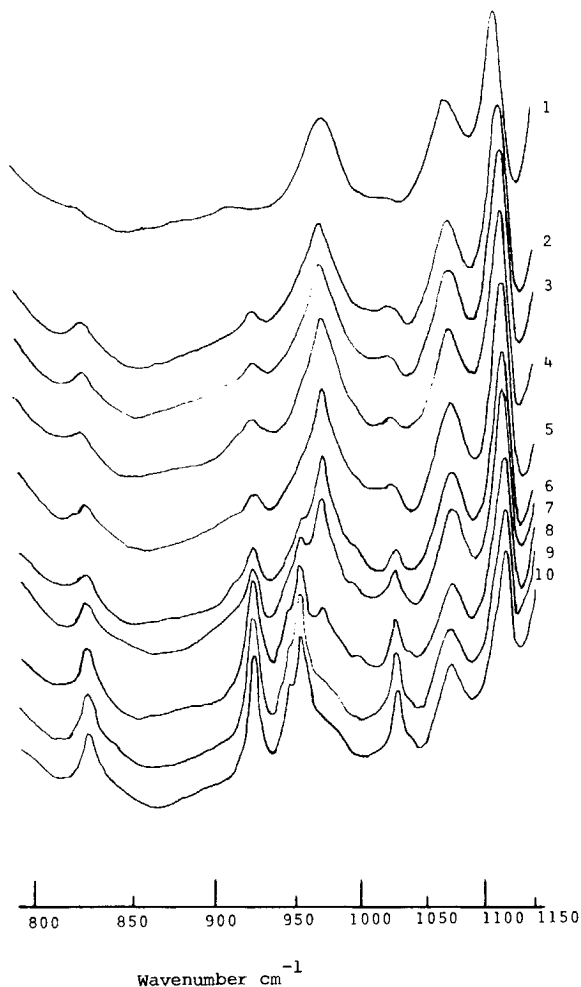


Fig. 1. Infrared absorption spectra of nylon 6 films. (1) amorphous (2) amorphous annealed in air at 50°C; (3) amorphous annealed in air at 100°C; (4) amorphous annealed in air at 125°C; (5) amorphous annealed in air at 150°C; (6) amorphous annealed in air at 170°C; (7) amorphous annealed in air at 180°C; (8) amorphous annealed in air at 190°C; (9) amorphous annealed in air at 200°C; (10) amorphous annealed in air at 210°C.

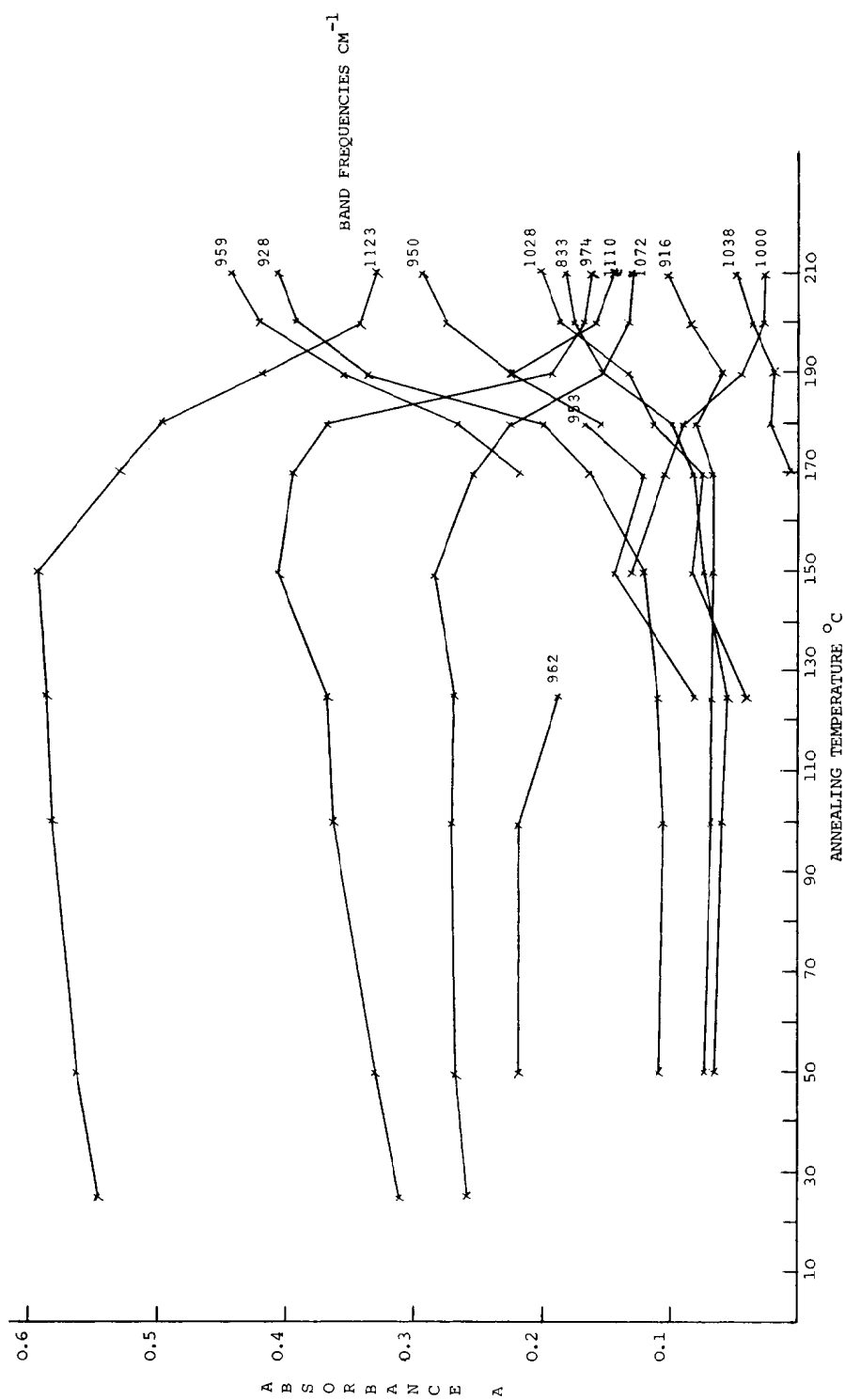


Fig. 2. Absorption band intensity changes in the region 1150-800 cm^{-1} following the annealing in air of amorphous nylon 6 films at various temperatures.

TABLE I
Variations in Long Period Spacings with Increase in Annealing Temperature for
Nylon 6 Films

Annealing temp (°C)	Long period spring (Å)
125	55
150	53
170	56
180	62
190	81
200	91
210	98

photographs long period spacings were calculated. These spacings together with their corresponding annealing temperatures are listed in Table I. Sample films annealed at temperatures below 125°C were insufficiently crystalline to produce a characteristic low angle diffraction pattern.

All the annealed samples were annealed for 30 min. After this time no further changes in the infrared spectra or x-ray diffraction patterns occurred at any particular temperature. In addition, no changes in sample thickness were detected following annealing.

Drawing

Infrared Studies. An amorphous film of nylon 6 was drawn to a draw ratio of 3, and the infrared absorption spectra of both amorphous and amorphous drawn films were recorded in the spectral region of 1150–800 cm^{-1} (Fig. 3). Amorphous drawn films were also investigated in the same spectral region using infrared radiation polarized both parallel and perpendicular with respect to the draw axis of the films. The spectra obtained appear in Figure 4.

Water Treatment

Infrared Studies. In order to investigate the effects of water on amorphous films of nylon 6, a derivative infrared spectrum was recorded. In absorption spectra, mutual overlapping of absorption bands can lead to an obscuration of the characteristics of one or more absorption bands. However,

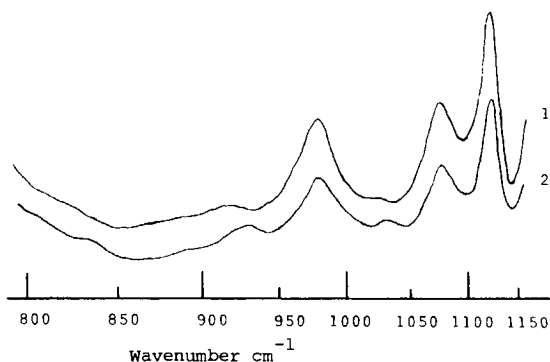


Fig. 3. Infrared absorption spectra of nylon 6 films: (1) amorphous; (2) amorphous drawn.

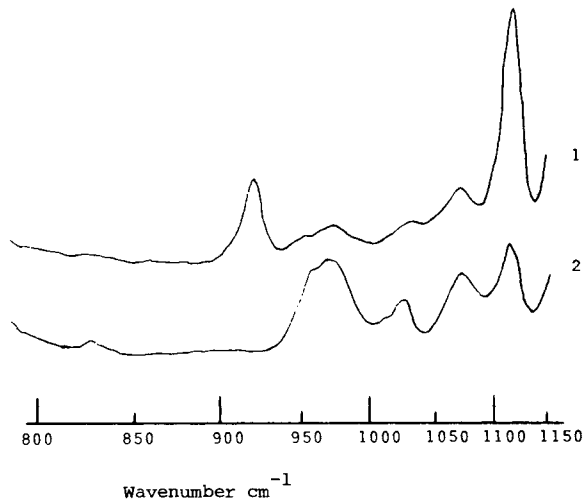


Fig. 4. Infrared absorption spectra of an amorphous drawn nylon 6 film. Spectra recorded using infrared radiation polarized both parallel and perpendicular with respect to the draw direction of the sample: (1) parallel; (2) perpendicular.

a second derivative spectrum produced by the electronic differentiator is much sharper than its parent absorption spectrum, and more fine detail is therefore apparent. The derivative infrared spectra of an amorphous film and an amorphous film treated in water at room temperature for 8 h appear in Figure 5.

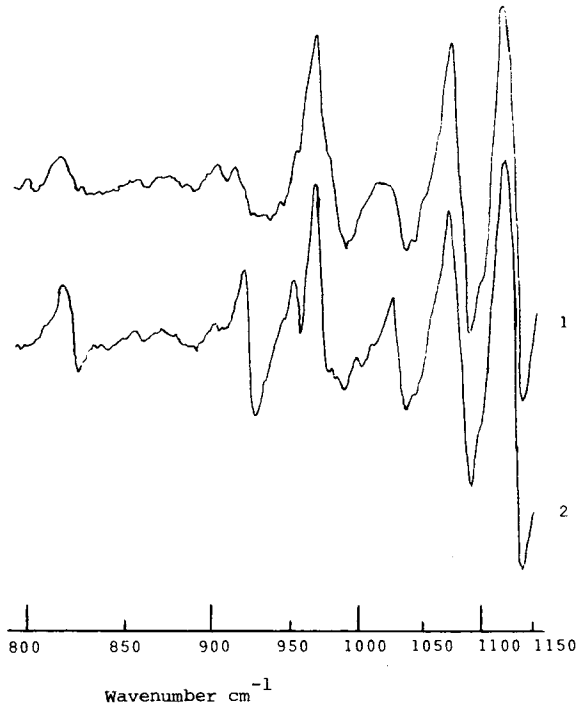


Fig. 5. Derivative infrared spectra of nylon 6 films: (1) amorphous; (2) amorphous treated in water at room temperature.

RESULTS AND DISCUSSION

The Effects of Annealing

Long period spacings have previously been equated with fold period in both nylon 6.6^{10,11} and nylon 6.^{12,13} The infrared and X-ray diffraction data in this study support these earlier observations.

Low-angle x-ray diffraction studies reveal that annealing between 125°C and 150°C in air results in a small decrease in the long/fold period (Table I). This can be explained if a regularization of irregular folds and/or fold intermeshing occurs¹ in this temperature range. Infrared studies in the same temperature range (Figs. 1 and 2) reveal that an absorption band at 974 cm^{-1} increases a little in intensity. This band actually increases steadily in intensity from room temperature up to 150°C, and the increase is interpreted as being due to a steady increase in chain fold content. Such an increase was proposed by Koenig and Agboatwalla¹ for melt quenched nylon 6.6 samples between 180°C and their melting point. However, this proposal appears to be incompatible with a doubling of the fold period in nylon 6.6 following such annealing.^{10,11} A doubling of the fold period would be expected to result in a decrease in the fold content. In this study annealing above 150°C results in a decrease in the intensity of the absorption band at 974 cm^{-1} (Figs. 1 and 2), and this is interpreted as being due to a decrease in the number of folds present. Between 150 and 180°C the decrease in intensity of the band at 974 cm^{-1} is only small and coincides with a steady increase in the long/fold period (Table I). However, between 180°C and 190°C a very large increase in long/fold period occurs (Table I), and this coincides with a very large decrease in the intensity of the band at 974 cm^{-1} (Figs. 1 and 2).

It appears that whenever the chain folds increase their fold period, they do so at the expense of the number of folds present. Above 190°C a further small increase in long/fold period occurs up to 210°C (Table I), and this is coupled with a further small decrease in the intensity of the band at 974 cm^{-1} (Figs. 1 and 2). It must therefore be assumed that a further small decrease in the fold content occurs between 190 and 210°C.

An approximate doubling of the fold period occurs between the smallest and largest values for long/fold period shown in Table I. However, this increase in fold period does not occur in discontinuous steps corresponding to a doubling or quadrupling of the long/fold period over an extremely small annealing temperature range as previously suggested for nylon 6.6.^{10,11} In fact, no evidence at all was found which supported a quadrupling of the long/fold period in nylon 6.

The intensity of the absorption band at 974 cm^{-1} falls to less than half its maximum intensity between annealing temperatures of 150 and 210°C (Figs. 1 and 2). This observation coupled with the fact that the maximum length of the long/fold period is in fact a little less than double its minimum length (Table I) can be explained if some folds unfold to become straight chain molecules without increasing their fold periods.

A slight yellowing of the sample films occurred at the higher annealing temperatures. However, a comparison between the infrared spectra of sam-

ples annealed in air with those of samples annealed in dry nitrogen revealed identical amide band and CH_2 stretching band intensities for any particular annealing temperature. Clearly the small amount of oxidative degradation which occurred during high temperature annealing in air had no significant effect on the molecular structures of the sample films.

Air annealed samples were chosen because the behavior of the band at 974 cm^{-1} was much easier to interpret than its behavior in samples annealed in dry nitrogen. Although the general behavior of this absorption band was similar in both types of sample, it exhibited two small intensity increases and decreases up to an annealing temperature of 195°C in dry nitrogen. This behavior suggested that changes in molecular conformation within the samples occurred in a disjointed manner due to the absence of water vapor from the annealing atmosphere. It has previously been shown that water molecules absorbed by noncrystalline thermoplastic polymers act as a "lubricant" and induce changes in molecular conformation particularly at high temperatures.^{14,15}

The Effects of Drawing

The decrease in the intensity of the infrared absorption band at 974 cm^{-1} observed when an amorphous sample film of nylon 6 was drawn (Fig. 3) supports the assignment of this band as a "fold band." Drawing would be expected to destroy (unfold) some of the chain folds present in an amorphous film.

The results of investigations using polarized infrared radiation further supports this view. It has previously been shown that the amino component of the molecular chains in nylon 6.6 constitutes the actual fold and also that the planes containing the folds are fully hydrogen-bonded.^{1,16} No free $\text{C}=\text{O}$ or NH group vibrations were detected in the infrared spectra of the nylon 6 films investigated in this study,¹⁷ thereby confirming that our nylon 6 samples were fully hydrogen-bonded and that they must therefore have folds which consist of five CH_2 groups.

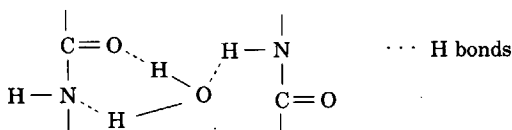
Any chain folds in amorphous drawn sample films of nylon 6 would be expected to align predominantly at right angles to the draw direction. Any CH_2 wagging or twisting vibrations in the nonamide vicinal CH_2 groups in the folds would therefore be expected to exhibit perpendicular dichroism. It is clear from Figure 4 that the band at 974 cm^{-1} exhibits strong perpendicular dichroism (dichroic ratio = 0.3) and may therefore be assigned to CH_2 wagging or twisting vibrations in the nonamide vicinal CH_2 groups in the folds. Such groups are likely by virtue of their positions to have unique vibrational frequencies because vibrations in one CH_2 group will be influenced by vibrations in neighboring CH_2 groups much more than in the straight portions of the molecular chains.

The Effects of Water

In order to confirm the assignment of the band at 974 cm^{-1} to nonamide vicinal CH_2 group wagging or twisting vibrations, an amorphous film of nylon 6 was treated in water at room temperature, and its infrared derivative spectrum was recorded (Fig. 5). No frequency shift occurred in this

band following water treatment, indicating that the band could not be assigned to any amide group vibration or even to any amide vicinal CH_2 group vibration.¹⁸ Both amide and amide vicinal group vibrations have been shown by Hallos¹⁹ and by Whittaker²⁰ to exhibit frequency shifts following treatment in water at room temperature.

The mechanism of hydration proposed by Hallos¹⁹ for amorphous nylon 6 satisfactorily explained such frequency shifts:



CONCLUSION

A band at 974 cm^{-1} in the infrared spectra of nylon 6 is representative of CH_2 wagging or twisting vibrations in nonamide vicinal CH_2 groups located in molecular chain folds.

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