FTIR Separation of Nylon 6 Chain Conformations: Clarification of the Mesomorphous and γ− Crystalline Phase

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FTIR Separation of Nylon-6 Chain Conformations: Clarification of the Mesomorphous and γ-Crystalline Phases

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SYNOPSIS

Specific infrared absorptions for each form of Nylon-6 have been identified. Quenched films were prepared by melt casting and converted in turn to the α-crystalline and γ-crystalline structures. The films were examined using Fourier transform infrared spectroscopy (FTIR) with the attenuated total reflection configuration and by X-ray diffractometry. The FTIR spectrum of the pure mesomorphous component of the quenched film was calculated by subtracting away the contribution of α-crystalline peaks present due to incomplete quenching. A curve-fitting procedure was applied to the pure mesomorphous and gamma crystalline spectra. Several peaks in the mesomorphous spectrum are observed to develop a shoulder upon conversion to the γ-crystalline form. This is due to the extra *gauche* character imparted to the C—N bond between the methylene unit and the amide group. These and other band assignments were confirmed by analysis of model compounds.

Keywords: infrared spectra of Nylon-6 chain conformation • Nylon-6 chain conformation, FT-IR separation of

INTRODUCTION

Numerous studies have been made of the infrared spectrum of Nylon-6 in its various structural forms. The two predominant crystalline forms and two disordered phases have been presented separately, but little work has been done to separate the components from a heterogeneous mixture. This has been due to the difficulty in differentiating the infrared spectra of the γ-crystalline and mesomorphous conformations. This has also prevented the use of infrared spectra to determine total crystallinity. In this study, specific infrared absorptions for each type of structure have been identified; and the α-crystalline, γ-crystalline, mesomorphous, and amorphous components can now be resolved simultaneously.

It should be made clear that in the following analysis, the noncrystalline components of the Nylon-6 films will be designated as mesomorphous following the convention of Doskocilova. These components are not to be confused with the amorphous material which exists in the melt or in quenched samples below the glass transition temperature. The purpose of this work is to demonstrate that the infrared spectrum of this mesomorphous phase can be distinguished from the spectra of both crystalline phases. Previously, only the dominant crystal form could be separately identified.

The two accepted crystalline forms of Nylon-6 have been well characterized by X-ray and FTIR analysis. In the α-crystalline structure as determined by Holmes et al.[1] the chain is fully extended and the amide group is in the same plane as the methylene groups. Arimoto et al.[2] have shown that in the γ structure, the chain is shorter by 3% with respect to the fully extended structure and the amide group is rotated 67° away from the main chain. Although there are many peaks unique to each crystal form, there have been no published attempts to separate these two forms from a sample containing fractions of each phase.

In addition to the normal amorphous form observed in the melt phase, a second disordered phase

has been reported. In this phase, many of the methylene groups in each chain are aligned parallel with neighboring chains, yet random orientation of each pendent group about the chain axis occurs. Sandemann and Keller[3] reported that this mesomorphous phase is obtained upon quenching the molten polymer and used the prefix meso, meaning intermediate, to distinguish this conformation from the truly amorphous material. Doskocilova et al.[4] asserted that the true amorphous form does not exist in the solid state above the polymer T_β at 65°C. In the same study, they presented a spectrum of the mesomorphous phase, which was virtually identical to that of the γ-crystalline form, and demonstrated the differences between these two forms and the amorphous melt.

Early attempts to determine the crystallinity of Nylon-6 by IR, made use of the absorbance band at 928 cm^{-1}, which monotonically increases during the annealing process. It was later shown by Doskocilova that this band is representative only of the α-crystalline component and thus does not give a good indication of overall crystallinity in the sample.[5] No previous work has reported any quantifiable differences between the infrared spectra of the γ-crystalline and mesomorphous phases, making overall crystallinity measurements impossible if the γ-form is present. In this study, several bands unique to the γ-crystalline form have been identified and explanations for their appearance presented. These band assignments have been supported by analysis of a model compound.

EXPERIMENTAL

Nylon-6 polymer for this study was produced using the ring opening polymerization of ϵ-caprolactam. Sodium hydride and phenylisocyanate, 1.5 mol % each were used as catalyst and initiator, respectively. All chemicals were purchased from the Aldrich Chemical Company and used as received. Films were cast onto heated aluminum foil by smearing melted blocks of the polymer across the surface of the foil. The film and support were immediately quenched in liquid nitrogen and then returned to room temperature to obtain mesomorphous films. The amorphous spectrum was obtained by examining Nylon-6 in the melt phase between KBr plates. The quenched films were converted to the α-crystalline form by annealing in a forced-air convection oven at 200°C for 3 hours. A slight yellowing of the film was observed after annealing in either air or nitrogen

due to oxidation of the end groups. Gel permeation chromatography measurements showed the molecular weight of the nylon to be approximately 6000.[6] Thus any reaction at the chain ends is not expected to be visible in the infrared spectrum of the polymer.

The γ-crystalline form can be prepared by treating the α-form with iodine as demonstrated by Kinoshita.[7] Following the procedure of Frayer et al.[8] the annealed films were placed in a solution of 15.2 g I$_2$, 17.6 g KI, and 120 mL H$_2$O, for two days. These were then transferred to a rinse solution of 8.4 g Na$_2$S$_2$O$_3$ in 120 ml H$_2$O for two additional days to remove the iodine from the treated polymer. After the rinse stage, the films were washed several times with deionized water and dried at room temperature.

The model compound was prepared by mixing 1,4-diaminobutane (dissolved in carbon tetrachloride) and butyric acid chloride (in a 10% solution of sodium hydroxide) vigorously for 15 minutes. The white precipitate was collected, washed with deionized water, and recrystallized from a methanol/water mixed solvent. Gel permeation chromatographic analysis showed a single peak for this product at the expected molecular weight. The structure, an aliphatic chain including two amide groups, was confirmed by proton nuclear magnetic resonance (NMR) measurements.

Specimens were examined using a Bomem Michelson 110 Fourier transform infrared spectrometer at a resolution of 4 cm^{-1}. The detector was a liquid nitrogen cooled mercury cadmium telluride (MCT) type having a specific detectivity (D*) of 2×10^{10} cmHz$^{0.5}$W^{-1}. Each sample was purged for 20 minutes with 80 cm^3/s of dry nitrogen before beginning collection of 50 coadded scans. The attenuated total reflection configuration was used with a KRS-5 prism ($50 \times 20 \times 2$ mm) having an incident angle of 45°. Samples were cut from the quenched film along and across the smear direction to check for any residual orientation effects caused by the smearing procedure. Polarization studies were made using transmission and attenuated total reflection, to confirm that the samples were isotropic. Confirmation of the crystalline form present at each stage of the treatment process was obtained by X-ray diffraction measurements.

RESULTS AND DISCUSSION

The polymer films were cast from the melt onto aluminum foil to avoid the use of exotic and toxic solvents normally needed to dissolve Nylon-6. Any in-

homogeneities in thickness introduced by this method are irrelevant for qualitative study but were nevertheless corrected for by use of internal standards for quantitative analysis.

The smearing technique employed could be expected to produce some degree of orientation of the polymer films. Specimens cut from the longitudinal and transverse directions were examined in transmission to discover if this had occurred. Spectra of the parallel (p) and perpendicular (s) polarization components of the films were identical, illustrating that an isotropic sample film had been cast. Specifically, all forms of Nylon-6 have a band absorbing between 1118 and 1124 cm^{-1} which interacts with parallel polarized light.[9] This band did not change in intensity when either p or s polarized light was passed through the sample. The spectra for the perpendicular components of the transverse and longitudinal films were also compared. The longitudinal film showed a higher overall absorbance, probably due to thickness variations or mounting differences between the two films. The relative intensities of the spectra are virtually identical, however.

Figures 1 and 2 show the spectra of the same nylon film at different stages of the treatment process. The differences between the spectra of the mesomorphous, α-crystalline, and γ-crystalline states of this film are recorded in Table I along with previous band assignments when available from the literature.[4,5,8-14] A curve-fitting procedure, using Lorentzian and Gaussian models, was used to separate the contributions of individual peaks in overlapped regions.

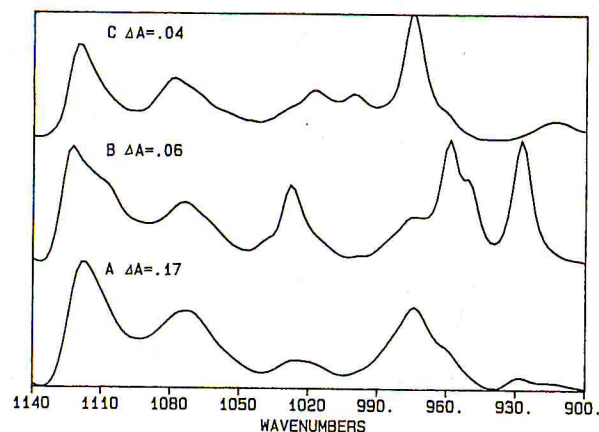The spectrum of the quenched film was observed to contain small peaks at 927, 959, and 1028 cm^{-1}.

Figure 1.   Nylon-6 ATR spectra of (A) quenched film, (B) annealed film, and (C) chemically treated film from 1140 to 900 cm^{-1}.
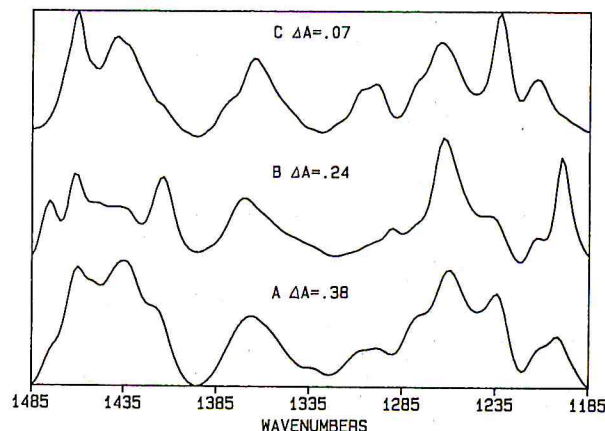

Figure 2.   Nylon-6 ATR spectra of (A) quenched film, (B) annealed film, and (C) chemically treated film from 1485 to 1185 cm^{-1}.

These peaks have been previously assigned to the α-crystalline form[4] and arise in this sample due to imperfect quenching. Confirmation of the identity of these bands was obtained by observing their monotonic increase during the annealing process, and upon slow cooling from the melt.

To compare quantitatively the γ-crystalline and mesomorphous forms, it is necessary to remove all contributions of α-crystalline material from the latter spectrum. Simak has done this qualitatively while following the annealing process, to obtain spectra of the 'crystalline' and 'amorphous' phases.[15] Using the ATR spectra presented in Figure 1 with the disappearance of α-crystalline peaks at 950 and 1199 cm^{-1} as the basis for subtraction, the pure mesomorphous spectrum has been calculated. This is presented in Figures 3 and 4 with the γ-crystalline spectrum for comparison.

The spectra obtained for the mesomorphous and γ-crystalline structures in this study are remarkably similar, yet are by no means indistinguishable. The change in bandwidth is easily explained by the ability of the molecule in the mesomorphous phase to rotate about the chain axis. Such motions would average to the position postulated for the γ crystal but would result in a broader range of transitional energies.

In addition to the sharpening of the bands in the γ-crystalline spectrum, the appearance of new bands unique to this conformation is noted. Frayer et al.[8] have assigned bands at 1212 and 1300 cm^{-1} to the fold in the γ-form crystal in support of their work on the α-form. Such bands would not be expected to occur in the mesomorphous spectrum, and thus provide a means of distinguishing it from the γ-form.

Table I. Band Assignments in Nylon-6 Position in Wavenumbers (Intensity in Arbitrary Units)

Mesomorphous	γ-Crystalline	α-Crystalline	Vibration type			Ref.
911 (0.6)	914 (2.6)	901 (1.7)	CO—NH	$\perp$		9
918 (0.4)						
		927 (18)	CO—NH	α	//	9
		950 (9.0)	CO—NH	α	//	9
961 (2.8)	962 (2.6)	959 (14)	CO—NH	$\perp$		9
973 (7.8)	975 (18)		CO—NH	m, γ		9
	1000 (2.1)			γ		10
1019 (1.7)	1018 (3.2)	1021 (2.8)				
		1028 (7.6)	CO—NH	α	$\perp$	9
1031 (0.5)	1028 (1.0)		CO—NH	m, γ	//	9
		1039 (1.7)	CO—NH	α	//	9
1054 (1.9)	1057 (1.6)					
		1062 (1.4)				
1068 (5.9)	1067 (2.6)		CO—NH	$\perp$		9
		1074 (2.5)	CO—NH	α		5
1079 (4.4)	1079 (7.9)		CO—NH			9
	1107 (4.2)	1106 (0.8)				
1113 (8.9)	1116 (6.8)	1114 (3.9)				
1120 (8.4)	1121 (8.4)		C—C & CO—NH	γ	//	9
		1124 (8.4)	C—C & CO—NH	α	//	9
1158 (4.7)	1161 (7.5)					
1168 (24)	1168 (28)	1168 (9.6)	CH$_2$ twist/wag			4
1172 (8.0)	1174 (4.9)		'Amorphous'			11
		1199 (32)	CH$_2$ twist-wag			4
1204 (4.0)						
1209 (7.5)	1213 (7.5)	1213 (7.5)	Amide III & CH$_2$ wag			8
1233 (24)	1232 (20)		Amide III & CH$_2$ wag			10
		1238 (7.1)	Amide III & CH$_2$ wag			10
	1264 (18)	1264 (15)	Amide III & CH$_2$ wag			4
1278 (13)	1279 (3.0)		Amide III & CH$_2$ wag			10
		1291 (5.6)	Amide III & CH$_2$ wag			10
1297 (3.0)	1298 (7.5)	1300 (1.2)	Amide III & CH$_2$ wag			10
1308 (5.6)	1308 (7.1)		(See text)			
	1319 (1.5)		(See text)			
1333 (1.4)		1331 (1.3)	Am III, CH$_2$ tw, CH ν			12
1357 (10)	1352 (6.8)					
		1364 (9.0)	Am III, CH$_2$ tw, CH ν			12
1367 (6.9)	1366 (15)		Amide III & CH$_2$ wag			10
		1372 (6.3)	Amide III & CH$_2$ wag			10
1378 (6.7)	1380 (6.0)		(See text)			
	1390 (1.5)		(See text)			
		1402 (0.8)				
		1413 (22)	CH$_2$ scissors	α		10
1434 (34)	1429 (94)		CH$_2$ scissors	γ, m		4
	1440 (17)		(See text)			
1462 (21)	1460 (24)		CH$_2$ scissors	γ, m		10
	1467 (4.5)		(See text)			5
		1476 (17)	CH$_2$ scissors	α		10
1499 (1.1)	1500 (3.0)	1504 (10)	Amide II			13
	1513 (4.5)					
1521 (18)	1530 (24)	1528 (56)				
1542 (55)	1549 (49)	1541 (28)	Amide II all			10
1562 (23)	1565 (23)	1564 (2.9)	Amide II all			10

Table I. Continued

Mesomorphous	γ-Crystalline	α-Crystalline	Vibration type		Ref.
1624 (60)	1623 (50)				
		1631 (79)	Amide I		12
1636 (48)	1641 (50)		Amide I		12
1650 (38)	1659 (7.9)	1661 (10)	Amide I		10
1673 (4.1)		1678 (1.3)	Imide from rxn.		14
2854 (20)	2852 (26)	2847 (3.6)	CH_2 sym. str. all		4
		2869 (2.5)	CH_2 sym. str.		12
		2896 (9.0)			
		2907 (3.8)			
2924 (32)	2929 (33)	2932 (5.6)	CH_2 asym. str.		4
		2943 (12)			
2954 (9.5)	2958 (8.6)				
3084 (8.6)	3087 (9.0)		Assoc N—H	γ, m	10
3201 (6.7)	3193 (6.4)	3181 (3.3)			
3286 (32)	3285 (30)	3273 (9.6)	Assoc N—H		12
		3293 (29)	Assoc N—H		10
		3318 (5.0)			

In these spectra, however, this is not the case. The new bands observed occur in the CH_2 deformation region, the Amide III and CH_2 wag region, and at 1000 cm^{-1}.

Several broad bands in the mesomorphous structure are observed to split into two sharper bands upon conversion to the γ-form. The band at 1308 cm^{-1} in the mesomorphous spectrum shown in Figure 5, for example, has a corresponding band at 1308 cm^{-1} and a shoulder at 1319 cm^{-1} in the spectrum of the γ crystal. Similar splittings are observed for bands at 1378, 1434, and 1462 cm^{-1} in the meso-

morphous structure. The resulting shoulders at 1319, 1390, 1440, and 1467 cm^{-1}, are not observed in the original mesomorphous spectrum and thus can be used to distinguish the γ-crystalline component from the disordered form. Only three of these bands have been tentatively identified with any structural feature in previous studies. The shoulder at 1467 cm^{-1} has been assigned by Doskocilova et al.[5] to the CH_2 scissoring motion in 'Form B' of Nylon-6, a combination of the mesomorphous and γ-crystalline structures. They also made similar assignments for bands at 1439 and 1460 cm^{-1}.[4]
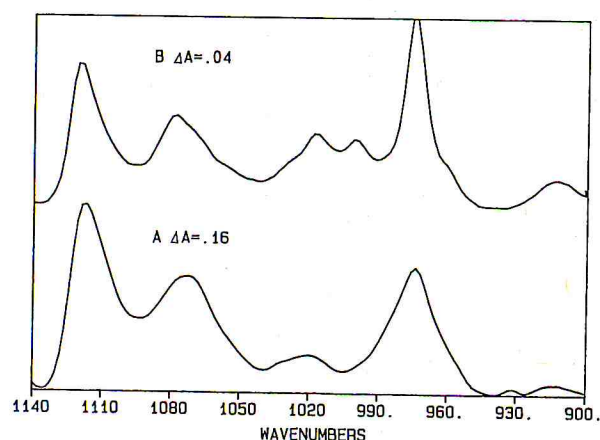

Figure 3. Comparison of (A) calculated mesomorphous Nylon-6 spectrum with (B) γ-crystalline spectrum from 1140 to 900 cm^{-1}.
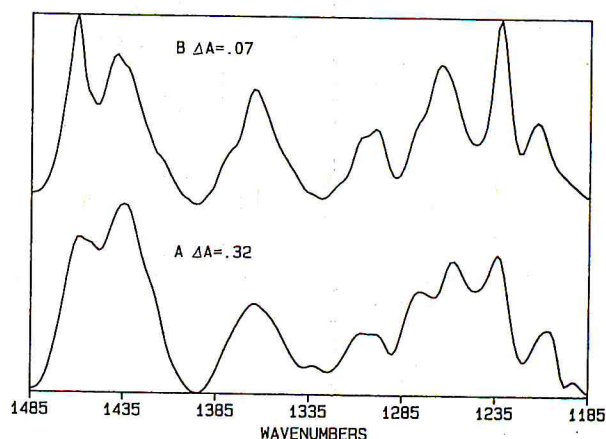

Figure 4. Comparison of (A) calculated mesomorphous Nylon-6 spectrum with (B) γ-crystalline spectrum from 1485 to 1185 cm^{-1}.

Since the intensity of the shoulder in each case is approximately one-fourth that of the main band, it is reasonable to assign the shoulder to a methylene unit immediately adjacent to the amide group. This methylene unit would be slightly strained as extra *gauche* character is imparted to the bond upon crystallization. In the γ-crystalline structure, the amide group is rotated away from the methylene chain, in a manner that is locally less favorable energetically than either the α-crystalline structure or the proposed mesomorphous state. This could explain the fact that each shoulder appears at a frequency approximately 10 cm^{-1} higher than the original broad band. The structure is stable with respect to the mesomorphous conformation, however, because of the increased hydrogen bonding between amide groups along the chain. Thus the shoulder frequencies in the γ-crystalline structure spectrum can be tentatively assigned to a coupling between the CH$_2$ wag of the methylene unit adjacent to the nitrogen atom, and the Amide III vibration.

A model compound consisting of two amide groups embedded in an aliphatic chain was prepared to test this assignment. Upon deuteration of the amide group, as shown in Figure 6, it was found that a peak at 1287 cm^{-1} shifted to 1279 cm^{-1}. Such a shift is expected for a band arising from the coupling of an amide group vibration with another mode. The assignment of this other mode is supported by the work of Snyder and Schachtschneider, who in their work on n-paraffins,[16] assigned peaks at 1290 cm^{-1} in n-butane and 1258 cm^{-1} in n-pentane to the methylene wagging vibration.

The mesomorphous to γ-crystalline conversion

Figure 6. Transmission spectra of the model compound (A) after and (B) prior to deuteration.

is also accompanied by three other peak shifts, from 984 to 1000 cm^{-1}, from 1078 to 1107 cm^{-1}, and from 1499 to 1513 cm^{-1}. These could also be explained by the slight strains imposed on the molecule upon crystallization and provide an additional means to differentiate the mesomorphous and γ-crystalline forms. The shoulder area in each of these cases is not however equal to one-fourth the area of the main peak.

CONCLUSIONS

It has been demonstrated that the mesomorphous and γ-crystalline conformations of Nylon-6 can be distinguished by analysis of their respective infrared spectra. The added *gauche* character imparted to the polymer chain in the γ-crystalline structure results in several new infrared absorbances not seen in the mesomorphous material. Model compound analysis has supported the assignment of these new bands. The three predominant room temperature forms of Nylon-6 (α-crystalline, γ-crystalline, and mesomorphous) can thus be separately identified.
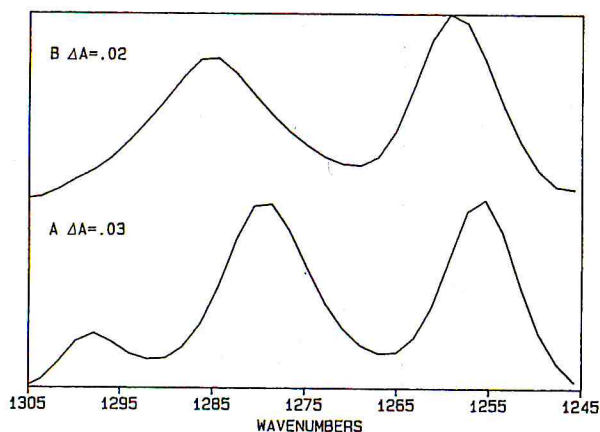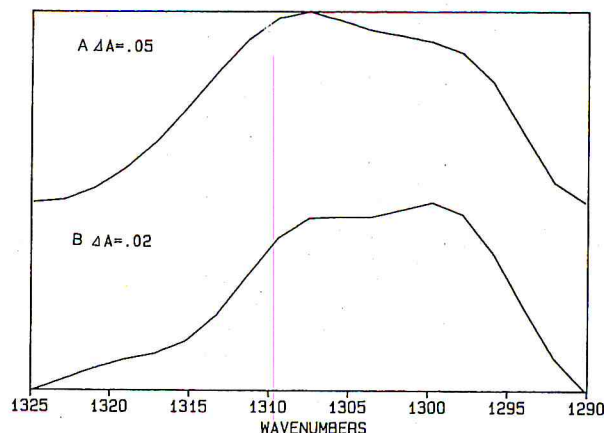
Figure 5. Comparison of (A) calculated mesomorphous Nylon-6 spectrum with (B) γ-crystalline spectrum in the CH$_2$ wag-Amide III region.

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