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Polymorphism in Nylon-11: Characterization using HTWAXS and HTFTIR

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Summary: Nylon-11 was crystallized into different crystalline phases by appropriate methods. The α phase was obtained by precipitating nylon-11 in 1,4-butanediol. The melt crystallized sample at 175 °C gave pseudohexagonal phase. The γ phase was obtained by casting nylon-11 in trifluroacetic acid (TFA). The change in the structure was monitored *in situ* by high temperature wide-angle X-ray scattering (HTWAXS) and high temperature Fourier transform infrared spectroscopy (HTFTIR). The studies have shown that nylon-11 is one of the few nylons that exhibit extensive degree of polymorphism. HTFTIR studies revealed, apart from the conformational differences between various phases of nylon-11, some information on the formation of γ phase.

Keywords: crystalline phases; FT-IR; nylon 11; polymorphism; WAXS

Introduction

Nylons are important semicrystalline polymers with many useful properties. The properties are dictated by the structure consisting of flexible methylene segments and rigid amide groups connected in an alternate manner along the chain axis. Among nylons, nylon-6,6 and nylon-6 are commercially successful and have been extensively explored scientifically. In the odd-nylons group, nylon-11 received considerable scientific attention because of its piezoelectric and ferroelectric properties. Nylon-11 exhibits polymorphism, and several researchers[1–8] have studied the polymorphism of nylon-11.

Hydrogen bonding dominates the crystal structure of nylons; hydrogen bonded sheets are the main feature of nylon structure, and the two strong reflections arise from this feature. The *d* spacings of these reflections at 0.37 and 0.44 nm are due to the intersheet distance between the sheets and the projected interchain distance within the sheet, respectively. Most nylons show a crystal-to-crystal transition on heating. This phenomenon was first observed in nylon-6,6 by Brill and hence is known as the Brill transition.[9] The room temperature triclinic α phase transforms into a pseudohexagonal (hexagonally packed) phase at elevated temperatures, and the transition is reversible. Crystalline transition is also reported for nylons -6,[10,11] -4,6,[12] -6,10,[12] -6,12,[12,13] and -12.[14]

Murthy et al.[10] suggested enhanced mobility of chains in the crystalline phase during transformation from one crystalline phase to another. The structural changes occurring in the Brill transition phenomenon for a series of nylons *m,n* and its model compounds have been studied by Tashiro et al[15–19] using HTFTIR and HTWAXS techniques in combination with the computer simulation method.

In the present paper, we report the results of the detailed characterization study made on the various polymorphs of nylon-11 at room temperature and on heating using HTWAXS and HTFTIR techniques for the first time with a view to understand the crystalline transition exhibited by the various polymorphs.

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Experimental Section

Nylon-11 pellets were obtained from Aldrich, USA. Nylon-11 was crystallized by precipitating in 1,4-butanediol.[20] The X- ray diffraction (XRD) experiments were performed using a Rigaku Dmax 2500 diffractometer with a copper target and the details are explained elsewhere.[20] The samples were scanned between $2\theta = 5$ to 30° at a scan speed of 2°/min. The diffraction pattern was collected while the sample temperature was held constant. The change in the diffraction pattern was monitored during heating/cooling by scanning at regular temperature intervals until the sample melted. The sample was cooled/heated at the rate of 20 °C /min, and when the sample temperature reached within 20 °C of the required set temperature, the cooling/heating rate was automatically reduced to 2 °C/min to minimize the over shooting of the set temperature. The temperature was maintained within 1 °C of the set temperature thereafter. The positions of the peaks were fixed by deconvoluting the peaks by profile-fitting, using Rigaku multipeak separation software available with the diffractometer system. For melt crystallization studies, a thin film of nylon-11 was formed on the copper block by melt pressing the sample.[20] The nylon-11 film cast from TFA solution was stuck in the copper sample holder and heated to melting, and the diffraction patterns were acquired at regular temperature intervals. Room temperature and high temperature infrared spectra of these samples were taken using a Perkin-Elmer FTIR Spectrometer (model: Spectrum GX) with a DTGS detector at a resolution of 2 cm^{-1} in the range of 400–4500 cm^{-1}.[20]

Results and Discussion

The room temperature diffraction pattern of the nylon-11 sample crystallized in 1,4-butanediol shows the characteristic reflections of nylons at $2\theta = 19.92$ and 23.74°. These reflections may be indexed as 100 and 110/010 based on the α phase having a triclinic unit cell proposed by Slichter,[2] Kawaguchi et al.,[4] and Kim et al.[5] The 001 reflection occurs at $2\theta = 7.54°$, corresponding to a d spacing of 1.171 nm. The behavior of the diffractograms and the d spacings of the α phase on heating from room temperature to melt is shown in Figure 1a and d, respectively. It is seen that, on heating, the two-peak nature of the diffractogram is preserved until melting. The d spacing of the 110/010 reflection shows a rapid increase after 110 °C and approaches the 100 reflection, indicating the transformation of the α phase into the pseudohexagonal phase. However, the transformation is not fully completed before melting. Indeed, Tashiro and co-workers[15–19] have shown that the Brill transition does not occur at only one temperature point but it occurs over a temperature region. Another notable feature of the nylon-11 α phase is the behavior of the 001 peak on heating, as shown in Figure 1d. The d spacing of the 001 reflection increases with increase in temperature; the increase is more rapid at about 110 °C, similar to the d spacing of 110/010 reflections. Nylon-11 crystallizes in the pseudohexagonal phase like nylon-6, 6[9,21] during isothermal crystallization at 175 °C from the melt. At 175 °C it shows two crystalline peaks at $2\theta = 6.93°$ and 20.69° and the corresponding d spacings are 1.274 and 0.429 nm respectively. The reflection at $2\theta = 6.93°$ may be indexed to the 001 reflection. The behavior of the diffractograms and the d spacings on cooling from the crystallization temperature (T_c) to room temperature is shown in Figure 1b and e, respectively. It is seen from the Figure 1b that, on cooling from the T_c, the single-peak nature of the diffractogram is preserved and the d spacings of the pseudohexagonal phase show small decreases with further decrease in temperature. However, two new peaks at $2\theta = 20.89°$ and 21.94° appear at about 100 °C. These peaks become prominent and separate out with further decrease in temperature, and concomitantly, the peak due to the pseudohexagonal phase decreases. This indicates a

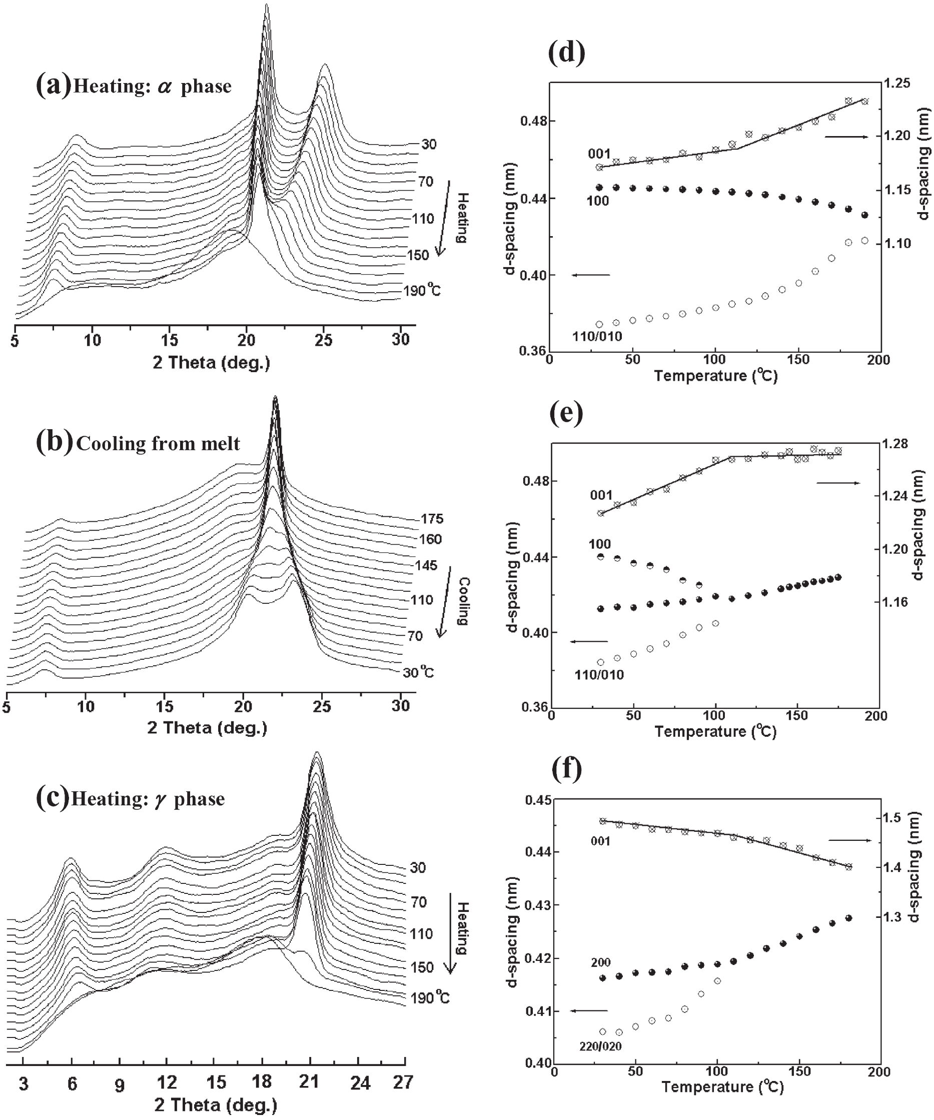

Figure 1.

Behavior of XRD patterns of nylon-11: (a) On heating from room temperature to melt for the α phase crystallized in 1,4-butanediol. (b) Melt crystallized at 175 °C on cooling to room temperature. (c) On heating from room temperature to melt for γ phase obtained by film casting from triflouoroacetic acid. The behavior of the d spacings for (d) 1,4-butanediol crystallized, (e) melt crystallized, and (f) trifluoroacetic acid cast nylon-11.

crystalline transition of the pseudohexagonal phase at about 100 °C. At room temperature, these new peaks appear at $2\theta = 20.17°$ and 23.13°, and the corresponding d spacings are 0.440 and 0.384 nm. The 001 reflection occurs at $2\theta = 7.20°$ at room temperature, and the corresponding d spacing is 1.227 nm. The d spacings at room temperature are different from the d spacings of the α phase discussed above. Furthermore, the behavior of the diffractograms with temperature is different from that of the α phase. Hence, we designate this phase as the α' phase[5] to distinguish it from the α phase obtained by crystallizing in 1,4- butanediol. At room temperature, the pseudohexagonal phase fraction is about 4% and that of the α' phase is about 46%. The 001 reflection, shows interesting behavior and is shown in Figure 1e. The *d* spacing of this reflection remains constant in the pseudohexagonal phase, but starts to decrease after its transformation to the α' phase at 100 °C. The variations in diffraction patterns and *d* spacings on cooling from T_c are found to be reversible on heating the sample from room temperature to melting.

The nylon-11 cast from TFA exhibits the γ phase and appears similar to the γ phase of nylon-6 obtained by treating in KI/I_2 solution, and the room temperature diffraction pattern can be seen in Figure 1c. Though at room temperature the diffractogram appears to have a single peak at $2\theta = 21.34^\circ$, the profile-fitting procedure clearly indicates the presence of a shoulder at $2\theta = 21.87^\circ$. The corresponding *d* spacings of these reflections are 0.416 and 0.406 nm, respectively. The peak due to the 001 reflection is seen at $2\theta = 5.91^\circ$, and the *d* spacing is 1.495 nm. Because the fully extended repeat unit of nylon-11 is 1.5 nm, in the γ phase, the chain axis coincides with the *c*-axis of the unit cell. Although the detailed structure of the γ phase is not available in the literature, it can be thought of as monoclinic, but it is different from the monoclinic structure of form II discussed by Kawaguchi et al.[4] The changes in the diffraction pattern and the *d* spacings during heating from room temperature to melting are shown in Figure 1c and e. On heating, the peak at $2\theta = 21.87^\circ$ moves closer to the peak at $2\theta = 21.34^\circ$ and merges into a single peak at about 110 °C. On further heating, the single peak remains as a single peak until melting. Concomitantly the 001 reflection shows a small decrease in its d-spacing. It is evident from the Figure 1c and e that the γ phase transforms into the pseudohexagonal phase at about 110 °C on heating and remains in the pseudohexagonal phase until melting. Above 110 °C, the *d* spacing of the pseudohexagonal phase increases with increase in temperature. The foregoing discussions indicate that nylon-11 exists in the pseudohexagonal phase at temperatures above 110 °C; however, the 001 *d* spacing and its variation with temperature depends on the starting phase. It also means that the pseudohexagonal phase obtained from the different phases has a different packing mode.

The forgoing discussions are primarily focused on the structure based on the data obtained from variable temperature WAXS studies, and in the following section, the discussion will be focused on the data obtained from variable temperature FTIR studies on the various phases of nylon-11. FTIR spectra of nylons are well documented in the literature[22] and have four important regions. The region 500–800 cm^{-1} comprises the amide V and VI bands. The 1000–1400 cm^{-1} region contains the so-called progression bands and is sensitive to the methylene segments. The region 1500–1700 cm^{-1} contains the amide I and II bands and is sensitive to N–H stretching and C–O bonds. The Amide A band occurs at about 3300 cm^{-1} and is assigned to N–H stretching vibration and is sensitive to the strength of the hydrogen bond.

Figure 2a–c shows the spectral region from 500 to 800 cm^{-1} for the various phases and comprises the amide V and amide VI bands. At room temperature the amide V and VI bands appear at 686 and 582 cm^{-1} respectively for the α phase (1,4-butanediol crystallized sample). These bands appear at 686 and 581 cm^{-1} for the α' phase (melt crystallized sample). The amide V band shifts from 686 cm^{-1} to 709 cm^{-1} for the γ phase (TFA-cast film). Furthermore in the case of the γ phase the amide VI band is shifted[23] from 582 cm^{-1} to 627 cm^{-1}. Similar to the γ phase of nylon-6[24] the spectra show a distinct additional band at 595 cm^{-1} which is characteristic of the γ phase.[24] The variation of amide V band position on heating for α, α' and γ phases is shown in Figure 2d–f. On heating, the wavenumber of amide V band of the α phase remains constant up to 130 °C and then increases on further heating. The α' phase also shows slightly different behavior;

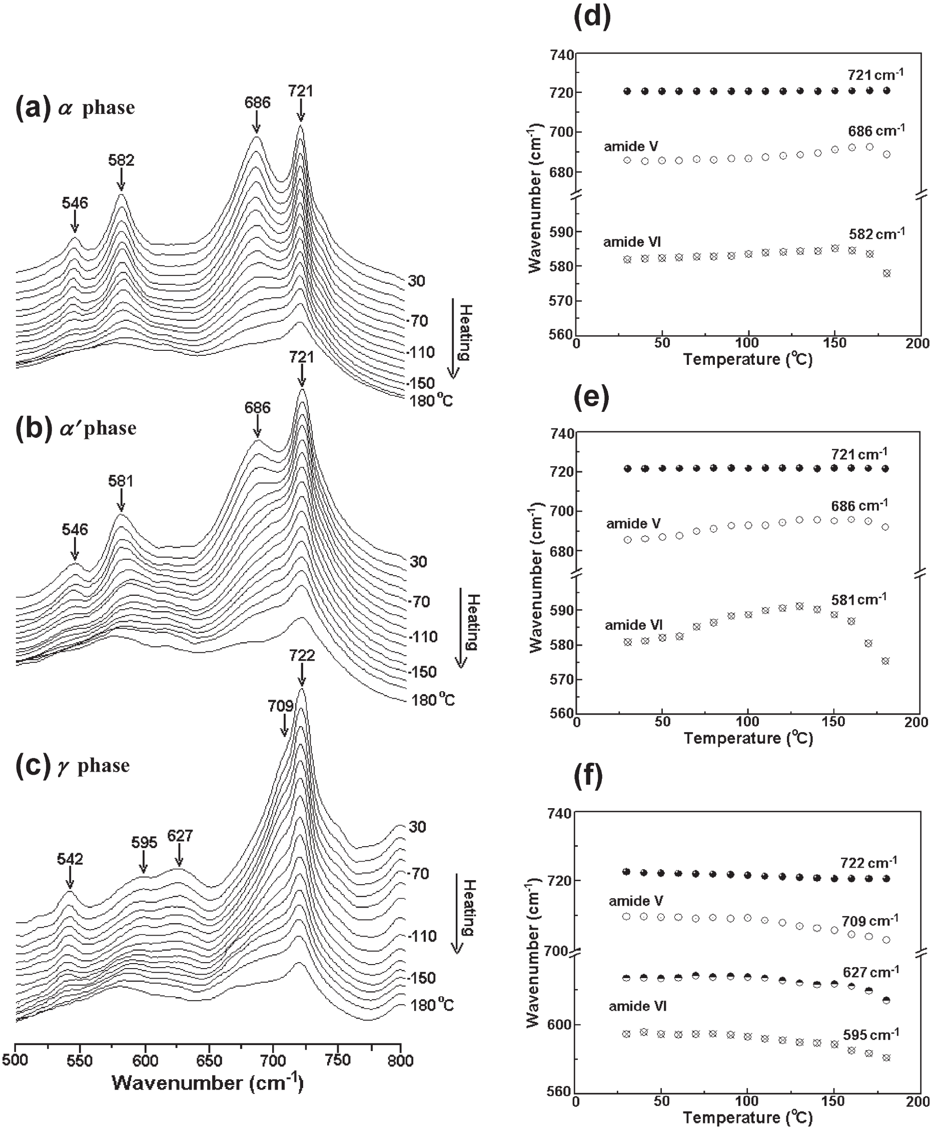

Figure 2.

Variable temperature FTIR spectra of the region 500–800 cm^{-1} of nylon 11 during heating from room temperature to melt: (a) α phase (1,4-butanediol crystallized), (b) α' phase (melt crystallized), and (c) γ phase obtained by casting in TFA. The variation of the wavenumber of amide V and VI bands during heating for (d) α phase, (e) α' phase, and (f) γ phase.

the wavenumber increases initially but above 120 °C it remains constant and towards the meting temperature it decreases. It may be pointed out here that the α' phase transforms into the pseudohexagonal phase at about 120 °C. In the γ phase, on the other hand, the wavenumber remains constant up to 100 °C and then it starts to decrease when the γ phase transforms into the pseudohexagonal phase. The amide VI band at 582 cm^{-1} in the case of the α and α' phases, does not change position during heating but decreases towards the T_m. On the other hand the amide VI bands at 595 and

627 cm^{-1} for the γ phase show a decrease with increasing temperature. The methylene rocking mode band at 721 cm^{-1} appears to be invariant towards heating for all the phases.

Another region of interest is from 1100 to 1400 cm^{-1} and is characterized by the progression bands from the methylene sequence. Figure 3a–c shows this region and the bands appear at 1126, 1159, 1190, 1223, 1240, 1279 and 1373 cm^{-1} for the α and α' phases at room temperature. These bands however appear at different position for the γ phase and occur at 1123, 1160, 1198, 1225, 1250, 1279 and 1371 cm^{-1} respectively. Upon heating almost all these bands show minor shift in position and decrease in absorbance but the major difference is observed between the α and γ phases. The 1160 and 1198 cm^{-1} bands are assigned to T_{10} and T_9 (CH_2 twisting) respectively and the 1190 cm^{-1} band arises from W_1 (CH_2 wagging).[22] Figure 3d–f depicts the variation of the band position and absorbance for various samples. In the case of the α phase the 1160 cm^{-1} shows a small shift towards the lower wavenumber with heating. The 1190 cm^{-1} band shifts to higher wavenumber with increase in temperature and the increment is more obvious above 120 °C. The absorbance decreases with increasing temperature for these bands and again the decrease is more prominent above 120 °C. The behavior of these bands shows minor variation for the α' phase. The 1160 cm^{-1} band position decreases with increase in temperature and is similar to the behavior of this band in the α phase. The 1190 cm^{-1} band also increases with increasing temperature initially and exhibits a more pronounced change in the temperature region 70 to 120 °C. Above this region the band position remains constant and from the HTWAXS data presented above, the sample exists in the pseudohexagonal phase above 120 °C. Such a behavior of progression bands is a common feature of nylons and is shown to arise due to the enhanced mobility of methylene segments with increasing temperature.[15,16] In the γ phase, the band at 1190 cm^{-1} is not obvious in the spectra but the band at 1198 cm^{-1} is prominent; furthermore, the behavior of 1160 and 1198 cm^{-1} bands with increasing temperature is different from that of the α and α' phases and is shown in Figure 3f. The wavenumber of these two bands decreases with increasing temperature but shows deviation at about 100 °C. The normalized integrated absorbance of 1160 and 1198 cm^{-1} band decreases with increasing temperature. The 1198 cm^{-1} band, which appears only for the γ phase, shows a rapid decrease above 100 °C when the γ phase transforms into pseudohexagonal phase.

The regions sensitive to hydrogen bonding are from 1500 to 1800 cm^{-1} and from 3000 to 3600 cm^{-1}. The region 1500 to 1800 cm^{-1} is shown in Figure 4a–c for the α, α' and γ phases and contains the amide I and II bands. The amide I band appears at 1640 and 1637 cm^{-1} for α and α' phases respectively, while for the γ phase it is again at 1639 cm^{-1}. The amide I band arises from the stretching of the carbonyl groups and the band has contribution from the hydrogen bonded carbonyl groups in the crystalline region (ordered), the hydrogen bonded carbonyl groups in the amorphous region (disordered) and the non hydrogen bonded carbonyl groups (free). Because of the contribution from the different carbonyl groups outlined above, the band usually appears highly asymmetric. Visual inspection of the Figure 4a–c shows that the behavior of the amide I band looks very similar for the α and α' phases at room temperature and on heating. The amide I band of the γ phase, however, shows variance from the α and α' phases; the band is considerably sharper. The amide II band appears at 1537 and 1544 cm^{-1} for the α and α' phases respectively. The band shifts to 1555 cm^{-1} for the γ phase. The amide II band arises mainly from the in-plane N–H bending and has contributions from ordered, disordered and free N–H groups. Consequently, the amide II band also appears highly skewed. Figure 4d–f shows the behavior of the peak position and the normalized absorbance for the various

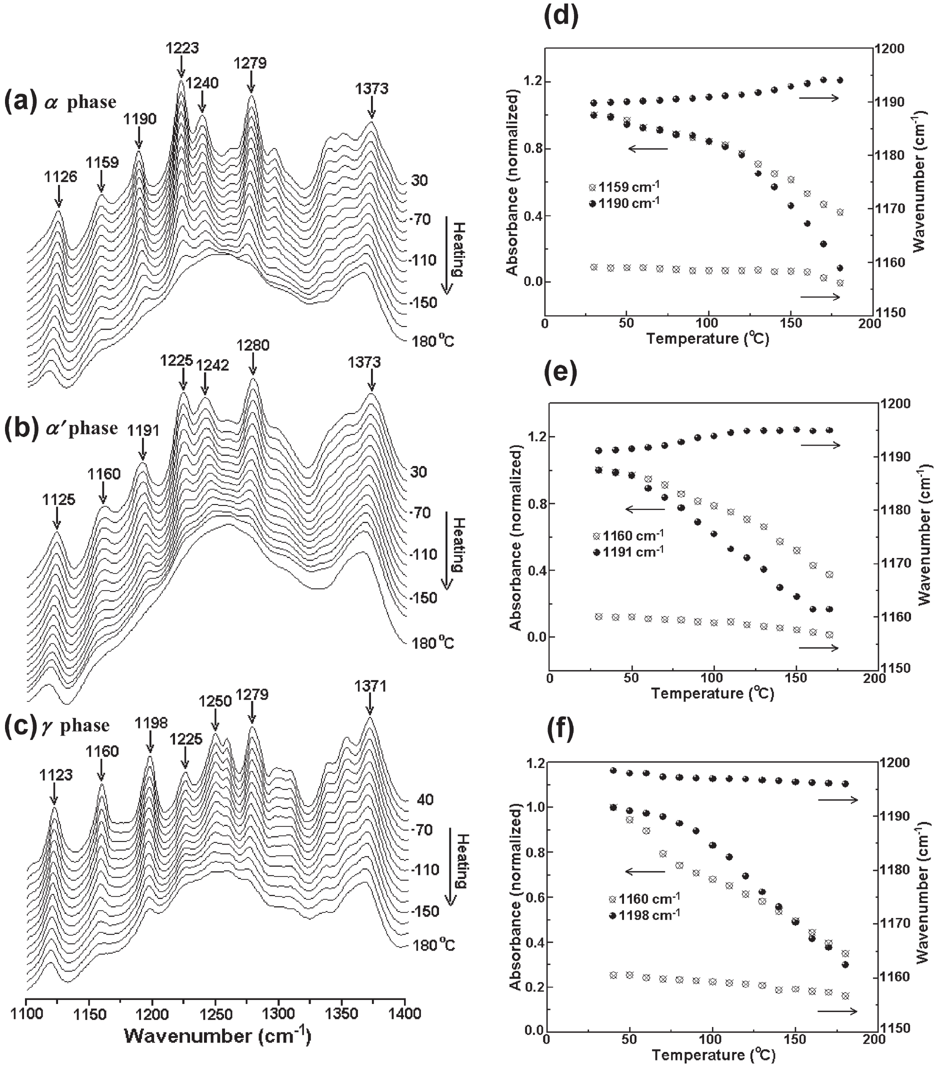

Figure 3.

Variable temperature FTIR spectra of the region 1100–1400 cm^{-1} of nylon-11 during heating from room temperature to melt: (a) α phase, (b) α' phase, and (c) γ phase. The variation of the wavenumber and normalized absorbance of bands 1160 and 1190 cm^{-1} during heating for (d) α phase, and (e) α' phase. (f) The variation of the wavenumber and normalized absorbance of bands 1160 and 1198 cm^{-1} during heating for γ phase.

phases. The wavenumber increases slightly with increasing temperature for the α phase and the shift is more pronounced close to T_m. The wavenumber 1544 cm^{-1} of the α' phase increases up to 120 °C and then decreases. The normalized integrated absorbance progressively decreases with increasing temperature for both the phases. The amide II band of the γ phase shows slightly different behavior. First of all, the band appears at 1555 cm^{-1}, at higher wavenumber than the α and α' phases. Secondly, the behavior of the band on heating is very different from the α phases. The band shifts to lower wavenumber on heating and becomes sharper.

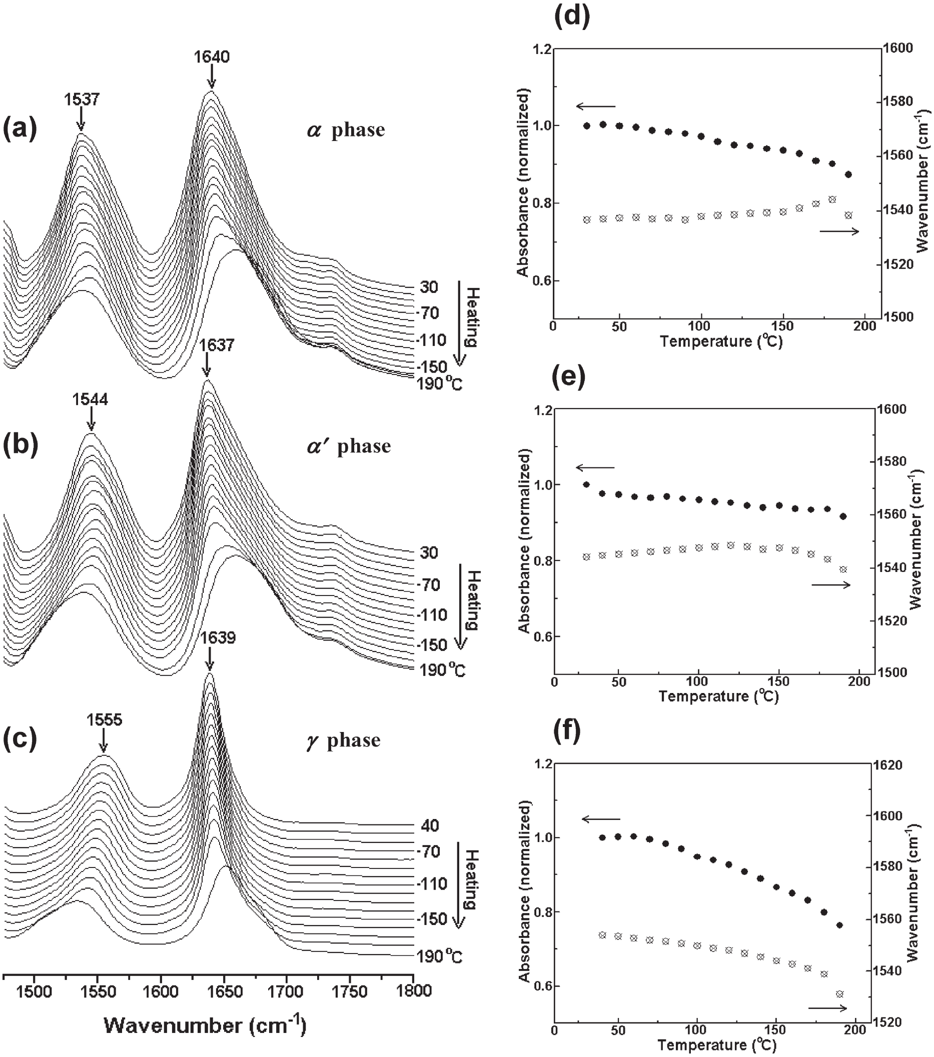

Figure 4.

Variable temperature FTIR spectra of the region 1500–1800 cm^{-1} of nylon-11 during heating from room temperature to melt: (a) α phase, (b) α' phase, and (c) γ phase. The variation of the wavenumber and normalized absorbance of amide I and amide II bands during heating for (d) α phase, (e) α' phase, and (f) γ phase.

The changes in the amide II band occurring during heating is also reflected in the amide A band and Figure 5a–c shows the variation in the spectra during heating for all the samples. The amide A band is assigned to N–H stretching vibration and is sensitive to the strength of the hydrogen bond. The contribution to the amide A comes from i) free N–H stretch at 3444 cm^{-1} ii) bonded N–H stretch at 3300 cm^{-1} arising out of crystalline fraction iii) bonded N–H stretch at 3310 cm^{-1} arising out of amorphous fraction. The region is too broad to deconvolute meaningfully into individual peaks and hence is discussed as a composite peak. The amide A band appears at 3309 and 3310 cm^{-1} for the α and α' phases respectively. In the case

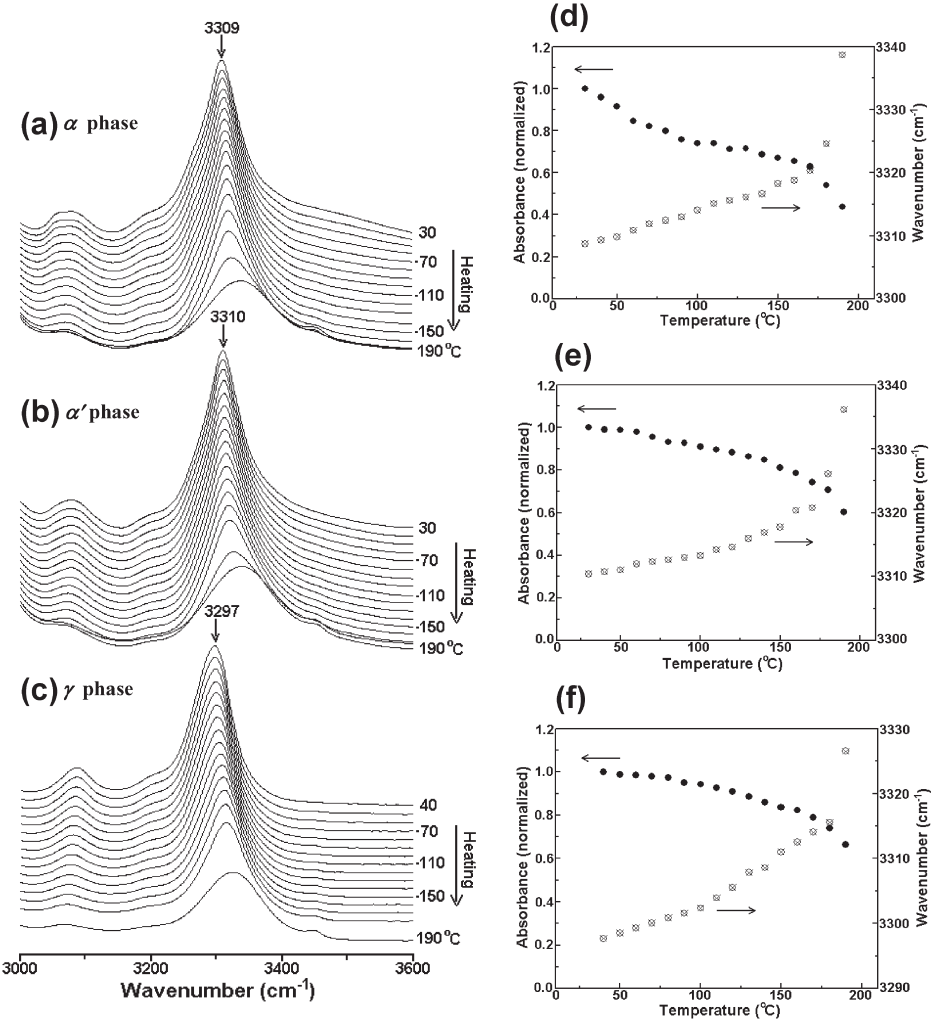

Figure 5.
Variable temperature FTIR spectra of the region 3000–3600 cm^{-1} of nylon-11 during heating from room temperature to melt: (a) α phase, (b) α' phase, and (c) γ phase. The variation of the wavenumber and normalized absorbance of amide A band during heating for (d) α phase, (e) α' phase, and (f) γ phase.

of the γ phase it shifts to 3297 cm^{-1}. Another noticeable difference between the α and γ phases is the absorbance of the amide A band in relation with the symmetric and anti-symmetric CH_2 stretch bands at 2851 and 2920 cm^{-1}.[22,25] The amide A band of the α and α' phases has comparable peak height with the band at 2920 cm^{-1} but the amide A band of the γ phase shows much reduced absorbance. The amide A band, in general is sharp and skewed and cannot be approximated to Gaussian profile. However, it may be noted that Skrovanek et al[26] observed symmetrical profile in samples cast from 1,1,1,3,3,3-hexafloro-2-propanol. Figure 5d–f shows the variation of the wavenumber and absorbance of the amide A band during heating. In the case of the α phase, the peak position shifts to higher wavenumber in a linear fashion until melting and after melting the peak shifts to

3338 cm^{-1} and the band has Gaussian profile. The normalized area decreases with increasing temperature; initially the rate is more which slows down after 90 °C. Again close to melting it decreases more rapidly. The α' phase shows similar behavior with the α phase; nevertheless minor variations are seen. The wavenumber increases with increase in temperature but more pronounced increase is at about 100 °C when the γ phase transforms into the pseudohexagonal phase. The integrated absorbance decreases progressively with increase in temperature. However, all the samples have Gaussian profile and wavenumber in the melt above 190 °C.

The WAXS studies presented above clearly indicate that the α and α' phases are distinctly different and on heating the α phase does not transform into the pseudohexagonal phase. The α' phase, however, transforms into the pseudohexagonal phase before melting. On the other hand FTIR spectra show subtle differences between these phases as highlighted in the Table 1, indicating these two phases have similar molecular conformation in the crystalline phase. The γ phase shows distinct differences in the FTIR spectra when compared with the α and α' phases. Since the conformation in the amorphous phase is expected to be the same for all the phases, the differences may be attributed to different conformation in the crystalline phase of the γ phase. In the case of nylon-6 the γ phase is obtained by KI/I_2 treatment or by melt crystallization with clay layers controlling the hydrogen bonds. In the case of γ phase obtained by KI/I_2 treatment, the iodine forms a complex with the nylon-6 and the removal of iodine from the complex leads to the γ phase.[27] In the case of nylon-11 – TFA system, in the solution the amide group in the nylon can be protonated[28,29] and can form an ion pair with TFA. During the evaporation of the solvent the ion pair disappears and the hydrogen bonding between nylon chains is gradually formed.

Conclusion

The HTWAXS and HTFTIR studies provided new information on the polymorphism of nylon-11. Nylon-11 precipitated in 1,4-butanediol crystallized in the α phase and did not fully transform into the pseudohexagonal phase on heating. Nylon-11 melt crystallized at 175 °C crystallized in the pseudohexagonal phase, and transformed into the α' phase at about 100 °C, which is different from the α phase. The γ phase transformed into pseudohexagonal phase on heating above 110 °C. Nylon 11 is the first nylon to exhibit variation in the pseudohexagonal phase packing mode depending on the starting phase.

The variable temperature FTIR studies indicated that the α and α' phases had a similar conformation in the crystalline phase. However, on heating there was variation among the phases, confirming the results of the XRD studies. The γ phase showed characteristic infrared bands at different positions from those of the α and α' phases. The differences may be attributed to different chain conformation in the crystalline phase of the γ phase. The

Table 1.
FTIR band positions for the various phases of Nylon-11

Crystalline phases	FTIR Band position (cm^{-1})							
	Amide		CH$_2$ Twisting		CH$_2$ Wagging	Amide		
	V	VI	T$_{10}$	T$_9$		I	II	A
α	686	582	1159	—	1190	1640	1537	3309
α'	686	581	1160	—	1191	1637	1544	3310
γ	709	627 595	1160	1198	—	1639	1555	3297

formation of the γ phase in nylons may be by externally regulating the hydrogen bond formation during crystallization. In the case of nylon-11, the TFA-amide ion pair controls the formation of hydrogen bonding leading to the γ phase.

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