

Investigation of Brill Transition in Nylon 6 and Nylon 6,6 by Infrared Spectroscopy

Nadarajah Vasanthan,* N. Sanjeeva Murthy, and Robert G. Bray

Engineered Material Sector Laboratories, AlliedSignal Inc., Morristown, New Jersey 07962

Received June 15, 1998

Revised Manuscript Received September 22, 1998

Introduction. Many semicrystalline polymers undergo phase transitions prior to melting.¹ The crystal to crystal transitions observed for nylons have come to be known as the Brill transition.² They belong to a general class of α transitions in semicrystalline polymers. Changes in the physical properties of the semicrystalline polymers during the α transitions are of practical importance.³ The Brill transition is easily seen in nylon 6,6 (N6,6), as the two strongest peaks at $\sim 20^\circ$ (200) and $\sim 24^\circ$ (002 + 202) in the wide-angle X-ray diffraction (XRD) scans merge into a single peak at the transition temperature (T_B).² Similar behavior was also reported for nylon 6 (N6).⁴ XRD studies in N6,6 have shown that the triclinic crystal structure at room temperature transforms into a different triclinic structure at T_B ;⁵ this high-temperature crystalline form was earlier characterized as a pseudohexagonal form. A similar monoclinic to monoclinic phase transformation has also been suggested for N6.⁴ NMR data confirm these structural changes in both N6,6 and N6.^{4,5} Although the Brill transition can be observed in the DSC scan of a solution-crystallized N6,6,⁶ it cannot be easily seen in N6, probably because T_B ($\sim 160^\circ\text{C}$) is close to its melting point (224°C). In this paper we describe our variable-temperature infrared measurements on N6 and N6,6 through the Brill transition temperature.

Experimental Section. Sample. Nylon 6 (Capron 8207 from AlliedSignal) and nylon 6,6 (Zytel 101 from Dupont) samples were dissolved in formic acid and a thin film of the polymer was cast over a KBr plate. The films were melted and slowly cooled to room temperature in the heating cell to obtain highly crystalline samples. These samples were used to observe the Brill transition. Thicker samples produced by the same method were used to estimate the crystallinity by XRD.

Infrared Spectroscopy. Infrared spectra were collected on a Fourier transform infrared spectrometer (Nicolet Magna 550) at a resolution of 4 cm^{-1} . Sets of 256 scans were used for signal averaging. Spectra were taken at selected temperatures using a variable-temperature cell. Selected IR bands were resolved using the Peak Solve fitting program (Jandell) to determine the area under the various peaks. The peaks were assumed to be Lorentzian with a linear baseline. It was found that the standard error for the areas over the temperature range used in our analysis is approximately 2–3%.

Results. Infrared spectra taken as a function of temperature for N6,6 in the frequency regions 1100–800 and 1350–1100 cm^{-1} are shown in Figure 1a,b, respectively. Infrared spectra at room temperature

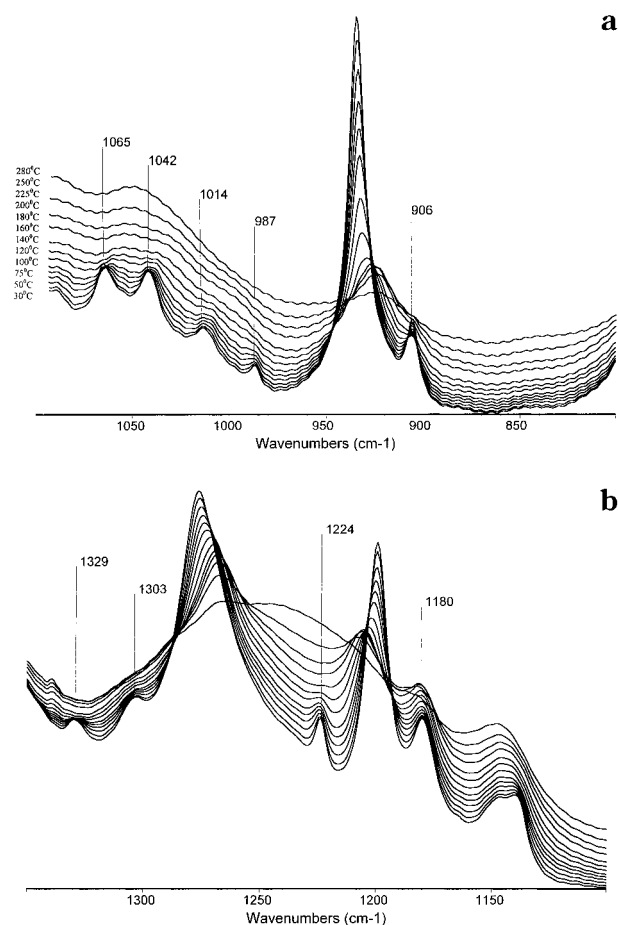


Figure 1. Infrared spectra of nylon 6,6 taken as a function of temperature from 25 to 280°C .

show bands characteristic of crystalline and amorphous components. The band assignments for N6,6 are reported in the literature.⁷ The bands at 1200 and 935 cm^{-1} are associated with the crystalline phase, while the bands at 1180 and 1144 cm^{-1} are associated with the amorphous phase. When a semicrystalline sample is heated from room temperature to the melting temperature (260°C), the sharp crystalline bands (e.g., 1200 and 935 cm^{-1}) become weaker and broader and disappear in the melt, and the broad amorphous bands (e.g., 1180 and 1144 cm^{-1}) remain essentially unchanged up to the melt. Careful examination of the spectra shows that some of the weaker crystalline bands (e.g., 1329, 1303, 1224, 1065, 1042, 1014, 987, and possibly 906 cm^{-1}) abruptly disappear between 160 and 180°C much before T_m . Comparison of the spectra obtained during heating the film to the melt and cooling (not shown) from the melt to room temperature show that these changes are completely reversible. We will call these weaker crystalline bands Brill bands because they disappear at T_B .

Figure 2 shows the integrated absorbances of the vibrational bands at 1224, 1200, and 1180 cm^{-1} , associated with the Brill transition, crystalline phase, and amorphous phase, respectively. It can be seen that the Brill band decreases in intensity with increasing temperature and reaches zero at the temperature between 160 and 180°C . On the other hand, the band associated with the crystalline phase continuously decreases in

* To whom correspondence should be addressed. Present address: TRI/Princeton, 601 Prospect Avenue, Princeton, New Jersey 08542.

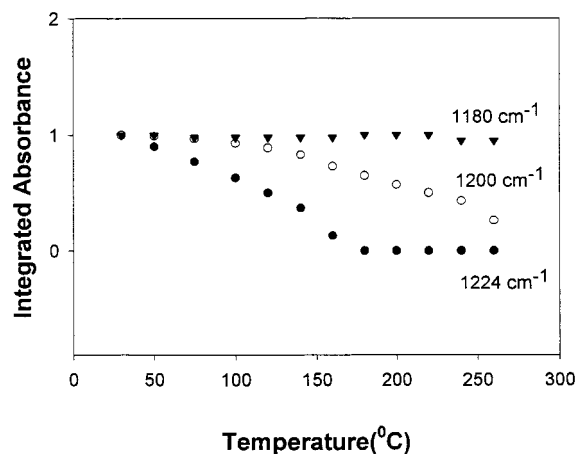


Figure 2. Temperature dependence of integrated absorbance of the bands associated with the Brill transition (1224 cm^{-1}), crystalline phase (1200 cm^{-1}), and the amorphous phase (1180 cm^{-1}).

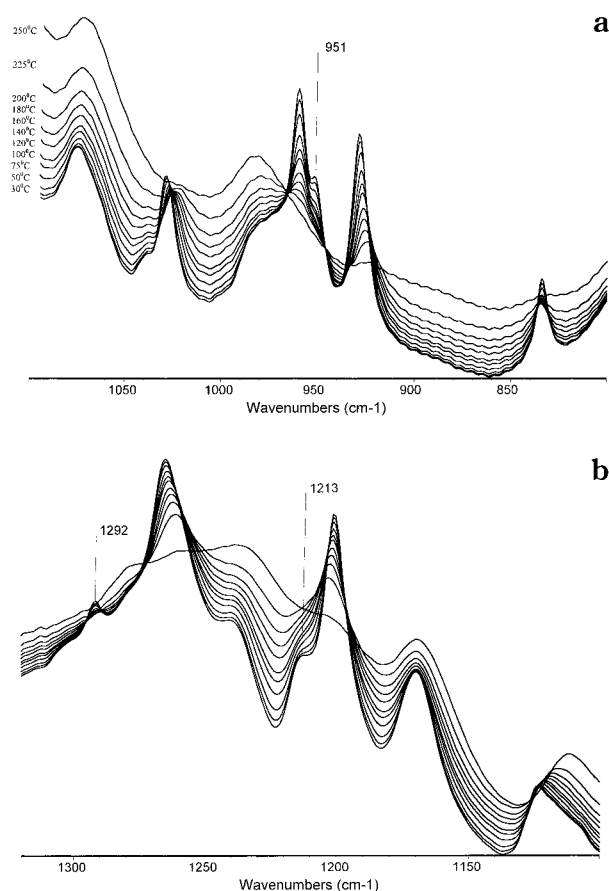


Figure 3. Infrared spectra of nylon 6 taken as a function of temperature from 25 to 250 °C.

intensity, and the band associated with amorphous phase stays almost unchanged at all temperatures up to T_m . Other Brill bands also show changes similar to the 1224 cm^{-1} band, but the broad amorphous transition underneath these bands prevented quantitative analysis of these bands.

Infrared spectra obtained as a function of temperature for nylon 6 in the frequency regions $1100\text{--}800$ and $1350\text{--}1100\text{ cm}^{-1}$ are shown in Figures 3a,b. The bands at 1200 , 1030 , 959 , and 930 cm^{-1} are associated with the α crystalline phase and bands at 1170 and 987 cm^{-1} are associated with the amorphous phase. As the

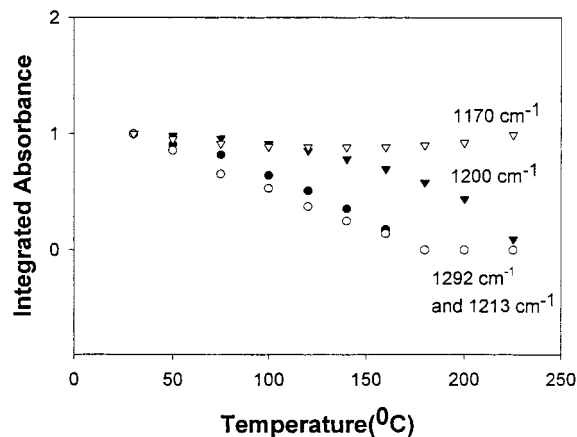


Figure 4. Temperature dependence of the integrated absorbance of the bands corresponding to the Brill transition (1292 and 1213 cm^{-1}), crystalline phase (1200 cm^{-1}), and the amorphous phase (1170 cm^{-1}).

temperature increases, the intensity of the crystalline bands decreases, similar to that observed in N6,6 and other semicrystalline polymers. Our infrared spectrum and XRD data suggest that the starting sample contains only the α crystal form. The presence of γ crystal form, if any, is negligible.

In addition to the expected changes in the infrared spectra, we observe, as in N6,6, additional changes in the bands at 1292 and 1213 cm^{-1} between 160 and 180 °C . As the temperature increases, the absorbance of these bands decreases and disappears completely at 160 °C . In analogy with N6,6, and on the basis of previously reported NMR and XRD data for N6, we associate these bands with the Brill transition in N6. Changes in the spectrum at T_B is much clearer in N6,6 than in nylon 6. Figure 4 shows the integrated absorbance of the infrared band associated with the amorphous (1170 cm^{-1}) and the crystalline (1200 cm^{-1}) phases and Brill bands (1213 and 1292 cm^{-1}) as a function of temperature. The Brill bands decrease with an increase in temperature and disappear at T_B (160 °C), while the crystalline band disappears only in the melt, and the amorphous band stays almost constant up to the melt.

Discussion. Variable-temperature XRD and solid-state NMR spectroscopic observations in N6 and N6,6 have shown that there is a change in the crystal structure during the Brill transition that occurs between 160 and 180 °C (T_B). The data presented above show that several IR bands ("Brill Bands") disappear at T_B , and this also represents the formation of a new structure, identified previously as the pseudohexagonal phase. Recent studies of the Brill transition in other nylons have shown that the details of the structural changes that occur at T_B depend on the type of nylon and crystallization conditions.^{6,8} Thus, it is not surprising that the changes in IR spectra during T_B in the N6 and N6,6 reported here are different.

The infrared spectrum for a semicrystalline sample consists of relatively sharp bands characteristic of the crystalline phase overlapping with broader bands due to the amorphous phase. The sharp bands for the crystalline component are a consequence of the restricted conformation in the crystalline phase. In contrast, because more than one energetically allowed conformation is possible in the amorphous phase, the bands due to the amorphous phase are always broader. In addition to these two classes of bands, our data show

that several rather weak infrared bands disappear at T_B , indicating significant structural changes at T_B . The numbers of vibrational bands that change during the Brill transition are few, weak, and difficult to interpret. The bands that show changes during the transition are 1329, 1303, 1224 1065, 1041, 1014, and 987 cm^{-1} for N6,6 and 1292 and 1213 cm^{-1} for N6. The bands at 1329 and 1224 cm^{-1} have been identified as "fold bands" arising from wagging and twisting modes of CH_2 groups coupled with the amide III mode CONH groups.⁹ The band at 1303 cm^{-1} is due to NH twisting, those at 1065, 1041, and 1014 cm^{-1} are the skeletal C—C stretch vibrations, and the one at 983 cm^{-1} is the NH rocking mode. The disappearance of these bands may be correlated with changes in the crystal structure at T_B . The changes in the structure may be associated with the librational motion of the methylene segments, which had been studied by deuterium NMR spectroscopy.¹⁰ Furthermore, the intensity of the crystalline band decreases continuously during heating to the melting point. Such a decrease has been interpreted in the case of polyethylene as due to "premelting" of the crystals, which includes melting of the lamellar surface and smaller lamella within the lamellar stacks.¹¹

Changes in the spectrum at T_B are more prominent for N6,6 compared to N6. We observed seven weak bands that undergo changes at T_B in N6,6 whereas only three bands undergo significant changes at T_B for N6. It is possible that the more complex spectra in N6 (due to the absence of center of symmetry that is present in N6,6) tends to mask the small changes at T_B . In addition, T_B (160–180 °C for both N6 and N6,6) is much closer to the melting point in N6 (224 °C) than in N6,6 (260 °C). It could also be because there is only one type of methylene segment in N6, while N6,6 has two different types. The line shape analysis of the deuterium NMR spectrum of N6,6 showed that below T_B , the methylene groups in the hexamethylenediamine moiety have less motional averaging than the methylene groups in the adipoyl moiety.¹⁰ Above 160 °C, the line shapes of all of the methylene groups appeared to be the same. The increase in the motional averaging of the hexamethylenediamine moiety above 160 °C could be associated with the disappearance of the Brill band that we observe in our IR data. Thus, the disappearance of the Brill bands may be due to local "melting" of the methylene segments, which makes the librational mo-

tion possible. Also, the chemical shifts of the new peaks observed in CP/MAS spectra of N6 at temperatures above 100 °C suggest that the conformational changes at T_B are small and are more likely to result from the differences in the packing of the crystalline segments within the lamellae.^{4,12}

To see the effect on hydrogen bonding during the Brill transition, we monitored the band shifts of the amide I (C=O stretching) vibration and N—H stretching vibration as a function of temperature for N6 and N6,6. Although we observed systematic shifts in the N—H stretching and C=O stretching vibrations with temperature, the discontinuities in these frequency shifts at T_B were not meaningful. This indicates that there is no significant change in the hydrogen bonding during the Brill transition and that hydrogen bonding is maintained up to the melting temperature.⁵

Conclusion. We report here the first observation of the changes in the infrared spectra of N6 and N6,6 at the Brill transition temperature. The disappearance of a sequence of bands, which we identify as "Brill bands", is more apparent in N6,6 than N6. These changes can be attributed to the onset of librational motions that bring about changes in interchain interaction (packing) rather than large scale conformational changes.

References and Notes

- (1) Turi, Edith A. *Thermal Characterization of Polymeric Materials*, 2nd ed.; Academic Press: New York, 1997.
- (2) Brill, R. *J. Prakt. Chem.* **1942**, 161, 49.
- (3) Aharoni, S. M.; Sibilia, J. P. *J. Appl. Polym. Sci.* **1979**, 23, 133.
- (4) Murthy, N. S.; Curran, S. A.; Ahroni, S. M.; Minor, H. *Macromolecules* **1991**, 24, 3215.
- (5) Hirschinger, J.; Miura, H.; Gardner, K. H.; English, A. E. *Macromolecules* **1990**, 23, 2153.
- (6) Ramesh, C.; Keller, A.; Eltink, S. J. F. A. *Polymer* **1994**, 35, 2483.
- (7) Jakes, J.; Krimm, S. *Spectrochim Acta* **1971**, 27A, 19.
- (8) Atkins, E. D. T.; Hill, M.; Hong, S. K.; Keller, A.; Organ, S. *Macromolecules* **1992**, 25, 917.
- (9) Koenig, J. L.; Agboatwalla, M. C. *J. Macromol. Sci., Phys. B2*, **1968**, 391.
- (10) Miura, H.; Hirschinger, J.; English, A. D. *Macromolecules* **1990**, 23, 2169.
- (11) Tanabe, Y.; Strobl, G. R.; Fischer, E. W. *Polymer* **1986**, 27, 1147.
- (12) Hatfield, G. R.; Glans, J. H.; Hammond, W. B. *Macromolecules* **1990**, 23, 1654.

MA980935O