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X-ray Determination of the Thermal Expansion Coefficient of Nylon 6,6 Fibers

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Abstract: *The thermal behavior of commercially available nylon 6,6 fibres has been analysed using wide angle X-ray diffraction data, collected in the temperature range 25 - 225 °C. The three axial directions a, b and c- characterized by concentrations of hydrogen bonds, van der Waal's interactions and covalent bonds respectively, respond differently to heat treatment. The crystallographic c- axis corresponding to the fiber axis, registers a contraction during heating and an expansion in the return cooling cycle. In a single heating and cooling cycle, a residual contraction of ~1.8% in the c-length is observed. The a- length manifests little change with heat treatment and in contrast, the b-axial length of the basal plane increases during heating, within the respective structure, be it triclinic or hexagonal. The unit cell volume increases with heating. The increase in crystallinity observed during heating matches with the suggested growth of crystallites and/or reduction in microstrain. All the structural parameters manifest a thermally induced hysteresis and also a sudden large change at ~125°C and 75°C respectively during heating and cooling respectively. The latter feature has been associated with structural transformations.*

Keywords: *Nylon 6,6, X-ray diffraction, thermal expansion coefficient.*

1. INTRODUCTION

Nylon 6,6 is among the very early set of man-made fibers developed[1] in the 30's. Nylons, in general have a range of applications, which includes limited use at high temperatures also. The service temperatures recommended for nylons range from 69 - 235°C[2]. Thermal expansion coefficient is an important property of any material, more so, for materials recommended for use at elevated temperatures. For a material commercialized nearly seven decades ago, data on the value of thermal expansion coefficient can be expected to be text book information and is indeed so. For nylon 6,6 the coefficient of linear thermal expansion reported in literature is ~1.0×10^{-4}/°C [3,4] and it refers to the macro thermal expansion. There could, however, be difference between the macro thermal expansion and the behavior at the level of crystal lattice. Such a difference is, understandable because the macro value refers to the polymeric sample as a whole, which invariably includes a less crystalline or amorphous fraction, defects of various types etc., whereas the X-ray data pertain to the crystalline fraction. A comparison between the crystalline and macro thermal expansion coefficients will indeed be useful in understanding the correlation between the two. It must be

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mentioned that our earlier X-ray investigations[5] on the aromatic polyamide Kevlar, established the difference in the thermal expansion behaviors of the polymer chains in the crystal lattice and the macro fibre. The axial thermal expansion coefficient of the polymer chains in the crystal lattice of Kevlar was found to be more negative than the value reported for the entire fiber.

The high temperature behavior of nylons, in general, has been a topic of interest and a large number of high temperature X-ray investigations on nylon 6,6 in particular, have been reported[6-17]. At this juncture, it may be appropriate to mention very briefly about few of these high temperature X-ray investigations. The oft-quoted work of Brill[6] concerns the triclinic (Tr) to hexagonal (H) structural transformation for melt-crystallized samples. Schichter[7] reports the thermally induced distortion of the unit cell. Colclough and Baker[8] describe the polymorphism in nylon 6,6. Itoh and Konishi[9] and Itoh *et al.*[10] have studied the solution grown crystals at elevated pressures and temperatures. Ramesh *et al.'s* [11] work concern the role of crystallization temperature on the Brill transition. A comparison of the temperature induced structural changes in few nylons has been reported by Radusch[12]. Hsiao *et al.*[13] have carried out synchrotron, online investigation on the structure and morphology development during continuous drawing of nylon 6,6 fibers at various temperatures. Murthy *et al.*[14,15] have studied the pre-melting crystalline relaxations, interactions between amorphous and crystalline domains. Ishikawa *et al.*[16] have examined the temperature dependence of crystal structures of several even-even nylons. Jain and Vijayan have analysed the effect of thermal aging on the crystal structural characteristics[17].

Much of the earlier work concerns the Tr – H structural change associated with the Brill transition. Influence of parameters like draw ratio, crystallization temperature etc on the structural characteristics have also been studied[11, 13]. Explicit analysis of the X-ray thermal expansion behaviour, however, seems to have received comparatively less attention. Murthy *et al.*[15] have derived the thermal expansion coefficient of the amorphous segments of nylon 6,6 in a semi crystalline sample, as $5.9\times10^{-4}/°K$, using small angle X-ray data. Jayanna and Subramanyam[18] have examined the thermal expansion behavior of gamma-irradiated nylon 6,6 in the temperature range 10 to 340° K. The present study is concerned with the elucidation of X-ray thermal expansion coefficient of commercially available, nylon 6,6 fibers using wide angle X-ray diffraction data collected with in situ heating, in the temperature range 25 to 225°C. In particular, attention has been focused on the behavior of the axial lengths of the crystallographic unit cell. Few other crystal structural changes, which accompany thermal treatment, have also been examined. It may be pointed out that although Ramesh et al[11] and Murthy et al[15] have dealt with both heating and cooling parts of a thermal cycle, the X-ray thermal expansion coefficients during both heating and cooling of nylon6,6 fibers have been compared for the first time, only in the present study.

2. EXPERIMENTAL

Nylon 6,6 fibers were obtained from M/s Goodfellow. A bundle of fibers ~ 0.3mm thick was held taut in the high temperature attachment for fibers supplied by M/s

Rigaku International Corporation, Japan, for the D/MAX 2200 Ultima X-ray powder diffractometer. CuKα radiation, scintillation counter and a monochromator in the diffracted beam were used to record the patterns at room temperature (~25°C) and at temperatures (T) 50, 75,100,125, 150, 175, 200 and 225°C, both during heating and cooling. The heater assembly consisted of a semi cylindrical metal foil surrounding the fibre sample. A chromel - alumel thermocouple placed near the sample measured the temperature. Heating rate was 5 °C per minute and after reaching the desired temperature, 10 minutes were allowed to stabilize. Fluctuation in temperature during the recording of any pattern was ±0.5°C. To distinguish between the two room temperature patterns viz., recorded prior to heating and that after a heating and cooling cycle respectively, the notations RT1 and RT2 are used.

Presence of the heater assembly necessitated the use of the θ_{fixed} mode for recording the patterns. All the patterns were recorded with $\theta_{fixed} = 5°$. Equatorial and meridional patterns were confined to the 2θ ranges of 14 to 31° and 34 to 43° respectively. Selection of such limited ranges was primarily to focus attention only on the intense reflections expected from nylon 6,6. Indexing of reflections was based on the crystal structure reported earlier[19]. Characteristics of individual diffraction profiles were derived by using the multi peak separation package utilizing a pseudo-Voigt function, supplied with the Rigaku diffractometer. In the case of some of the equatorial patterns where the initially distinct diffraction profiles merged into a single profile, multipeak separation could be effected only with the package Sigmaplot, version 9.0[20]. The equatorial and meridional patterns included three reflections each in the chosen 2θ ranges. Although the number of observed reflections was low, it was nevertheless sufficient to derive all the parameters of a triclinic unit cell, by combining the experimentally derived parameters with appropriate formulae[21]. The estimated standard deviations for the 2θ values range from 0.02 to 0.09°. The higher values of the standard deviations are in general, for the angles obtained by deconvolution of a single profile into three independent ones, by using the Sigma plot package. Although the standard deviation is rather high for these data sets, they appear reliable enough to indicate the trend.

It must be mentioned that the data used in the present study pertain to a single heating and cooling cycle (RT1→T→RT2) with no intermediate excursion to ambient conditions. Thus, the influence of abrupt drop to room temperature, often accidental, on the sample has been consciously avoided.

3. RESULTS AND DISCUSSION

3.1. Shift and Merging of Profiles

(a) *Equatorial*

Figure 1 shows some of the equatorial profiles. Based on the triclinic (Tr) unit cell of dimensions $a = 4.9$, $b = 5.4$, $c = 17.2$ Å, $\alpha = 48.5$, $\beta = 77$ and $\gamma = 63.5°$ given by Bunn and Garner[19], the observed maxima at $2\theta \approx 20.2$ and 23.3° in Figure 1 have been indexed as (100) and ((010)+(110)) respectively. Here, the + sign refers to overlap of reflections. The patterns corresponding to T = 50, 75 and 100 °C during heating and 75, 50 °C and

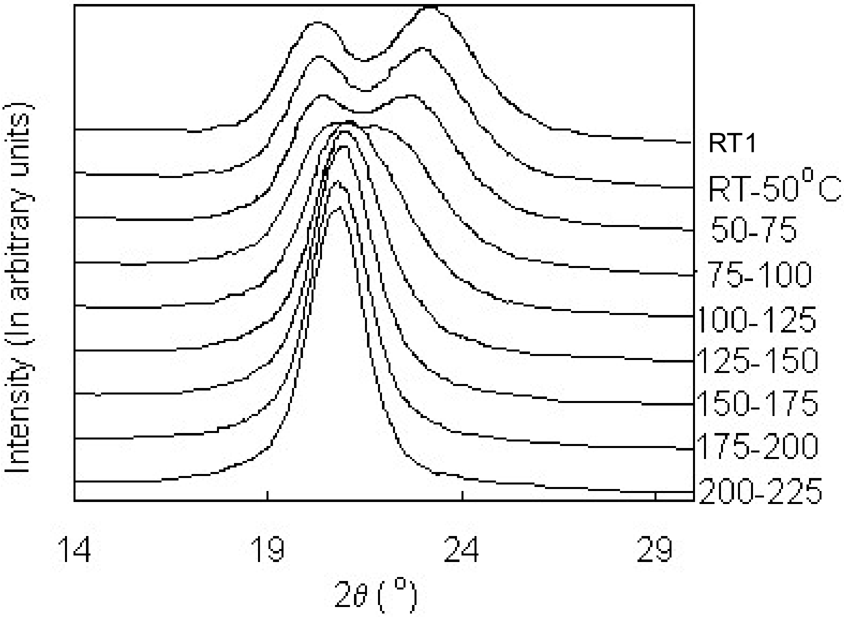

Figure 1a: Composite Diagram Showing the Equatorial Diffraction Profiles during Heating

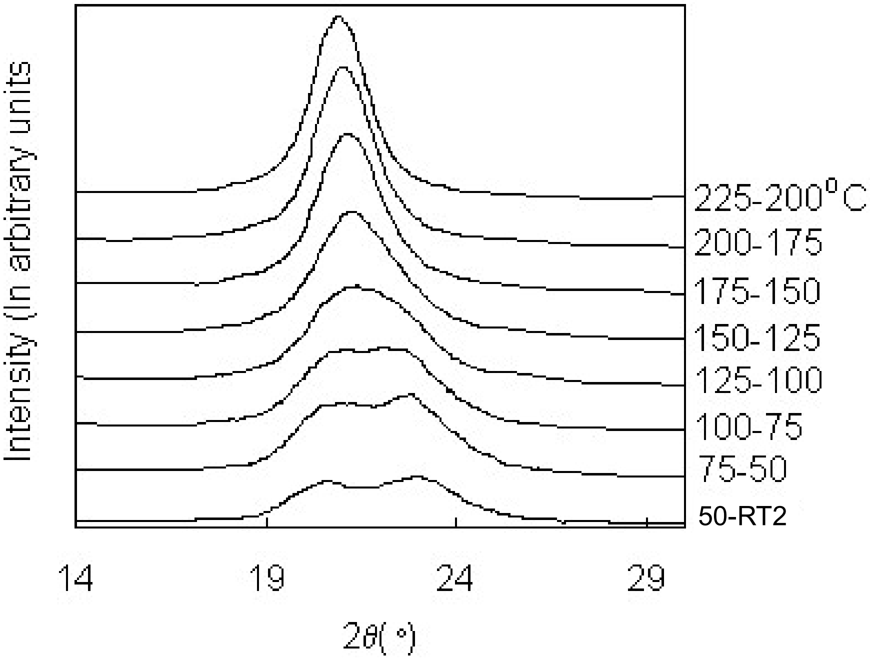

Figure 1b: Composite Diagram Showing the Equatorial Diffraction Profiles During Cooling

RT2 during cooling are similar to the pattern recorded at RT1 thereby suggesting that the initial structure is substantially retained at these temperatures. At the rest of the temperatures, the two diffraction maxima characteristic of RT1, merge into a single peak. Major contribution to the merger arises from the shift towards lower angle of the second reflection at $2\theta \approx 23.3°$. During heating, the merger observed first at 125°C persists up to 225 °C and while cooling, the single profile is retained upto 100 °C beyond which , it splits into two different maxima, similar to the pattern at RT1. The merging of reflections, which is part of both the heating and cooling cycles, conforms well with the structural transformation to a hexagonal (H) crystal system, reported earlier for nylon 6,6. This is also the well-known Brill transition mentioned earlier[6]. A hexagonal system necessitates the merging of (100), (010) and (110) reflections. Thus, in a single heating and cooling cycle, the nylon 6,6 sample gets characterized by two crystal systems Tr and H in the order Tr (heating) → H (cooling) → Tr. It is interesting to note that the temperature at which the merger corresponding to the Tr → H transformation takes place during heating, viz., 125 °C is higher than the temperature, 75 °C, at which the demerger or splitting corresponding to the reverse, H → Tr transformation takes place during cooling. Such a difference suggests thermally induced hysteresis indicative of different rates at which the changes occur during heating and cooling respectively. Ramesh et al [11] have also reported a hysteresis in the d-spacings recorded from samples crystallized at various temperatures where they deal with an initial hexagonal Brill structure changing to triclinic during cooling.

Some of the earlier studies [9,10,12,13,16] contend that the merger of reflections is not due to a Tr → H structural, Brill transition but is a result of anisotropic thermal expansion of the triclinic unit cell. According to Hsiao et al, the initial triclinic structure persists above the Brill transition temperature also. Ishikawa et al also mention that the Brill transition reported for nylons is not a phase transition, but an abrupt thermal expansion. Although such anisotropic thermal expansion of a triclinic cell leading to an ideal hexagonal symmetry appears rather fortuitous, it is not impossible because the crystal structure of nylon 6,6 is characterized by concentration of distinctly different types of bonds along the axial directions of the unit cell. It is found that the axial directions *a*, *b* and *c* correspond to concentration of hydrogen bonds, van der Waal's interactions and covalent bonds respectively. Such a structural anisotropy can indeed evoke differences in their response to changes in temperature and α consequent anisotropy in the thermal expansion behaviour. In particular, the β-direction corresponding to concentration of inter layer, van der Waal's interactions can be expected to expand more than the *a*- or *c*- dimensions. The comparatively higher shift observed in the present study, for the reflection (010) towards lower angle, does indeed favour this view. However, the unit cell dimensions, to be described subsequently in this paper, do not provide conclusive evidence that an anisotropic thermal expansion has led to an ideal hexagonal structure and a consequent merger of the equatorial reflections. The present study has therefore been carried out based on the former view viz., the thermally induced Tr (heating) → H (cooling) → Tr transformations are responsible for the merger and demerger of the equatorial reflections respectively.

(b) *Meridional*

The meridional patterns include the reflections (017), (127) and (027) occurring at 2θ values of 37.5, 38.6 and 40.4° respectively. The first two reflections overlap to form a single, broad profile. In contrast with the equatorial pattern, there is no temperature-induced merger of meridional reflections. However, the angular separation between the two observed maxima registers changes, which could be attributed, primarily, to thermally induced variations in the unit cell parameters. It may be mentioned that in the case of the aramid fiber Kevlar, similar changes in angular separation of equatorial reflections were correlated with variations in the tensile strength of the fiber[22].

3.2. Axial Dimensions – Anisotropic Behavior

In the crystal structure of nylon 6,6, the crystallographic *c*-axis is the fiber axis. Figure 2 shows the variation of the *c*-axial length with temperature. Heating and cooling are accompanied by contraction and expansion respectively, along with a suggested hysteresis. The *c*-lengths corresponding to the two room temperatures RT1 and RT2 differ by ~1.8%, which is the residual effect of a single heating and cooling cycle. Decrease of this order in the axial dimension of the polymer suggests that minor, localized changes from the initial all trans conformation of the poly (hexa methylene adipamide) or PHMA chains of which nylon 6,6 is made of, are perhaps introduced during the heating and/or cooling cycle and the changes are not fully recovered on returning to ambient conditions. Conformational changes of this type can indeed affect

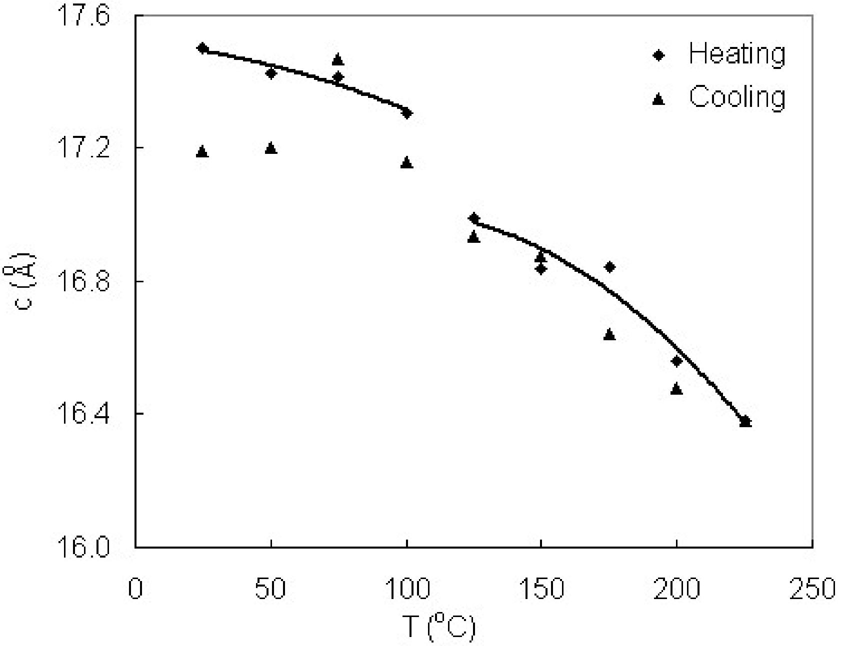

Figure 2: **Variation of The c-axial Length with T. The Discontinuity in The Line Corresponds to The Region of Large Change**

the initial tensile characteristics of the fiber. Our earlier studies on the effect of thermal aging of nylon 6,6 provide evidence for such a correlation between deterioration in tensile properties and heat treatment[17]. It may also be mentioned that in the case of the aramid fiber Kevlar, excursion to low temperatures up to -100 °C led to ~ 2.5% reduction in the initial, fiber axial length of the polymer[23]. Thus, the temperature induced hysteresis in the fiber axial length seems to be a feature common to both aliphatic and aromatic polyamides.

Figure 2 also shows that in the course of heating as well as cooling, a sudden, large change in the *c*-value occurs in the region 100 → 125 °C and 100 → 75 °C respectively. Such behaviour suggests possible structural changes, which as mentioned earlier, are of the Tr - H type, occurring at these temperatures. Hsiao et al[13] have also observed such large changes in unit cell dimensions during heating and they attribute such 'step-changes' to a pre melting of small crystals and a subsequent anisotropic expansion of the remaining larger crystals. It must be pointed out that as per the present data, step-changes are characteristic not only of heating but also of cooling. Associating the concept of premelting to cooling does not appear quite acceptable. In contrast, a reverse H → Tr transition accompanying cooling can well account for the observed large change in the cell dimension.

Figure 3 presents the variation of the thermal expansion coefficient, $\alpha_{c,}$ with *T* calculated using the *c*-values depicted in Figure 2. The α_c values pertaining to the heating and cooling parts of the cycle are calculated with respect to the values *c* (RT1) and *c* (225°C) respectively. Interestingly, α_c is not constant during either heating or cooling. As could be expected, during heating, α_c is negative. It gets more negative with increase in temperature and then nearly stabilizes at ~200 – 225°C. Cooling is characterized by a progressive increase in the α_c value. The average values of α_c during heating and cooling are -2.5×10^{-4} / °C and 3.4×10^{-4} / °C respectively. The thermal expansion coefficient of $\sim 1 \times 10^{-4}$ / °C reported[3,4] for the entire fiber, during heating, is indeed different and could be attributed to the presence of less crystalline fraction, impurities etc in the fiber, whose response to temperature could vary from that of the crystalline fraction. The α_c values presented here represent the behavior of the crystalline fraction only. There is also a remarkable similarity in the behavior of nylon 6,6 and the aramid fiber Kevlar. In both the cases, the X-ray thermal expansion coefficient during heating is more negative than the macro thermal expansion coefficient.

Figures 4 and 5 depict the effect of temperature on the basal plane dimensions *a*- and *b*- respectively. But for a cusp at ~125 °C (Figure 4), the *a*- length manifests very little change during either heating or cooling. In the crystal structure of nylon 6,6 the *a*- axis is characterized by a concentration of inter chain hydrogen bonds. The near retention of the *a*- length could be associated with the intrinsic propensity of most polyamides to form and retain the inter chain hydrogen bonds which act as a scaffolding in the respective crystal structures [24]. In the case of the aramid Kevlar, such a propensity was found to persist even at temperatures very close to its decomposition temperature of 500 °C [25]. The cusp seen at ~ 125 °C provides further support for the structural transformation referred to earlier.

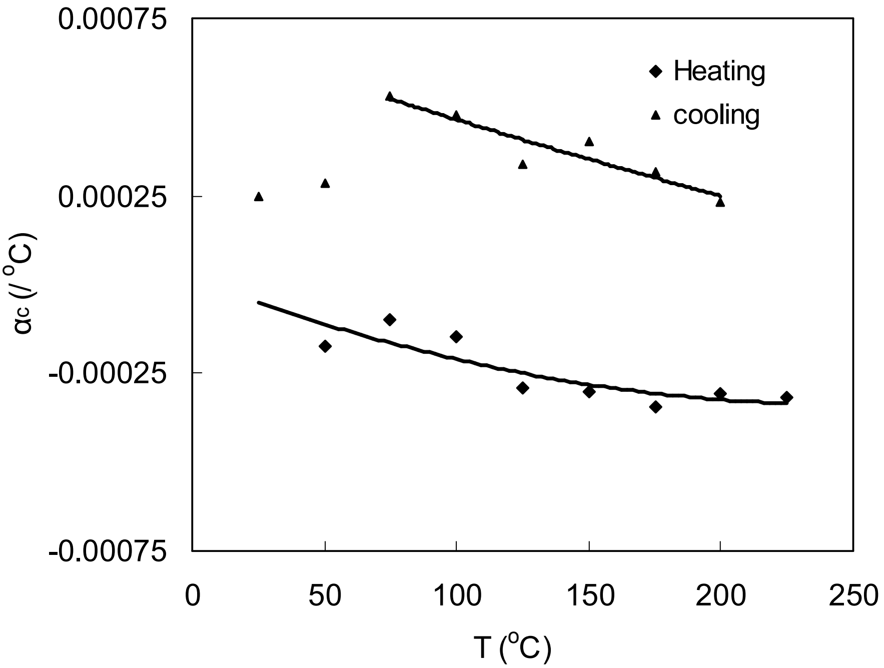

Figure 3: Variation of α_c with T

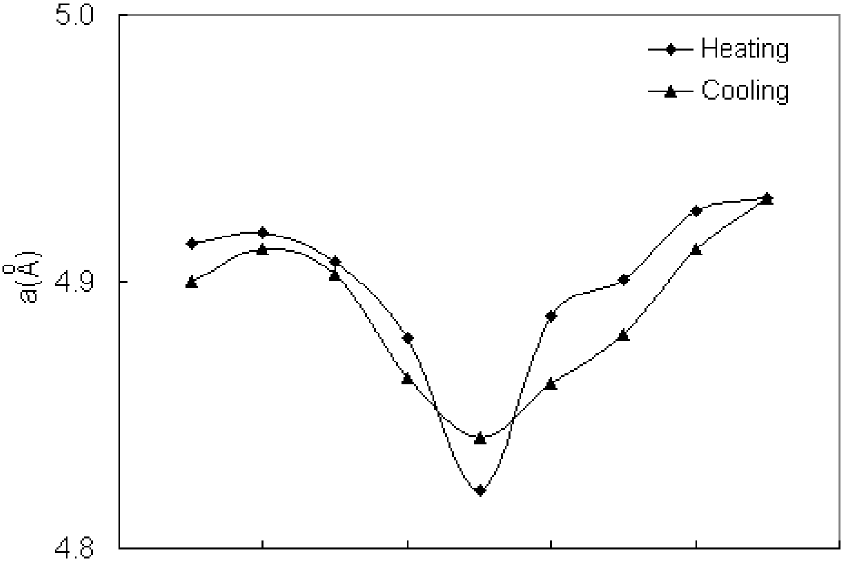

Figure 4: Variation of *a*- length with T

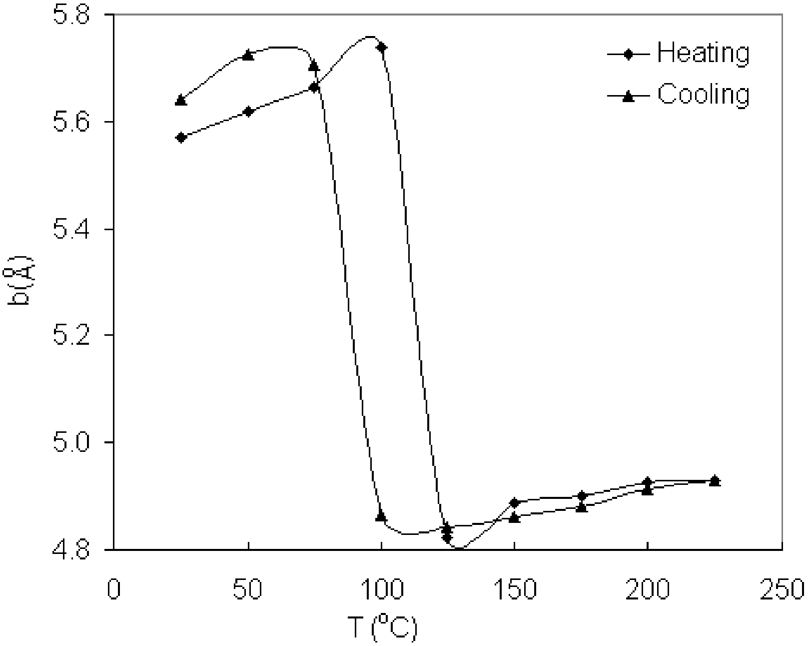

Figure 5: Variation of *b*- length with T

In contrast with the *a*-dimension, the b-length manifests conspicuous changes (Figure 5). The difference in the behavior of the two basal plane dimensions *a*- and *b*- may be correlated with the difference in the types of bonds distributed along these directions viz., hydrogen bonds and van der Waal's interactions respectively. During heating, the *b*-length increases, irrespective of the structure being Tr or H and vice versa during cooling. The sudden, large changes in the *b*-value observed at ~ 125 and 75 °C and the hysteresis are very similar to the behavior of the *c*-axial length. It is also found that b_{RT2} is > b_{RT1} by 1.2%. The basal plane area increases with heating in the respective Tr and H structures. As a consequence, despite the contraction of the fiber axial dimension, the unit cell volume registers an overall increase during heating and contraction during cooling (Figure 6) along with a hysteresis. Table 1 compares the contrasting behavior of the volume and axial thermal expansion coefficients.

The possibility of a triclinic crystal structure being retained at all stages of heating and cooling has also been examined in the present study. In a 'triclinic all along' situation, as mentioned earlier, the merger of reflections is due to fortuitous, anisotropic behavior of the unit cell leading to an ideal hexagonal symmetry. The triclinic cell dimensions corresponding to 125°C and beyond, during heating and upto 75 °C during cooling does not, however, provide evidence for a perfect hexagonal symmetry. Large deviations from the ideal hexagonal symmetry are found to exist. Thus, the present analysis favors the Tr - H - Tr transformations more than an all-triclinic structure during heat treatment.

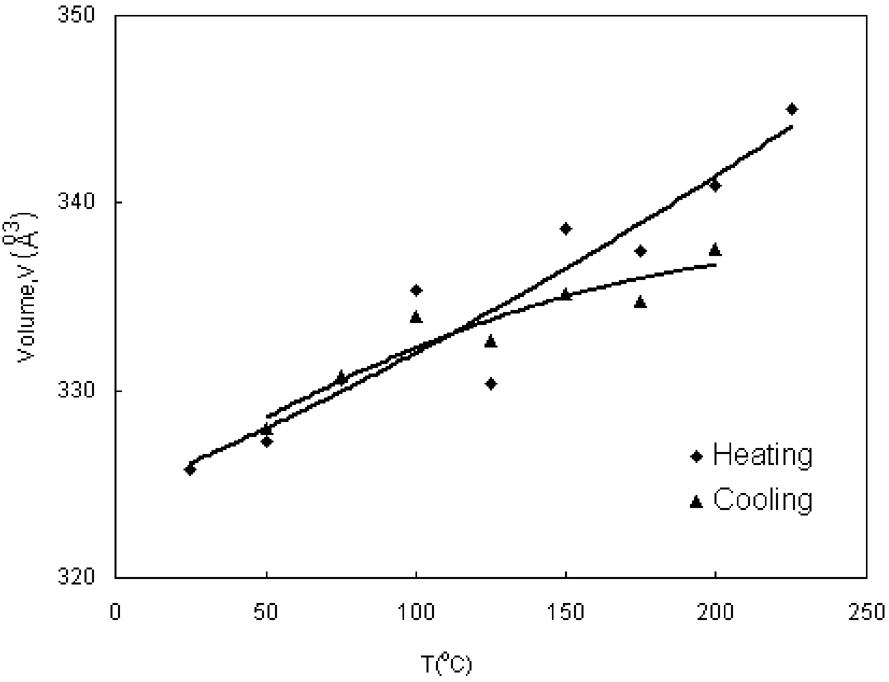

Figure 6: Variation of Unit Cell Volume, V with T

Table 1
The Contrasting Behavior of the Volume and Axial Thermal Expansion Coefficients

Parameter	*Heating*	*Cooling*
$\alpha_v \times 10^4$/°C	3.874	-1.769
$\alpha_c \times 10^4$/°C	-2.477	3.416

3.3. Crystallinity

Using the well known correlation between X-ray integrated intensity and crystallinity[26], the residual crystallinity, k/k_0, at various stages of heating and cooling have been estimated (Figure 7), using the equatorial intensities. Here, k_0 and k represent the crystallinity values prior to and after heat treatment respectively. Interestingly, the crystallinity increases with heating. The improved crystallinity also coincides with the growth of crystallites suggested by the half width values, the details of which are presented in the next section. The noticeable feature is the large change in crystallinity in the vicinity of 125 °C, providing further support for a structural change. The earlier observed hysteresis in unit cell lengths is manifested by crystallinity also. In a single heating and cooling cycle, ~9% reduction is found to occur.

3.4 Half Widths

Figure 8 depicts the fractional variation in the half width of the overlapping equatorial reflections. Here w_0 and w refer to the values prior to and after heat treatment respectively. As in the case of crystallinity, the 125- 225 -125°C regions correspond to sharpening or growth of crystallites and/or reduction in microstrain. The half width values manifest hysteresis and also provide evidence for structural transformations.

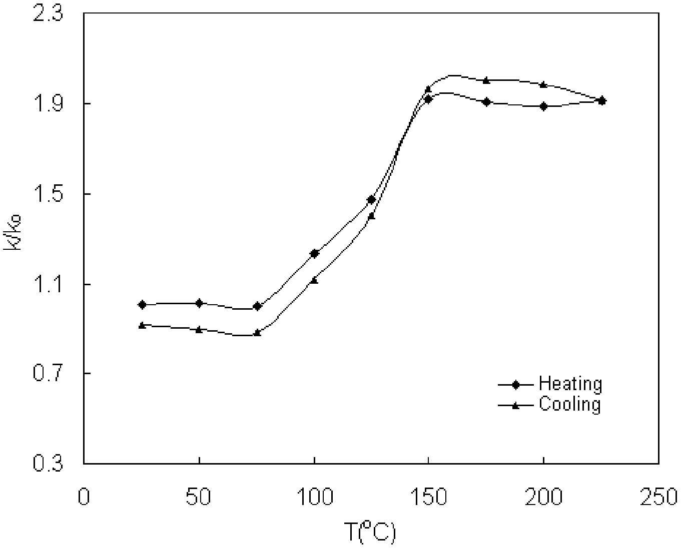

Figure 7: **Variation of the Residual Crystallinity, *k*/*k*$_0$ with T**

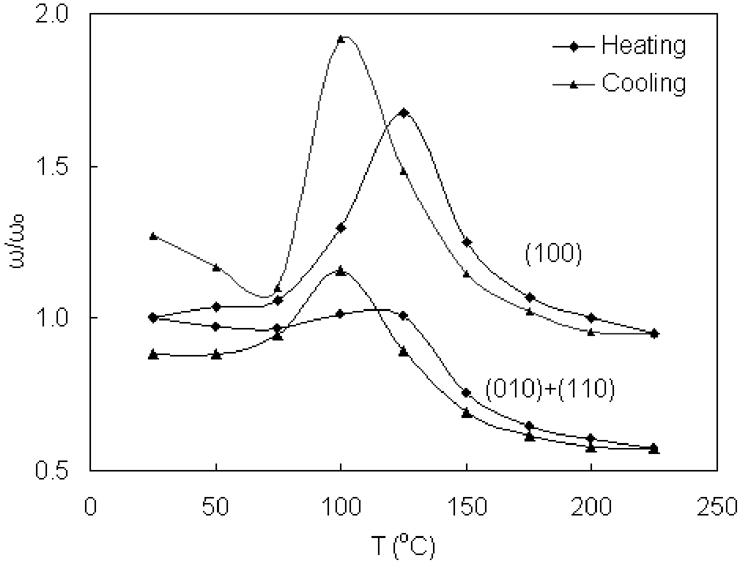

Figure 8: **Fractional Value of Half Widths of Equatorial Reflections versus T**

4. CONCLUSIONS

X-ray diffraction data collected with in situ heating from 25 to 225°C and subsequent cooling have been analysed on the basis of structural transformations of the type Triclinic(heating) → Hexagonal(cooling) → Triclinic. All the crystal structural parameters manifest a conspicuous hysteresis. In addition, a large change in structural parameters observed at ~125°C during heating and ~75-100°C during cooling favour the structural transformations mentioned above. The *c*-axial length corresponding to the fibre axis and hence a concentration of covalent bonds, contracts during heating and in contrast, expands during cooling. At the end of a single heating and cooling cycle, the c- length suffers a residual contraction of ~1.8%. The X-ray, axial thermal expansion coefficient observed during heating is $-2.477 \times 10^{-4}/°C$ compared to the value $\sim 1 \times 10^{-4}/°C$ reported for the macro fiber. The *b*- length of the unit cell, corresponding to a concentration of van der Waal's interactions expands during heating, irrespective of the phase. The *a*- length characterized by the inter chain hydrogen bonds is little affected by heat treatment. Despite the axial contraction, the unit cell volume registers an overall increase with temperature and a corresponding decrease with cooling. The increase in crystallinity observed during heating matches with the increase in crystallite dimension and/or reduction in microstrain.

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