

POSITRON LIFETIME STUDY OF THERMALLY INDUCED MICROSTRUCTURAL CHANGES IN NISTARI SILK FIBER

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Abstract Positron lifetime measurements have been made in natural polymer-Nistari silk fibers as a function of isochronal annealing temperature in the range of 27°C to 280°C. The variations in the positron results indicate the structural changes occurring in the Nistari silk fibers and determine the glass transition temperature as 170°C. Activation energies were measured separately for the crystalline and amorphous regions indicating the versatility of the technique. These values are close to the N—H bond dissociation energy, suggesting N—H bond dissociation as the most probable process occurring during thermal treatment. As an extension of the positron results, the molecular weight of the Nistari silk fibers was determined to be 10.7×10^5 based on free volume, which lies within the range suggested for the silk fibers. There seems to be an indication that cross-linking changes the spiral structure of cotton fibers to network type. However, this needs to be validated by other techniques.

Key words Nistari silk fiber, Positronium, Free volume, Molecular weight, Activation energy

INTRODUCTION

The mechanisms that control membrane permeability are most important in the function of biological membranes. Large domains of proteins existing in the biological lipid bilayer membranes are known to control the permeability of chemical substances^[1]. Natural polymers like silk fibers are continuous high molecular weight fibrous proteins consisting of many kinds of amino acids. These are produced by different species of silkworms of which the principal species is *Bombyx mori* or mulberry silkworm^[2]. From the applications point of view, these are excellent biomaterials for enzyme-immobilized membranes used as biosensors. This property is due to the insolubilization of the silk and immobilization of the enzyme. These factors are mainly due to the conformational transition of silk fibroins from water-soluble random coil to water insoluble silk II in the absence of any chemical reagent^[3]. It is of interest to note that silk fibroin is presently being tested as blood compatible material^[4]. In particular, the pure state of protein can be obtained from silk so that its study will be helpful for the improvement of silk quality but also in the manufacturing of synthetic fiber using silk as a model^[4]. Because of these special properties, and their importance in industrial and bio-related applications, recent research activity has been focused on the structural studies of silk fibers.

Silk has a high elastic modulus with a limited though useful extensibility and high strength in both its dry and its wet states mainly due to its peculiar microstructural characteristics such as crystallinity, strong hydrogen bonds between C=O and N—H groups of adjacent molecules and content of bulky side chains^[5]. Silk being a natural polymer is a polypeptide made up of four amino acids, namely glycine, alanine, serine and tyrosine, of which the major contributors are glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) and alanine ($\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$). Silk is hygroscopic in nature and its moisture regain is around 11%. If silk contains a high degree of moisture, its tenacity and

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number of breaks during winding, doubling and warping in the process of weaving are decreased and the feeling of silk becomes soft.

Multivoltine races of silk fiber like Nistari has lesser denier compared to cross breed races of silk fiber like bivoltine. Nistari silk fiber is one of the popular Indian silks distributed in eastern parts of India. Similar to bivoltine fibers, Nistari fibers show significant improvement in crystal size with annealing temperature. The sericin content in Nistari fiber is greater (about 25%) compared to bivoltine race, suggesting the protection of the fiber is better and it cannot be easily damaged. The X-ray diffraction (XRD) studies of Nistari silk reveal the presence of both amorphous and crystalline regions, suggesting its semicrystalline nature and more amorphous than bivoltine. Sericin is a kind of protein mainly consisting of shapeless particles and it is more soluble than the fibroin in water because of the highly hydrophilic amino acid molecules. These are globular and have irregular and diffusely formed structure.

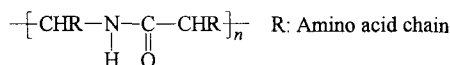
Natural fibers are readily biodegradable, abundantly available, and eco-friendly. In contrast, synthetic fibers are durable, sustainable but not biodegradable in the environment, thereby causing pollution after their end use. It is therefore necessary to improve the characteristic properties of these natural fibers by various physical and chemical treatments^[6]. From the positron annihilation studies on bivoltine silk fibers, we learnt that the random coil form of silk fibroin^[7] changes from silk I type (α form) to silk II type (β form)^[8, 9] under the influence of temperature^[10], UV irradiation^[11] and tensile stress^[3]. Motivated by these interesting results of bivoltine silk fibers, the author has extended the positron annihilation studies to Nistari silk fibers with specific interest in investigating the influence of sericin content on the T_g , melting point and other conformational changes in this silk fiber. The purpose is to understand the thermal behavior of the silk fibers at molecular level in terms of free volume fraction using a novel technique such as Positron Lifetime Spectroscopy (PLS). It is expected that a thermal study of the silk fibers would provide useful information on the thermal expansion of free volume holes, coagulation of free volume holes and the activation energies involved in such processes.

The microstructural changes of polymers due to thermal treatment have been studied by various research groups using PLS since it is sensitive to free volume changes and is a non-destructive technique^[12–15]. Positrons have been successfully used for materials research, as they are extremely sensitive to defects, phase transitions and inhomogeneities. The following is a brief outline of the PLS technique. The utility of positrons in the study of polymers is enhanced by the fact that the positron can capture an electron and form a bound system called positronium (Ps). Ps can exist in two forms: ortho-positronium (*o*-Ps) where the positron and electron spins are parallel and which has a mean lifetime of 142 ns in free space. The second form is para-positronium (*p*-Ps) where the spins of both the particles are anti-parallel and which decays with a lifetime of 123 ps. In condensed media like polymers, *o*-Ps lifetime is shortened to a few nanoseconds or less because of the pick-off process in which the positron of *o*-Ps picks an electron of anti-parallel spin from the surrounding medium and annihilates. Still, this has a relatively long lifetime compared to *p*-Ps and hence its component is well defined in the lifetime spectrum. Therefore, it is possible to make a precise measurement of the *o*-Ps lifetime and its intensity (fraction of positrons that annihilate as *o*-Ps). Another aspect of *o*-Ps annihilation in polymers is that this species is preferentially trapped or formed in regions of low electron density regions or what we call free volume holes or cavities. Since the *o*-Ps annihilation rate is proportional to the overlap of the positron and pick-off electron wave functions, it is natural to expect that *o*-Ps lifetime is strongly dependent on the size of the free volume cavities. It has also been shown that the intensity of *o*-Ps or in other words the probability of *o*-Ps formation is related to the number of free volume sites in the polymer^[12]. Therefore, the pick-off annihilation of *o*-Ps in a polymer can be interpreted as an indicator of the change of the cavities and change in the number of such cavities. A detailed theoretical description of the positron annihilation process can be found in references^[12–15].

EXPERIMENTAL

The Nistari silk fiber strands were wound on a centrally holed (1.5 cm diameter) aluminum sheet to a thickness of 1.5 mm. Two pieces of this kind were used for positron lifetime measurements in sandwich geometry. The isochronal annealing of the samples was done by keeping the sample for 1 h in a tubular oven and then quenching

it in an ice water bath to preserve the structure at the annealing temperature. The samples were then thoroughly dried before use in lifetime measurements. The oven temperature was controlled to within $\pm 1^\circ\text{C}$ with a proportional temperature controller. Isochronal annealing of the samples was done in the temperature range from 27°C to 280°C . XRD measurements showed the semi-crystalline nature of the Nistari silk fibers. The chemical structure of Nistari silk fibers which is similar to a polypeptide chain is shown below:



The positron lifetime spectrometer consists of a fast-fast coincidence system with a time resolution of 340 ps determined by measuring the coincident γ photons from ^{60}Co source with 40% energy window setting to receive ^{22}Na γ events. The lifetime spectra were collected so as to have at least one million counts under each spectrum. The experiment was repeated at each annealing temperature to check the reproducibility of the measurements. A detailed description of the present PLS system can be found elsewhere^[16, 19]. Using the program PATFIT-88^[20], measured PLS spectra were analyzed with appropriate source and background corrections. The source and background corrections were determined from a lifetime spectrum taken with a defect free aluminum sample and analyzed with the program RESOLUTION^[20]. Differential scanning calorimetric scans were taken using a Mettler DSC system FP90 with a heating stage FP84. 10 mg of the silk sample was taken in a glass crucible of 7 mm diameter and a heating rate of 10°C per minute was used for the scan.

RESULTS AND DISCUSSION

All positron lifetime spectra were subjected to two, three and four lifetime component analysis. Invariably, three-lifetime component analysis gave better χ^2 values and standard deviations than the two and four component analysis. Hence the results of three component analyses are presented and discussed here. The attribution of the three lifetimes to various states of positron annihilation is as follows: The first short lived component τ_1 with intensity I_1 is attributed to p -Ps and free annihilations. There seems to be some difference of opinion with regard to the assignment of the intermediate lifetime component τ_2 with intensity I_2 . We follow the prescription of Goldanskii *et al.*^[21], according to which this component is thought to arise due to the trapping of positrons in the defects present in the crystalline regions or in the crystalline-amorphous interface regions. The longest lived component τ_3 with intensity I_3 is attributed to pick-off annihilation of the o -Ps in the free volume sites present in the amorphous regions of the silk matrix^[12-14].

As described earlier, the free volume cavity radius (R) is related to the o -Ps pick-off lifetime (τ_3) by a simple relation. This relation is based on the quantum mechanical model first developed by Tao^[22] for molecular liquids. This was later modified for solid polymers by Eldrup^[23] and Nakanishi *et al.*^[24]. The underlying assumption in the formulation of this relation is that o -Ps atom in a free volume cell can be approximated to a particle in a potential well of radius R_0 . The potential is infinite if $r > R_0$ and constant for $r \leq R_0$. Further, it is assumed that there is an electron layer in the region $R < r < R_0$, with $R_0 = R + \delta R$ where δR represents the thickness of the electron layer. The o -Ps in the electron layer has a spin averaged lifetime of 0.5 ns. The expression connecting the free volume radius R (in nm) and the o -Ps pick-off lifetime τ_3 (in ns) according to Nakanishi *et al.*^[24] is

$$(1/\tau_3) = 2 \left[1 - (R/R_0) + (1/2\pi) \sin(2\pi R/R_0) \right] \quad (1)$$

Here, the value of $\delta R = 0.1656$ nm was determined by fitting experimental τ_3 values to data from molecular materials with well-known hole sizes like zeolites^[12]. Using this value of R , the free volume size (V_f) is calculated as $V_f = (4/3)\pi R^3$. The fractional free volume F_v is then calculated as

$$F_v = CI_3V_f \quad (2)$$

where the structural constant C for Nistari silk fibers was evaluated by first determining the free volume expansion coefficient α from the positron results which gives $\alpha = 1.4 \times 10^{-4} \text{ K}^{-1}$ and with this, C for silk fibers

turns out to be $0.003 \text{ \AA}^{-3}$.

Thermal Behavior of Free Volume Sites in the Amorphous Regions

From the positron results, plots of *o*-Ps lifetime τ_3 , average free volume size V_f and *o*-Ps intensity I_3 are made as a function of annealing temperature and shown in Figs. 1(a) and (b), respectively. Similarly, the second lifetime τ_2 and its intensity I_2 are plotted as a function of annealing temperature and shown in Figs. 2(a) and (b), respectively. The fractional free volume F_v calculated from Eq. (2) is also shown in Fig. 3.

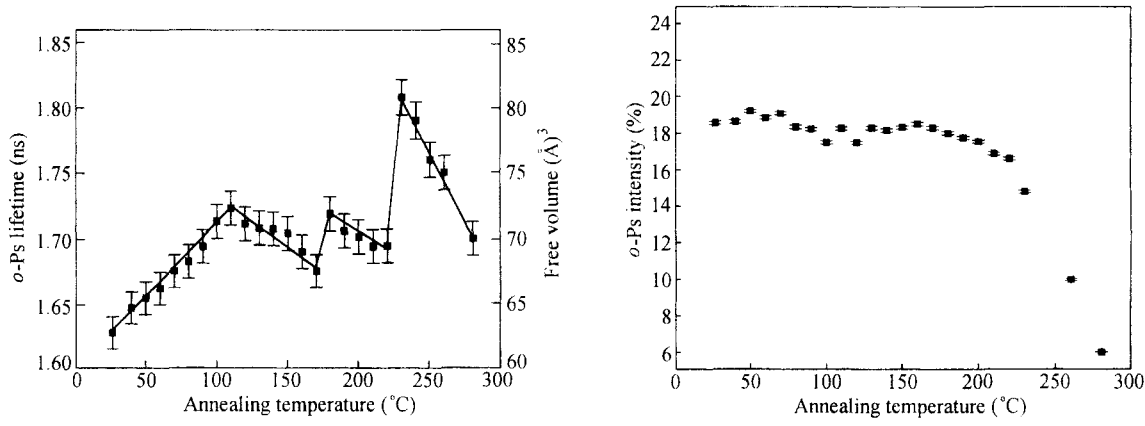


Fig. 1 Variation of *o*-Ps intensity I_3 as a function of annealing temperature (a) and variation of *o*-Ps lifetime τ_3 and free volume V_f as a function of annealing temperature (b). The solid line is drawn to guide the eye.

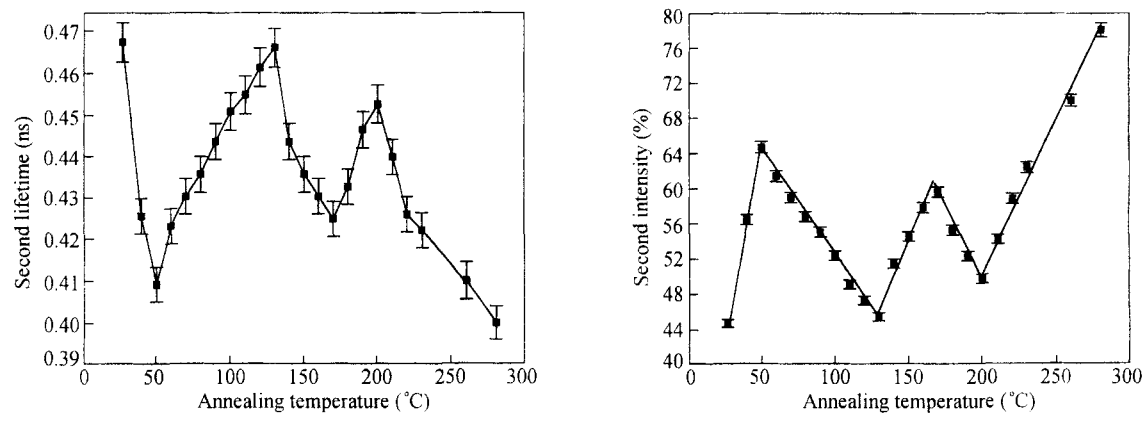


Fig. 2 Variation of intensity I_2 (a) and second lifetime τ_2 (b) as a function of annealing temperature. The solid lines are drawn to guide the eye.

Figure 1(a) shows that τ_3 and hence V_f initially increases with annealing temperature up to 100°C and during the same time the number density of free volume sites decreases. Thereafter the free volume decreases till 170°C whereas I_3 remains almost constant and then falls throughout the annealing temperature range. These variations in annealing parameters can be explained as follows: We know from literature that water molecules are embedded in the amorphous regions of the fiber matrix and their removal results in the contraction of the fiber. This contraction can lead to different effects on the amorphous as well as the crystalline regions of the silk matrix^[4]. It was reported that fibroin molecules in the silk matrix will have a limited swelling capacity^[2]. But water can easily penetrate into the flexible stretching structure of sericin, which protects the fibroin. This swelling increases the pressure among the sericin molecules and causes disjoining and division of the molecular bonds^[2]. With the increase in annealing temperature, removal of water molecules takes place. As a result an increase

in the average V_f and o -Ps lifetime is expected. Figure 1(a) supports this argument. With the removal of water, the pressure among the sericin molecules is withdrawn. With this some of the free volume holes may get coagulated leading to an increase in the average size of the free volume and hence o -Ps lifetime. Due to this coagulation the o -Ps intensity decreases in this temperature range (till 110°C). After 110°C V_f and τ_3 begin to decrease whereas I_3 remains almost constant in this region. Normally, the glass transition temperature of a polymer is characterized by the on-set of co-operative motion of segments of the molecular chains in the amorphous regions. Below T_g , only limited local motion of a small fraction of the molecules is possible^[25]. In the present case, it appears that this type of motion actually starts from 100°C and at each annealing temperature, the molecular segments can diffuse into some free volume holes leading to a reduction in the average V_f . Interestingly, the number density is not affected by this process.

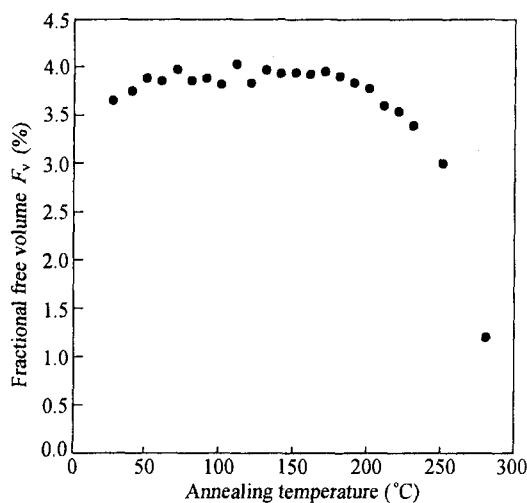


Fig. 3 Variation of fractional free volume as a function of annealing temperature

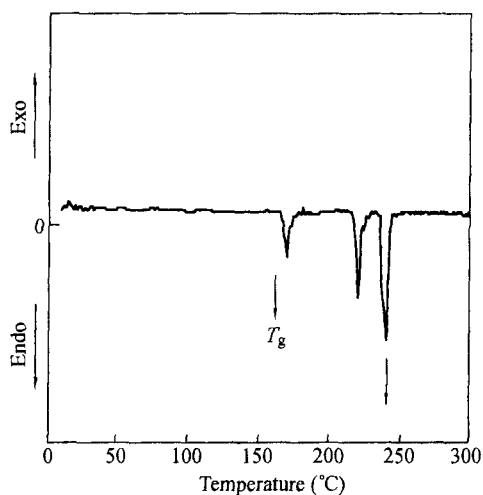


Fig. 4 DSC scan of Nistari silk fibers
Arrow marks indicate the glass transition and other transition temperatures (see text for details)

At 170°C, the slopes of V_f , τ_3 and I_3 are all changed. The F_v , which remained constant until 170°C, also shows a decreasing trend starting from this temperature. All these variations indicate that the T_g of Nistari silk fiber is 170°C. This is in good agreement with the value obtained from the DSC scan shown in Fig. 4. Compared to the bivoltine variety, the T_g of Nistari is 30°C higher which is probably due to the high sericin content in the Nistari. After T_g , segmental motion in the fiber increases. This leads to an increase in the average size of the free volume and hence an increase in τ_3 is observed. The increased molecular motion of the fibroins above T_g is attributed to the intra-molecular and intermolecular hydrogen bond dissociation in the random coil structure^[7]. Above 180°C the conformational change favours a more orderly β form similar to bivoltine silk fibers. Since this ordering results in the decrease of average V_f and hence the value of τ_3 . This process seems to continue up to 220°C indicating the completion of thermally induced crystalline modification to the β -form. The DSC scan shows an endothermic peak similar to a transition around this temperature. It can not be construed as the crystallization peak because crystallization is an exothermic process and it will appear as an exothermic peak in the DSC scan. The observed endothermic peak at 220°C can be interpreted in the light of positron results as that resulting from crystal modification similar to polymorphism where the material can exist in distinct crystal modifications. These different crystal modifications may change from one to another and this kind of change usually results in a transition of the kind noticed at 220°C and this transition is more favorable towards an ordered form. The rapid decrease in I_3 is a good indication of this. Beyond 240°C, thermal degradation of the fiber sets in resulting in a decrease in the value of V_f and hence τ_3 . The DSC scan (Fig. 4) shows that an endothermic peak at this temperature is suggestive of this change in the fiber structure or it could be due to the

melting of the silk fibers.

Thermal Behavior of Crystalline and c-a Interface Regions

The Figs. 2(a) and (b) show the variation of τ_2 and I_2 as a function of annealing temperature. These changes correspond to the crystalline regions as per the treatment of Goldanskii *et al.*^[21]. The value of τ_2 in Nistari silk is 0.47 ns and that in Bivoltine is 0.35 ns. This indicates Nistari silk has a bigger sized crystalline defects compared to Bivoltine. The variations in τ_2 and I_2 can be interpreted as follows; The presence of water molecules in the amorphous regions give rise to strain in the crystalline regions too^[5]. When the removal of water molecules starts, the strain on the crystalline regions will be withdrawn and the molecular chains get some freedom to rearrange. This rearrangement may lead to the splitting of large size defects to smaller size defects, which should result in a decrease of τ_2 and an increase of I_2 . This is what we observe in Figs. 2(a) and 2(b) till 50°C. Beyond 50°C, τ_2 increases whereas I_2 decreases. This might be due to the limited local motion of the chains resulting in coalescence of crystalline defects. This coalescence results in an increase of the value of τ_2 and a decrease of the I_2 value. This will proceed up to 130°C. Above 130°C, the random coil conformation seems to change into a mixture of α - and β -form^[7]. It has been reported that the α -form has a loose helix structure and less ordered in comparison to the more ordered β -form^[26]. In the α -form the helical chain may get twisted in a manner such that the average defect size becomes smaller and their number increases. If this happens, we should observe a decrease in τ_2 and an increase in I_2 . This process seems to proceed till 170°C. At 170°C, the slopes of both τ_2 and I_2 will change indicating the T_g of Nistari fibers is 170°C. Above T_g , the segmental motion of the fiber increases. The increase of I_2 above 200°C indicates that the sample has attained the more ordered β -form. Similar to bivoltine, the transformation from random coil to α -form can be seen in the crystalline regions of the silk fiber matrix and the conformational change to β -form is observed in the amorphous regions. The change in τ_2 and I_2 around 220°C are opposite in trend which is usually observed at a transition^[27]. The explanation given with regard to α -Ps parameter variation in the amorphous regions of the fibers holds well here also.

Activation Energies

Positron results have been further used in estimating the activation energies corresponding to the ordered regions (crystalline regions) and disordered regions (amorphous regions). In order to do this, we have used Goldanskii *et al.*^[21] kinetic relations corresponding to the two regions of the fiber matrix. They are

$$\nu_o = [I_2/(1 - I_2)] [1/\tau_1 - 1/\tau_2] \quad (3)$$

$$\nu_d = 4I_3[1/\tau_1 - 1/\tau_3]/(3 - 4I_3 - 3I_2) \quad (4)$$

Here ν_o and ν_d are the trapping rates for positrons and positronium in ordered and disordered regions respectively. Arrhenius plots of trapping rates as a function of $1/T$ for disordered and ordered regions are shown in Figs. 5(a) and (b), respectively. The activation energies obtained from the slopes of these plots are $E_d = 8.3$ kJ/mol and E_o is almost equal to zero. The total activation energy turns out to be $|E_d| + |E_o| = 8.3$ kJ/mol. These activation energies correspond to the temperature region above T_g . At higher temperatures, the sample moves towards the more ordered β -form. This highly ordered β -form results through hydrogen bond dissociation [N–H bond], which needs an energy around 8.4 kJ/mol. The activation energy of 8.3 kJ/mol obtained in the present experiment is in good agreement with the expected value, *i.e.* 8.4 kJ/mol. This suggests that the N–H bond dissociation is the most probable process that occurs in the Nistari silk fibers under thermal treatment mainly in the amorphous regions of the fiber matrix since the E_o is almost zero.

Molecular Weight Estimation

To the best of our knowledge, up to now, there is no method to determine the molecular weight of a polymer in solid form experimentally. Here we attempted to extend the positron measurements, which are non-destructive in nature, to estimate the molecular weight of the natural polymer-Nistari silk fibers by exploiting the connection between free volume and viscosity. Free volume is inversely proportional to the viscosity, which in turn is related to the molecular weight through the well-known Mark-Houwink relation^[6]. For this purpose, we have plotted free

volume cell size as a function of molecular weight for different polymers (data collected from literature^[14–16, 21, 25–30]) and these data fit well to a power relation of the type

$$V_f = AM^\beta \quad (5)$$

Where A and β are evaluated from the fit and their values are 5287 and 0.32, respectively, with a correlation coefficient of 0.93. Using these values and the free volume cell size from present measurement, we estimate the molecular weight of the Nistari silk fibers as 10.7×10^5 . This value lies in the range 8.0×10^5 to 3.0×10^6 suggested for natural polymers^[2, 3]. However, there is no independent measurement to compare the present result.

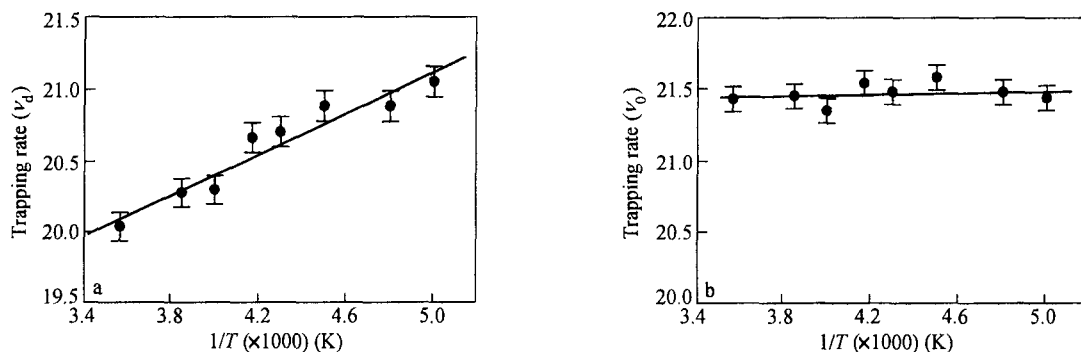


Fig. 5 Arrhenius plots for disordered (a) and ordered (b) regions
The solid lines are fit to the experimental data

CONCLUSIONS

The following are the conclusions drawn based on the present positron results. (1) It has been demonstrated that PLS is a versatile tool in probing the thermal behavior of Nistari silk fibers through free volume measurement. (2) PLS measures the T_g of Nistari silk fibers as 170°C , which is in good agreement with the DSC result. This high T_g may be due to the presence of high sericin content in Nistari. (3) Molecular weight of the Nistari silk fibers is determined to be 10.7×10^5 based on free volume, which lies within the range suggested for natural polymers. (4) Activation energies are measured separately for the crystalline and amorphous regions, thereby demonstrating the versatility of the technique. The values corresponds to the N–H bond dissociation energy, suggesting that N–H bond dissociation is the most probable process occurring in Nistari silk fibers. (5) There is an indication that the conformational change from α - to β -form has a pronounced effect on the free volume number density than its size. However, this needs to be validated from other measurements to support this observation.

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