

Free volume study of poly(chlorotrifluoroethylene) using positron annihilation spectroscopy as a microanalytical tool

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Positron lifetimes and X-ray diffraction measurements were carried out on poly(chlorotrifluoroethylene) films annealed between 25 and 215°C. The positron lifetime results were used to determine the free volume and XRD data were used to determine the apparent crystallite size and crystallinity. The glass transition temperature (T_g) of 52°C obtained from positron results is in agreement with that obtained by thermal analysis. The average free volume cell size is 74 Å³ in films annealed below T_g , and increases to 84 Å³ in samples annealed above T_g . Although the observed changes in positron lifetime parameters as a function of annealing temperature are small, they are significant for the kind of material investigated. Our observations are explained in terms of thermally activated chain mobility, local relaxations and long-range motions. We further estimate, for the first time, the activation energies in the amorphous and crystalline regions of the polymer using the Goldanskii kinetic relations. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The utilization of polymers in industrial applications requires a basic understanding of their material properties. A key problem in this regard is relating the macroscopic mechanical properties (e.g. impact strength, elastic moduli etc.) to atomic-scale free volume holes¹. The existence of free volume holes in polymers has been postulated for more than three decades². Many of the visco-elastic properties of polymeric materials can be based on free volume theory³. Now, it is possible to understand the kinetic and dynamic behaviour of polymeric molecules under varying conditions, if we can understand how free volume holes in the polymer matrix behave.

Although a great deal of research has been expended in the past decade towards understanding the influence of free volume on the physical properties of polymers, only limited information with regard to free volume size,

concentration, and shape has been forthcoming. In fact, reports of direct experimental measurement of these parameters are very scanty. In recent years, positron annihilation spectroscopy (PAS)^{4,5} has turned out to be one of the useful methods currently available for the study of polymers at a molecular level.

When energetic positrons enter a condensed medium, they first thermalize and then annihilate with the electrons of the medium via free annihilation, trapped annihilation, or form a bound state (e^+e^-) called positronium (Ps). Positronium decay, particularly o-Ps pick-off annihilation is important because, Ps is trapped in free volume sites. A measurement of lifetime and intensity of o-Ps, therefore provides a sensitive measure of polymer properties associated with free volume, degree of crystallinity, crosslinking, molecular weight, etc.^{6–10}.

Polymers are known to be admixtures of amorphous and crystalline regions. A typical amorphous polymer contains about 95% of bulk (excluded volume) and 5% of free volume. On the other hand, a crystalline polymer having regular crystal like structure, does not have free volume. Recent positron lifetime measurements in

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semicrystalline polymer PEEK¹¹ give strong evidence that Ps is formed and annihilated only in the free volume and not in the excluded volume. When a polymer is subjected to heat treatment, the molecular mobility and relaxation rate of local motion of chain varies. This molecular mobility affects the free volume of the polymeric material. Because of the sensitivity of Ps to free volume changes, PAS turns out to be a novel technique in this field.

Films of poly(chlorotrifluoroethylene) (PCTFE) are characterized to have high heat stability and fire resistance in the temperature range -200 to 180°C . They are utilized in reservoirs containing liquid oxygen at very low temperature. The films are impermeable to water and resistant to ageing and radiation damage. They are found to be useful in chemical engineering because of their chemical stability, high permeability and wear resistance. In addition, they are used in nuclear, space, electrical, and medical engineering and in computer manufacture¹².

Because of the potential technological applications of this polymer as mentioned above, it was felt desirable to study, for the first time, the positron lifetimes and hence free volume related properties, such as the glass transition temperature T_g and other thermally activated structural changes in the polymer matrix. X-ray diffraction was used to complement the PAS results.

EXPERIMENTAL

Sample preparation

PCTFE film used in this study is marketed by AlliedSignal Inc. as Aclar, type 22A film. These films contain about 3.5% vinylidene fluoride as a comonomer and the weight average molecular weight of these films is about 250 000. The films were cast on a cold casting roll so as to obtain a film of low crystallinity. Isochronal annealing of the films was done in the conventional way using a tubular oven. The oven temperature was controlled to within $\pm 1^{\circ}\text{C}$ with a temperature controller. In this method of annealing, the sample is heated at a predetermined annealing temperature, held for 1 h, and then quickly quenched into ice water so as to preserve the structure in the sample at elevated temperatures.

X-ray diffraction

X-ray diffraction (XRD) scans were obtained on a Philips diffractometer in parafocus geometry using Cu radiation and a graphite monochromator in the diffracted beam. The scans were resolved into amorphous and crystalline peaks by methods described elsewhere¹³. A crystalline index (%) was calculated from the ratio of the areas of the crystalline peaks to total scattered intensity over an angular range of 10 – 22° (2θ). The coherence length of the crystallites or the apparent crystallite size (L) was calculated from the full width at half maximum (b) of the crystalline peaks using the Scherrer equation

$$L = 0.9\lambda / (b \cos \theta) \quad (1)$$

where λ is the wavelength (1.542 \AA) and b is the peak width corrected for the instrumental broadening (0.09°).

Positron lifetime measurements

Films of thickness $76 \mu\text{m}$ were stacked together to make a source sample sandwich for positron lifetime

measurements. Spectra were measured with a fast-fast coincidence system, the details of which can be found in references 14–17. A time resolution of 0.340 ns was measured with ^{60}Co radiation for 40% energy gating with ^{22}Na . In actual analysis, the instrumental time resolution and source corrections obtained from the measured spectra of a metal of known lifetime (well annealed aluminium) fitted to the program RESOLUTION¹⁸ were used. The lifetime spectra of the sample were resolved using the program PATFIT-88¹⁸. Under each spectrum a total of more than 10^6 counts was accumulated. The experiment was repeated at each annealing temperature to check the reliability of the results and consistently reproducible spectra were used in the final analysis.

RESULTS AND DISCUSSION

X-ray diffraction results

Figure 1a shows XRD scans from some of the annealed samples used in this study. These scans can be interpreted as due to pseudo-hexagonal packing of the helical chains with varying degrees of lateral and chain-axis disorder. The data are consistent with the published unit cell dimensions of $a = 6.438 \text{ \AA}$, $c = 41.5 \text{ \AA}$ ¹⁹. The reported densities for the amorphous and crystalline phases are 2.077 and 2.152 g cm^{-3} respectively¹⁹. The XRD scans were resolved into crystalline and amorphous peaks as illustrated in the profile fitted scan shown in the inset. The resolved curves were used to obtain the crystallinity and the apparent crystallite sizes. The variation in the crystallinity and the crystallite sizes with annealing temperature are shown in Figure 1b. The crystallite size (this size refers to the linear dimension of the crystallites perpendicular to the chain axis) remains constant up to 80°C and then begins to increase. The slope changes again around 160°C . On the other hand, crystallinity which is unchanged up to 80°C increases linearly thereafter from 25% crystallinity to 65%.

Positron lifetime results

Positron lifetime spectra in molecular substances generally contain multiple exponential decay components. The majority of polymers show three to four lifetime components. In the present investigation, measured lifetime spectra were fitted to two-, three- and four-component analysis. The three-component analysis gave better χ^2 values and standard deviations, both in the as-received state and in the heat treated samples up to 215°C . Hence the results of three-component analysis are reported here. The shortest lived component is attributed to contributions from p-Ps self annihilation and free positron annihilation and it provides no useful information in the case of polymers. The intermediate lifetime component $\tau_2 = 0.370$ – 0.386 ns with intensity $I_2 = 80$ – 84% is attributed to the annihilation of positrons trapped at the defects (without forming Ps) in the crystalline regions or trapped at the crystalline–amorphous interface of the polymer. The variations of τ_2 and I_2 are presented in Figures 2a and 2b respectively. The third or long lived component with lifetime $\tau_3 = 1.74$ – 1.86 ns with intensity $I_3 = 4$ – 6% is attributed to the pick-off annihilation of o-Ps in free volume sites in the amorphous region of the polymer matrix. The variation of o-Ps lifetime and its intensity are

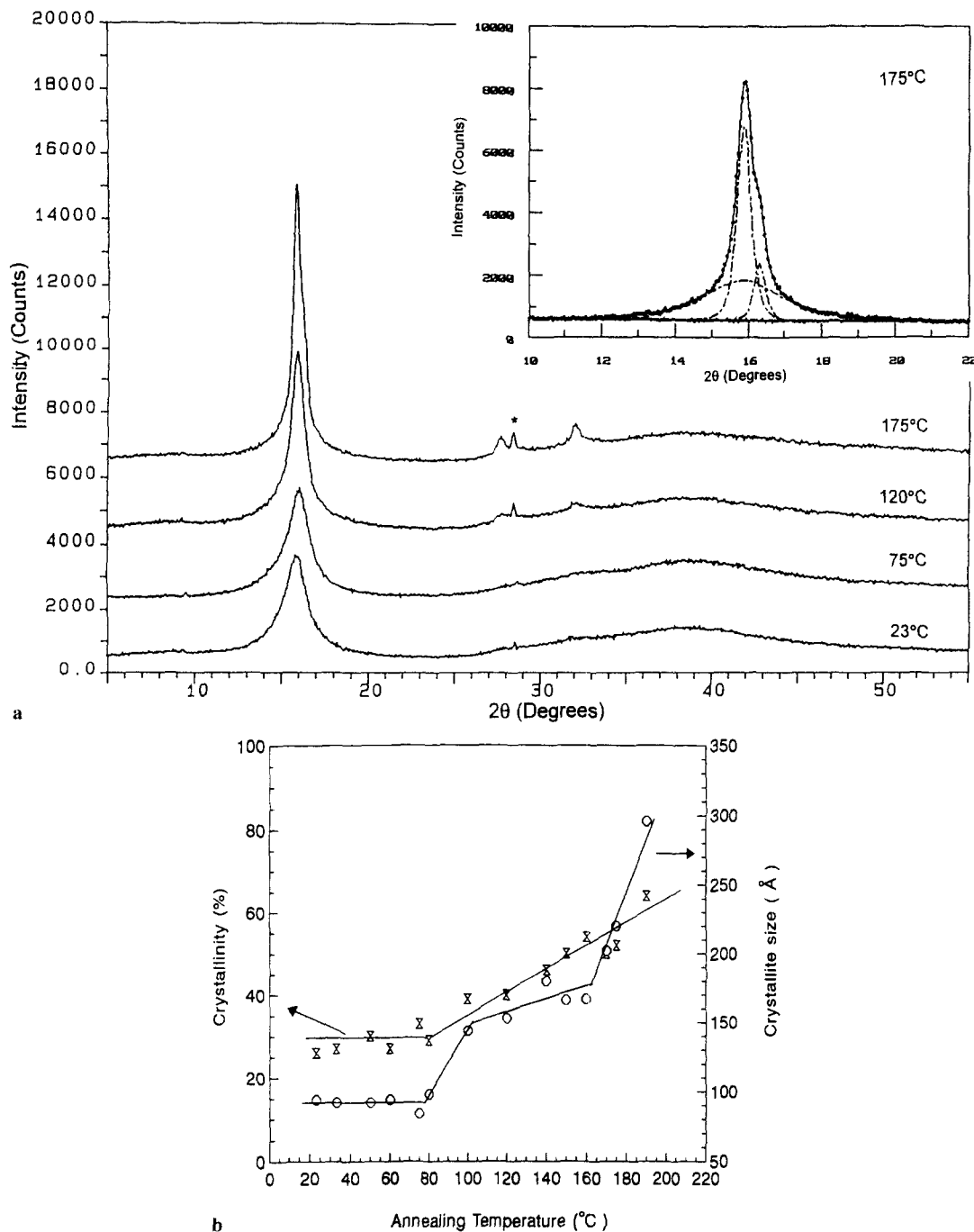


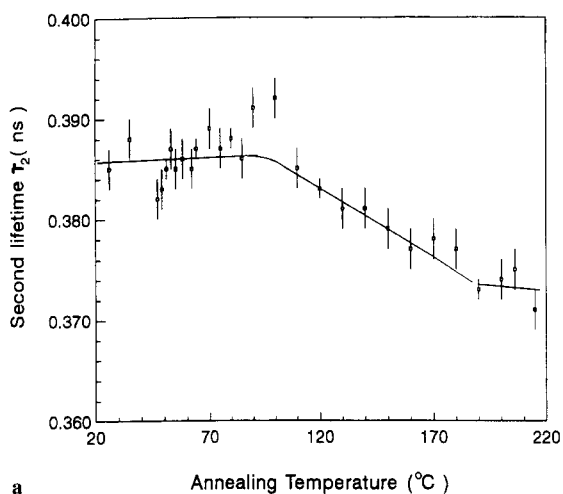
Figure 1 (a) Representative X-ray diffraction scans of PCTFE films at different annealing temperatures. The peak marked with an asterisk is due to the sample holder. The inset shows an example of the profile fitted scan used in the calculation of crystallinity and crystallite size. The fitted curve is shown by the full line through the data points (open circles). The resolved crystalline peaks and amorphous halo are shown by dotted curves. The difference between the observed data and the fitted curve is shown by the dotted line oscillating above and below the base line. (b) Crystallite size and degree of crystallinity as a function of annealing temperature (solid line is drawn to guide the eye)

shown in *Figures 3a* and *3b* respectively as a function of annealing temperature. The relation between the average free volume size and positron lifetime was quantified in a model first used by Tao²⁰ for molecular liquids. Following Tao, Nakanishi *et al.*²¹ have given a relation between o-Ps lifetime τ_3 (ns) and the free volume radius R (nm) under the assumption that the positronium atom in a free volume cell can be approximated by a particle in a spherical potential well of radius R_0 . The potential is infinite if $r > R_0$ and constant for $r < R_0$. In this model, it is further assumed that there is an electron layer in the region $R < r < R_0$, where $R = R_0 - \Delta R$, and ΔR represents the thickness of

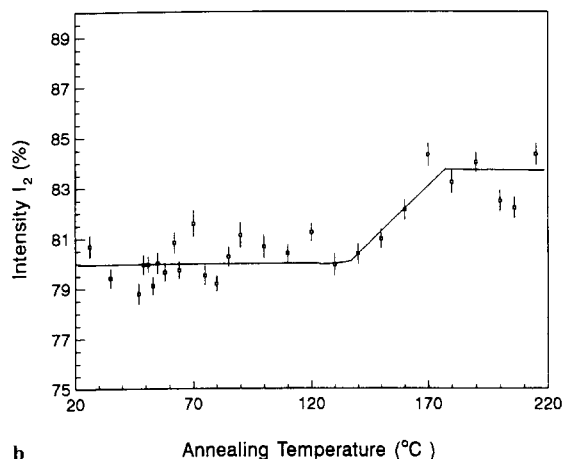
the electron layer. The o-Ps in the electron layer has a spin-averaged positronium lifetime of 0.5 ns. The relation given by Nakanishi *et al.*²¹ is

$$1/\tau_3 = 2[(1 - R/R_0) + 0.159 \sin(2\pi R/R_0)] \text{ ns}^{-1} \quad (2)$$

By fitting equation (2) to measured values of the o-Ps lifetime in molecular media having the known hole sizes from literature^{11, 14, 26}, we obtained a value of 0.166 nm for ΔR which agrees well with the value reported by Nakanishi *et al.*²¹. Using the free volume radius obtained from equation (2), the free volume V_f is calculated as $V_f = (4/3)\pi R^3$ and its variation with temperature is



a Annealing Temperature (°C)



b Annealing Temperature (°C)

Figure 2 (a) Second lifetime component τ_2 as a function of annealing temperature. (b) Intensity I_2 of the second lifetime component as a function of annealing temperature (solid line is drawn to guide the eye)

shown in *Figure 4*. The average free volume cell size varies from 74 \AA^3 to 84 \AA^3 with annealing temperature. The fractional free volume is calculated from the relation

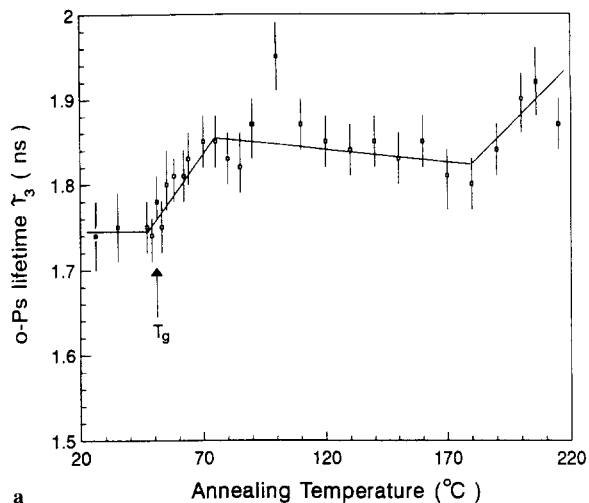
$$F_v = CV_f I_3 \quad (3)$$

where C is the structure constant derived from the coefficient of thermal expansion (CTE). CTE calculated from the free volume hole radius at two temperatures is $1.67 \times 10^{-3} \text{ K}^{-1}$ and this value is slightly higher than that reported in the literature²². Using this value of CTE, constant C was calculated to be 0.19 \AA^{-3} . The fractional free volume calculated from equation (3) is plotted in *Figure 5*. It should be emphasized here that there has not been a rigid test of equation (2) by an experiment with a sample in which the free volume cells are nearly spherical. Nevertheless, it provides reasonable values for comparison and interpretation of the experimental results.

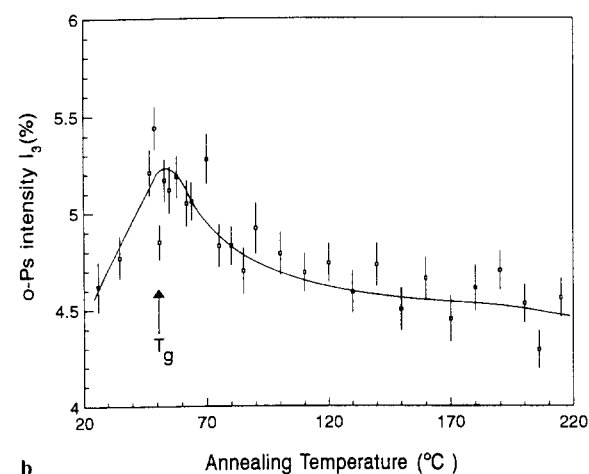
Glass transition temperature

Data in *Figure 2a* show that as the temperature of annealing is increased, τ_2 remains almost constant up to 80°C and then begins to decrease. The intensity of the second lifetime I_2 (*Figure 2b*), also remains almost unchanged up to $\sim 140^\circ\text{C}$, then begins to increase.

Data in *Figure 3a* show that the o-Ps lifetime (τ_3) which is related to free volume V_f remains almost



a Annealing Temperature (°C)



b Annealing Temperature (°C)

Figure 3 (a) o-Ps lifetime τ_3 as a function of annealing temperature. (b) Intensity I_3 of o-Ps lifetime as a function of annealing temperature (solid line is drawn to guide the eye)

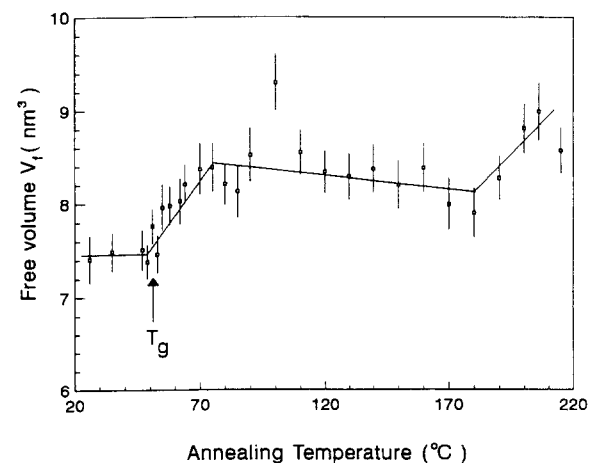


Figure 4 Free volume size V_f as a function of annealing temperature (solid line is drawn to guide the eye)

constant in the initial stages of annealing, begins to increase at 52°C , reaches a maximum around 80°C and thereafter is more or less constant up to 180°C and increases after 180°C . The fractional free volume F_v vs temperature plot (*Figure 5*) shows a small but significant increase up to 52°C and thereafter remains almost

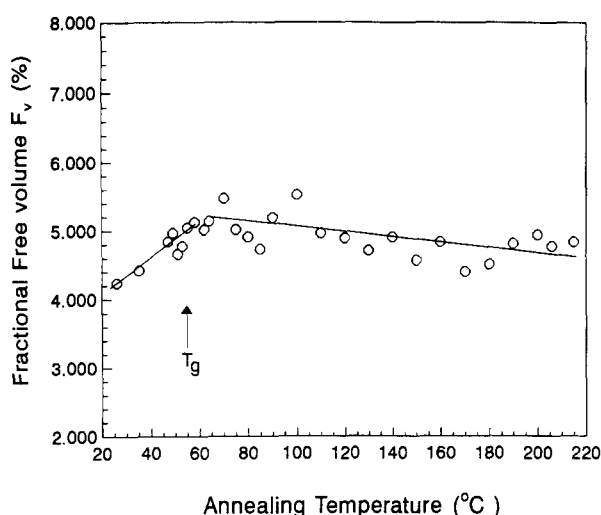


Figure 5 Fractional free volume F_v as a function of annealing temperature (solid line is drawn to guide the eye)

constant. All these variations indicate the presence of a clearly identifiable glass transition at 52°C for PCTFE. This value agrees well with the value obtained by various thermal analysis methods²², including our unpublished differential calorimetric data.

Defects or micro-voids in the crystalline phase

The changes in the annihilation parameters in the crystalline regions are small but significant. The second lifetime component τ_2 remains almost constant up to 80°C indicating that below T_g the defect structure in the crystalline domains of the polymer is not very much affected and this is consistent with the XRD results (Figure 1b). The intensity of the second component I_2 increases at temperatures above T_g . This increase in I_2 seems to correlate with the increase in the crystallinity as measured by XRD (Figure 1b). This correlation may suggest that as the volume fraction of the crystallites increases, it is possible that the total number of defects within the crystalline region also increases. We suspect that the density of defects would decrease under isothermal annealing at elevated temperature (~160°C). It should be noted here that the crystallite size derived from Scherrer equation is only an apparent crystallite size and it is a combined measure of the size of the crystallites and the order within them. The variation of crystallite size with annealing temperature (Figure 1b) indicates that two identifiable transitions, one around 80°C and the other around 160°C. However, positron results (Figure 2a) seem to show only the first one.

Free volume in the amorphous phase

Our data show that τ_3 (Figure 3a), and hence free volume (Figure 4), remain constant up to T_g indicating that changes in segmental motions are rather small in this region. The nature and magnitude of these motions depend on the size and geometry of the polymeric chain, the flexibility of the chain segments and the type of molecular aggregates. The intensity I_3 increases by a small amount up to T_g and then begins to decrease. The decrease in I_3 above T_g could be explained as due to decrease in the amorphous fraction, i.e. the increased crystallinity in samples annealed at elevated temperatures. Annealing below T_g does not significantly affect the

crystallinity, and as such, one would expect I_3 to be constant from room temperature to 60°C. The increase in the free volume contributions observed upon annealing below T_g suggests that, the amorphous chain segments are mobile at sub- T_g temperatures, but this mobility contributes to the increase in free volume content (Figures 3b and 5) upon quenching. At temperatures above T_g (after 80°C) the number-density of the free volume holes (since I_3 is a rough measure of these) decreases continuously with increase in annealing temperature (Figure 3b). This is obviously due to the onset of large scale mobility of the polymer chain⁸ as the amorphous phase transforms from glassy to rubbery state. This motion in the rubbery state requires more free volume than the short-range excursions of the atoms in the glassy state. The increase in the free volume size with increase in temperature suggests an increase in volume expansion coefficient above T_g . As can be seen from Figure 5, the total free volume content of the polymer decreases above T_g (not significantly). This correlates with the decrease in amorphous content, or the increase in the crystallinity at $T > T_g$. At higher temperatures (above T_g) these results help to distinguish the structural changes that occur in the ordered and the disordered regions^{15-17, 21, 23, 24}.

Beyond 80°C up to 180°C, the molecules naturally take up random, coiled configuration as a result of free rotation about a single covalent bond (C-C bond) in the chain backbone²⁵. This might cause diffusion of molecular segments into the free volume cells resulting in the decrease of τ_3 . But free volume size remaining almost constant within the experimental errors (Figure 4) indicates that there is no diffusion of molecular segments.

The variation of τ_3 above 180°C shows that o-Ps lifetime increases with temperature up to 210°C whereas I_3 remains constant in this region, suggesting that the number-density of holes does not change. But as this temperature is close to the melt, the increase in average free volume hole size with temperature predicts coalescence of angstrom sized holes²⁶.

Activation energies

Based on the kinetic equations of Goldanskii *et al.*²⁷ the positron results have been further extended to calculate the trapping rates in the ordered regions or crystalline domains (ν_0) and in disordered regions or amorphous domains (ν_d) of the polymer matrix. Here it is assumed that the probability of positrons forming Ps in the ordered regions is taken as zero and for disordered regions as $(1 - I_2)$. Arrhenius plots of trapping rates as a function of $1/T$ are shown in Figures 6 and 7 respectively.

The activation energies obtained from the slope of the Arrhenius plots for the ordered region (E_0) and disordered region (E_d), respectively, are $E_0 = -1.61$ meV (-0.16 kJ mol⁻¹) and $E_d = -14.50$ meV (-1.4 kJ mol⁻¹). These activation energies correspond to the temperature regime above T_g . It is an established fact the diffusion in amorphous alloys shows Arrhenius behaviour. Our observation in the present study indicates Arrhenius type of behaviour both in the crystalline and amorphous regions. In the case of metals, the activation energies tend to increase with increasing atomic size. By analogy, the values of E_0 and E_d may correlate with this concept but as of now we do not have a proven equation to evaluate the defects size just as we did in the case of

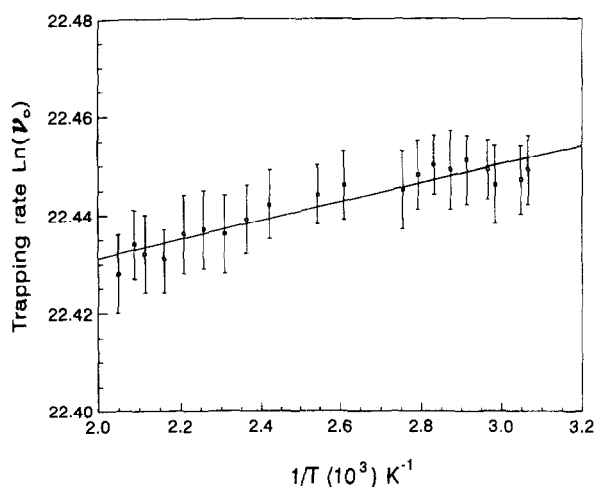


Figure 6 Positron trapping rate ν_0 in the ordered regions versus $1/T$ (solid line is a linear fit to experimental data)

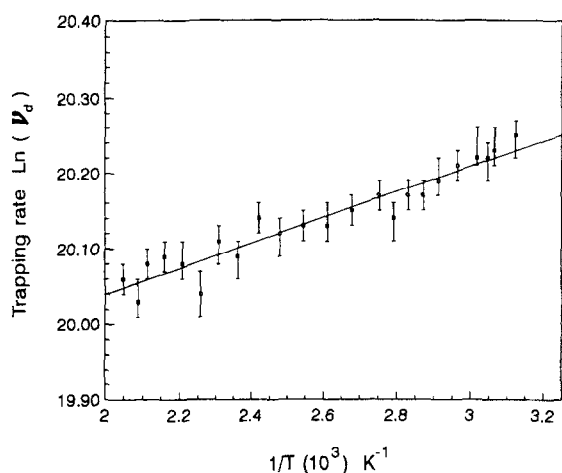


Figure 7 Positron trapping rate ν_d in the disordered regions versus $1/T$ (solid line is a linear fit to experimental data)

free volume (equation (2)). To draw definitive conclusions, more measurements of this kind, and a suitable relation to calculate the defects/microvoids size in the crystalline domains of the polymer using τ_2 values are needed. Nevertheless, it is evident that positron results differentiate between the crystalline and amorphous domains of the polymer matrix. Under annealing treatment, we observe the change in free volume as the polymer goes from glassy to rubbery state. The rigidity or flexibility of the free volume depends more or less on the co-operative motion of the chains, rotation or flexibility of the side groups. In the rubbery state, the free volume is more flexible than in the glassy state as evidenced by constancy in free volume up to T_g (Figure 4).

CONCLUSIONS

Positron annihilation technique is a very useful method in the study of the free volume related microstructure of the polymer as it gives simultaneously both the average free volume size as well as its fractional number density. The glass transition of PCTFE (Aclar) is obtained from the variation of the annihilation parameters. No change in free volume up to T_g suggests segmental motions in the

polymer chain are rather small. Above T_g , the changes in free volume indicates the onset of large scale mobility of the polymer chain as the amorphous phase transforms from glassy to rubbery state. After 180°C, the increase in free volume size is inferred as being due to coalescence of angstrom sized holes. There seems to be a correlation between the number of defects in the crystalline domains of the polymer and the increased crystallinity as indicated by XRD and lifetime results. Activation energies for the ordered and disordered regions are measure separately. More detailed measurements of this kind may provide a good insight into the diffusion process of positrons trapped in the crystalline regions and positronium in the amorphous regions respectively.

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