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Thermally induced microstructural changes in undoped and doped polyacrylonitrile: A positron-annihilation study

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Positron-lifetime measurements have been made in undoped and polymers 0.8 wt %–iodine-doped polyacrylonitrile (PAN) under annealing from room temperature to 160 °C. From the measured lifetimes, the free-volume size is calculated following the treatment of Nakanishi, Jean, and collaborators. The variation in free-volume size as function of temperature seems to suggest molecular-chain-folding processes in amorphous regions of the polymer, positron trapping at kink-type defects, and at the interface between crystalline and amorphous regions at lower temperatures. This study indicates that in the undoped state, the polymer has a glass transition temperature at 90 °C which is shifted toward lower temperature in the doped state by 30 °C. The results also suggest the degradation of the polymer in the two states after 100 °C and the effect of annealing is only on the size but not on the density of free-volume sites.

I. INTRODUCTION

Recently, polymers have attracted a great deal of interest from both physicists and technologists as a result of their active electronic properties and potential applications in storage batteries, semiconducting devices, etc.[1,2] The application of these polymers depends on a good understanding of their electronic structure and defect states. Knowledge of the defect states is essential, as it affects such important factors such as optical quality, electron mobilities, and trap states. The key problem in this regard is in relating the macroscopic mechanical properties of the polymers to the atomic-scale (a few angstroms) free-volume holes.[3]

The existence of free-volume holes in polymers was postulated almost three decades ago, and since then it has been a topic of considerable interest in polymer research.[4] The explanation of viscoelastic properties in polymeric materials has been based on free-volume theory,[5] which describes the kinetic and dynamic behavior of polymeric molecules and free-volume holes in the matrix. It is evident from numerous experiments that a variety of structural changes, such as first-order phase transitions, glass transitions, and relaxation processes in polymers, are known to be connected with the free volume as an intrinsic material parameter. The basic idea underlying this approach to relaxation phenomena is that molecular mobility at any temperature is dependent on the available free volume in the polymer matrix at this temperature. Unfortunately, it appears, that there has been little experimental observation of such parameters as hole size, hole concentration, and the shape of free volumes.

For a better understanding of these key parameters, it is necessary to apply a wide variety of physical methods, which can supply complementary information. Notable probes along this line of microanalysis include the positron-annihilation technique (PAT), photochromatic and fluorescent spectroscopy, and small-angle diffractions. The diffraction method becomes very difficult to use for hole sizes below 10 Å, whereas photochromatic and fluorescent methods induce additional perturbation by incorporating a sizable probe into the holes; thus, the extracted information about hole sizes can be considered only as being roughly estimated. In recent years the positron-annihilation technique has emerged from the level of basic research into the field of applied science and is probably one of the most useful methods currently available for the study of polymers at the molecular level.[6,7] The method is capable of probing directly properties of free-volume holes in polymeric materials.

When an energetic positron enters into a condensed medium, it diffuses through the lattice and thermalizes to thermal energy. After thermalization, the positron either annihilates via free annihilation or forms a bound state with an electron, i.e., a neutral entity called positronium (Ps). Ps has two spin states: One is orthopositronium (*o*-Ps), in which the spins of the two constituent particles are parallel, and the other is parapositronium (*p*-Ps), in which the spins are antiparallel. *p*-Ps decays into two photons with a mean intrinsic lifetime of 0.125 ns. *o*-Ps has an intrinsic lifetime of 140 ns and in free space produces three photons. In condensed matter, however, the positron of *o*-Ps annihilates predominantly with an electron of the medium possessing opposite spin. In this so-called pickoff process, only two photons are emitted and the mean lifetime of *o*-Ps is reduced to the order of a few nanoseconds. The most important feature of *o*-Ps in a polymer is that this species is preferentially trapped or formed in regions of low electron density or the so-called free-volume holes. Since the annihilation rate of *o*-Ps is proportional to the overlap of the positron wave function and the pickoff electron wave function,[8] the *o*-Ps lifetime is expected to depend strongly on the size of the hole. It is also shown that the intensity of this lifetime component depends on both the Ps-formation probability and the number of free-volume sites in the polymer matrix; therefore, the positron lifetime and intensity of the *o*-Ps pickoff component are closely related to a great deal of polymer properties, including phase transition, thermal degradation, degree of crystallinity, molecular weight, degree of cross linking, density, etc., that are influenced by the free volume.[9]

Thin polymer films are known to be mixture of amorphous and crystalline regions. The conductivity of such polymers is dominated by properties of the amorphous regions. The presence of amorphous regions gives rise to localized states. Since there are many localized states, the release or excitation of carriers in these states dominates the conduction process. Dopant molecules in such polymers enter either the amorphous regions or the micrograins such as chain folds.[10] A study of the electrical conductivity in the iodine-doped poly (*p*-phenylene oxide) (PPO) (Ref. 11) indicates that the presence of dopants in amorphous regions results in a decrease in the area of the amorphous and crystalline interface because of the formation of charge-transfer complexes. It is well known that lattice vibrations, thermal fluctuations, and molecular motion cause a smearing of the electron-density distribution in the lattice, effectively raising the local electron density in the free volume. This higher local electric field can directly influence the *o*-Ps yield by trapping positrons and also the annihilation characteristics. As a result, microstructural variations are directly connected to the annihilation parameters.[12]

It is interesting to study the variation of annihilation parameters, and hence free-volume-related properties, such as the glass transition and other thermally active structural changes within the polymer matrix. With this in mind, we have studied the semicrystalline (i.e., containing both crystalline and amorphous regions) polymer polyacrylonitrile (PAN) both in the undoped state as well as in a doped state, with 0.8 wt % iodine, by making positron-lifetime measurements as a function of annealing temperature. The results obtained in these two cases are discussed and conclusions drawn.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Polyacrylonitrile in powder form, obtained from the manufacturer M/s. Bayer, Germany was used in casting the polymer films. Spectroscopic-grade*N*,*N*-dimethylformamide (DMF) was used as the solvent. The PAN films were cast using the solvent casting method. The polymer powder was completely dissolved in DMF. Then the solution was poured on a fine flat and clean glass plate, and a film of thickness around 80–100 μm was obtained when the solvent was evaporated under an ir lamp, taking care that the temperature does not exceed 85–90 °C. Doping of the polymer with iodine was done by mixing accurately weighed quantities of PAN and iodine and by again completely dissolving the two in DMF and then drawn into films as before. The films were washed in distilled water, dried, and stored in vacuum desiccator for 24 h. The film characterization was done by an x-ray-diffraction measurement, and it was found that these films contained both amorphous and crystalline regions (i.e., semicrystalline polymer film).

B. Annealing treatment

Isochronal annealing of the sample was done using a standard procedure. We have used a tubular furnace with a temperature control with an accuracy of ± 1 K by using a proportional temperature controller. The sample films in stacks were kept for a fixed time period of 4 h at each temperature and then quenched in an ice-water bath. They were thoroughly dried before use in the actual experiment.

C. Lifetime measurements

Positron-lifetime spectra were measured with a fast-fast coincidence system which consists of a KL-236 plastic scintillator coupled to an RCA 8575 photomultiplier assembly as detectors. A carrier-free ^{22}Na of 15 μCi activity evaporated on a thin (1.2-μm-thick) nickel foil was used as the positron source, and the standard source-sample sandwich geometry (ten layers of the polymer films were stacked together on either side of the positron source) was employed for positron-lifetime measurements. A time resolution of 340 ps for the spectrometer was obtained with ^{60}Co radiation for 40% ^{22}Na energy gating.[13] In the actual analysis, the instrumental time resolution and source correction terms were obtained from the measured spectra of a metal of known lifetime fitted with use of the computer program RESOLUTION.[14] After source and background corrections, the lifetime components of the sample under study were resolved with use of the program PATFIT.[14] A total of about 10^5–10^6 counts were accumulated for each spectrum. Lifetime measurements were made at room temperature. Care was taken to check periodically the effects of electronic drift if any, although the experimental arrangement was housed in an air-conditioned room. For each annealing step in the temperature range 25–160 °C, several runs of lifetime spectra were taken to check the reproducibility of the results. Consistently reproducible spectra were used in the final analysis.

III. RESULTS AND DISCUSSION

A. Undoped sample

All the measured spectra were resolved into three components which consistently yielded better stability and χ^2 parameters than the two- and four-component analysis. The attribution of these three lifetime components to various states of positron annihilation is similar to the one given in previous papers.[13,15] The short-lived component characterized by (τ_1, I_1) is attributed to the contributions from *p*-Ps and free annihilation. The intermediate component (τ_2, I_2), which ranges from 0.395 to 0.414 ns in the undoped sample, is mainly due to the annihilation of positrons at the defects present in the crystalline regions or those trapped at the crystalline and amorphous interface. The third component (τ_3, I_3), whose value ranges from 1.42 to 1.79 ns, is attributed to pickoff annihilation of *o*-Ps in the free-volume sites present mainly in the amorphous regions of the polymer matrix. The lifetime τ_3 represents the mean value of *o*-Ps

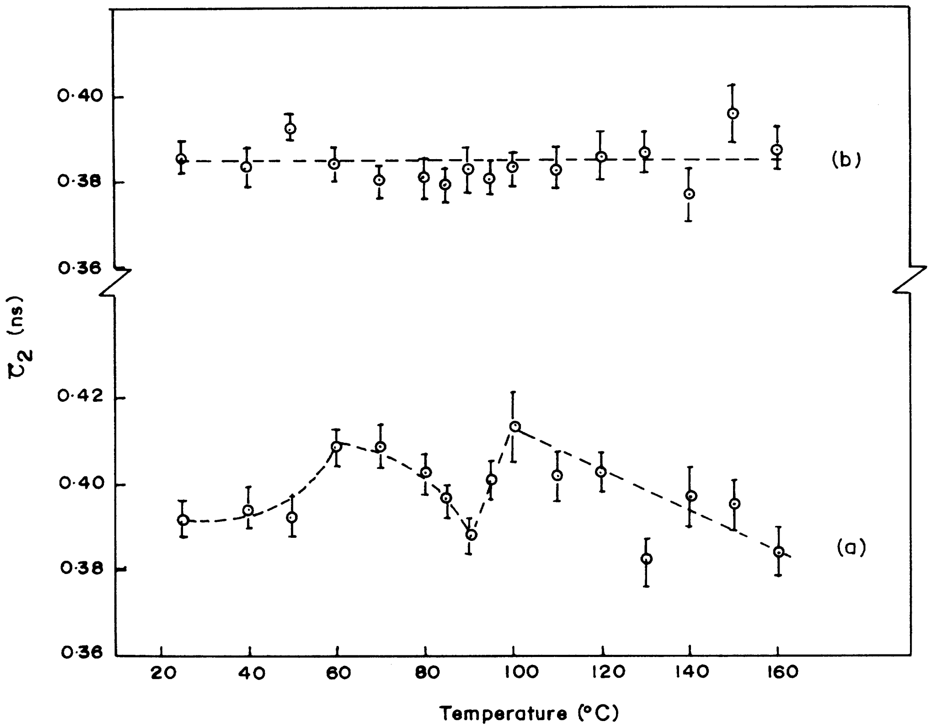

FIG. 1. Variation of the lifetime component τ_2 as a function of the annealing temperature (a) for a pure PAN (undoped) polymer and (b) for a 0.8 wt % iodine-doped PAN polymer.

pickoff lifetimes as the voids (free volume) are of different sizes. On the other hand, the intensity I_3 is proportional to the available number of free-volume sites in the polymer matrix. The variation of τ_2 and the corresponding intensity I_2 with annealing temperature are shown in Figs. 1(a) and 2(a), respectively. The variation of τ_3 as a function of annealing temperature is displayed in Fig. 3(a).

Since positronium formation and the subsequent decay can be correlated with the free volume present in the polymer matrix,[16] one can estimate the free-volume size in a polymer which is related to the value of the long-lived component. The relation between free-volume size and the orthopositronium lifetime (*o*-Ps) has been quantified in a model used by Tao for molecular liquids.[17] Following Tao,[17] Nakanishi, Wang, and Jean[18] gave a simple rela-

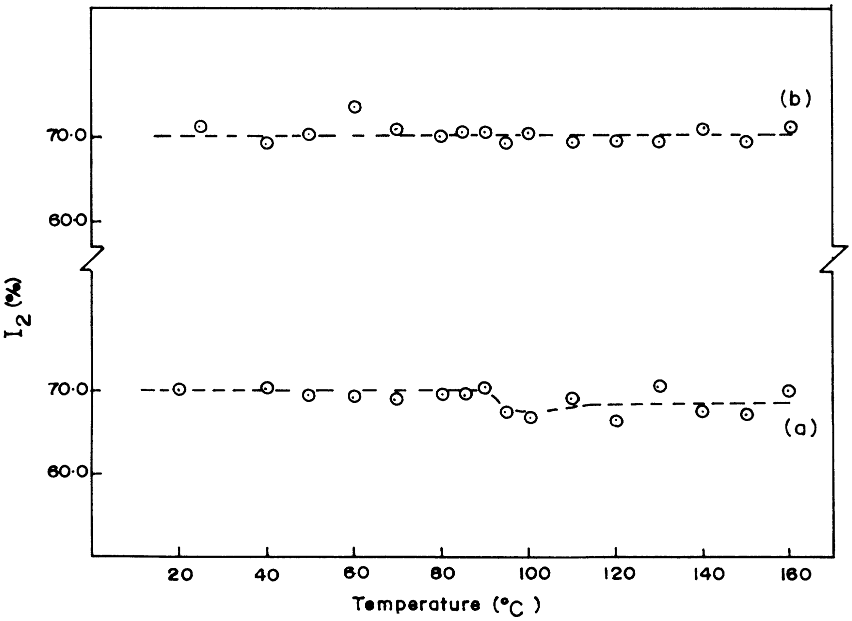

FIG. 2. Variation of the intensity I_2 as a function of the annealing temperature (a) for a pure PAN (undoped) polymer and (b) for a 0.8 wt % iodine-doped PAN polymer.

tion between the long-lived component τ_3 and the free-volume radius R. Here it is assumed that the orthopositronium atom in a free-volume site of the polymeric material can be approximated by a particle in a spherical potential well of radius R_0. The potential is infinite for $r > R_0$ and constant for $r < R_0$. 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 orthopositronium atom in the electron layer has a spin-averaged positronium lifetime of 0.5 ns. The relation between R and the orthopositronium lifetime τ_3 is of the form[18]

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

Nakanishi, Wang, and Jean have also shown that the above equation with $\delta R = 0.1656$ nm gives a correct estimate of τ_3 for known free-volume sizes in porous materials.[18] By fitting Eq. (1) to the measured values of the orthopositronium lifetime in the molecular media having known hole sizes (τ_3 in the range 2–5 ns) extracted from the literature,[19–24] we have obtained a value of 0.166 nm for δR which agrees well with the result of Nakanishi, Wang, and Jean. The various values of τ_3 and the hole radius are plotted in Fig. 4. Using this value of δR, we have calculated the hole radius using Eq. (1) and the measured value of τ_3 for the undoped PAN sample. When this is plotted on the same graph (Fig. 4), it lies at the appropriate position, justifying the fact that the value of $\delta R = 0.166$ nm is quite correct in the present case too. Using this hole radius, the free volume V_f was calculated as $4\pi R^3/3$. Figure 5 displays the free-volume size plotted as a function of annealing temperature. As is usually done, we assumed here that the concentration of free-volume sites is proportional to the intensity of orthopositronium in the polymer which has been tested in semicrystalline polyarylethevetherketone (PEEK) by others.[19] A plot of I_3 is shown in Fig. 6(a). It is found that for PAN the value of V_f ranges from 0.04 to 0.08 nm^3 for the annealing cycle 25–160 °C.

It is interesting to study the variation of the lifetime (τ_2) parameter as a function of annealing temperature from Fig. 1(a), where τ_2 is seen to increase from 25 to 60 °C. In Fig. 5 the free-volume size varies with temperature, whereas from Fig. 6(a) we observe that the intensity of *o*-Ps, which is closely related to both the positronium formation probability and the number density of free-volume sites, is almost constant throughout the annealing

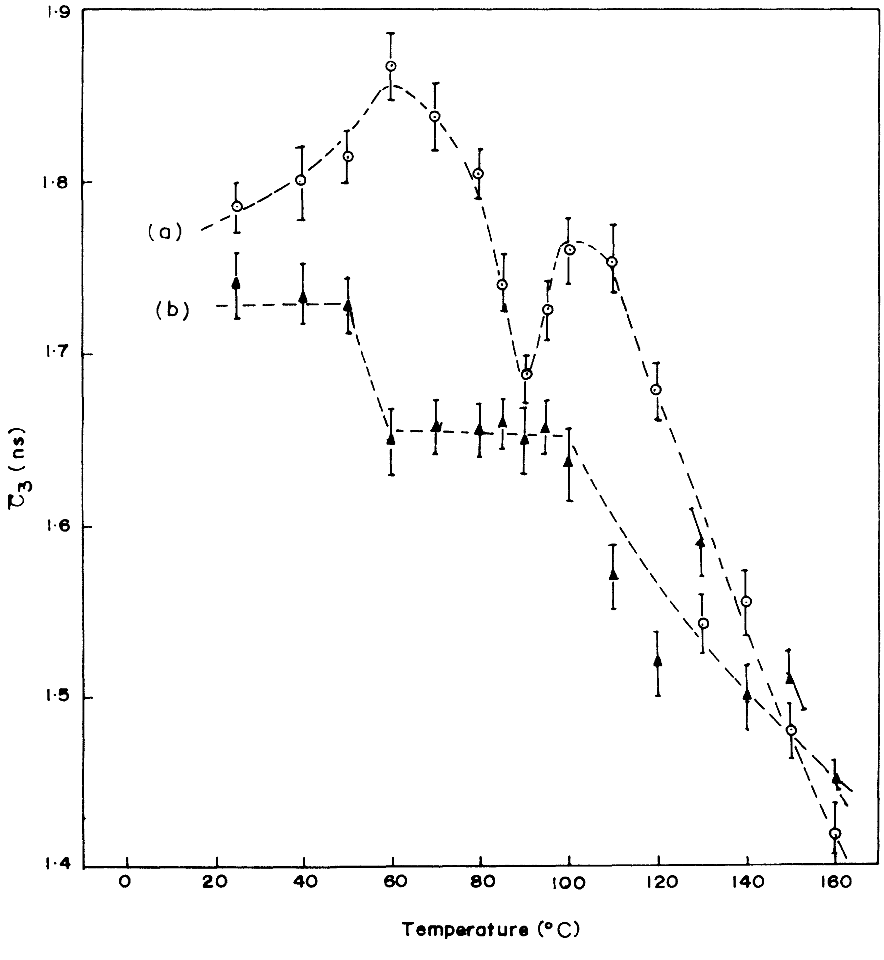

FIG. 3. Variation of the orthopositronium lifetime (τ_3) as a function of the annealing temperature (a) for a pure PAN (undoped) polymer and (b) for a 0.8 wt % iodine-doped PAN polymer.

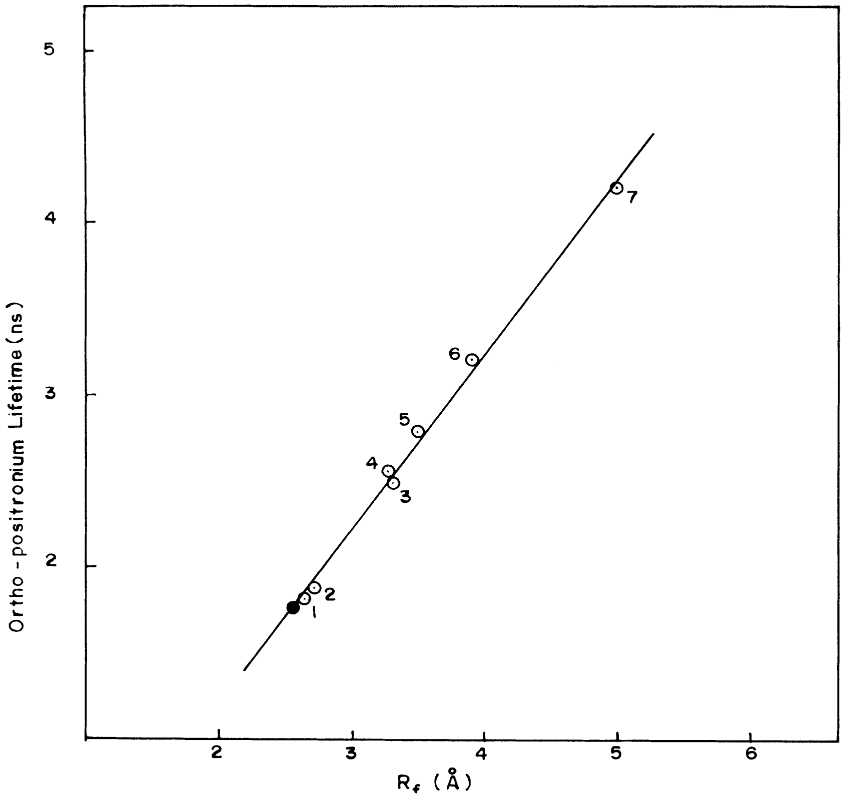

FIG. 4. Variation of the orthopositronium lifetime versus the hole radius: open circles are taken from the literature (Refs. 19–24), and the solid circle is from the present measurements.

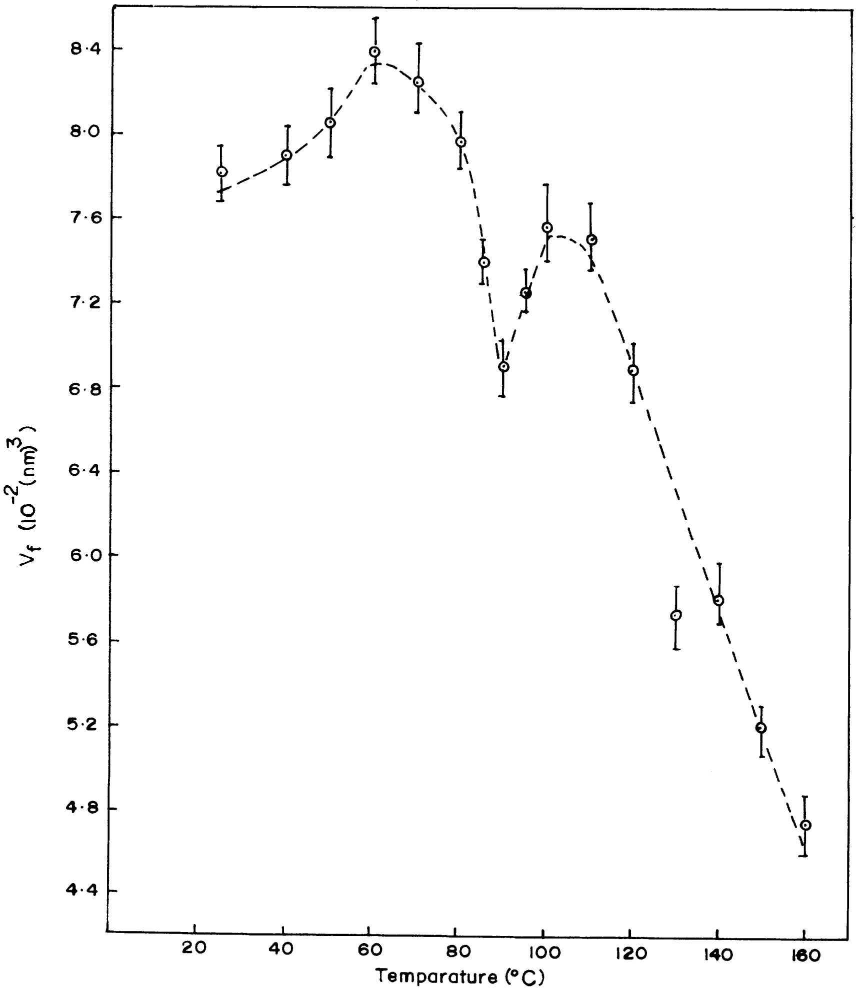

FIG. 5. Variation of the free-volume size as a function of the annealing temperature for a pure PAN (undoped) polymer.

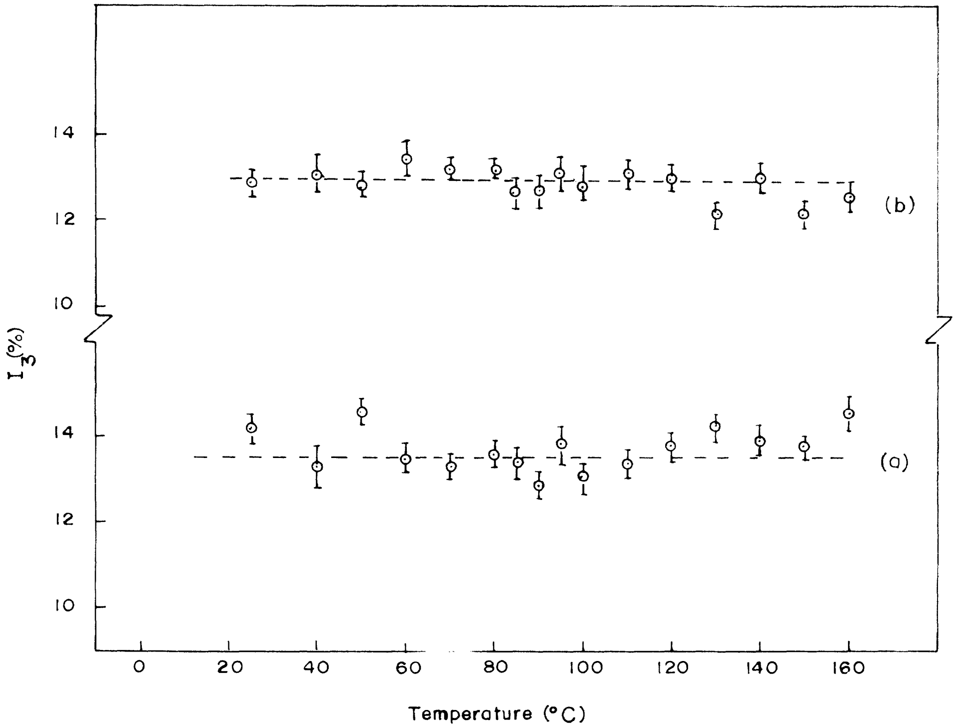

FIG. 6. Variation of the intensity I_3 as a function of the annealing temperature (a) for a pure PAN (undoped) polymer and (b) for a 0.8 wt % iodine-doped PAN polymer.

temperature. Initially, τ_3 and the free-volume size increase from 25° to 60 °C and after that it decreases up to 90 °C; then it increases suddenly until 100 °C, and thereafter it starts to decrease. The monotonic increase of τ_3, and hence the free-volume size and τ_2, up to 60 °C can be explained as follows: It is known that in semicrystalline polymers the variation of τ_2 with temperature is small, though significant. This could be due to additional positron states which are closely related to defects in crystalline regions or trapping sites at the crystalline and amorphous interface. Because of the presence of the bulky steric side group and intermolecular dipole repulsions in PAN, one can expect a shift to an irregularly twisted backbone chain configuration. These molecular chains pack like rigid rods in the lattice array and, as such, only lateral ordering between the chains is possible, but not the longitudinal ordering along the chains; therefore, one can expect the heat treatment to cause chain folding, which results in an increase of the hole size and hence an increase in τ_3. This chain folding does not affect the free-volume number density in the amorphous region. On the other hand, in the crystalline region some positrons may be trapped at kink-type defects which are due to the molecular arrangement. This is reflected in τ_2, which shows an increasing trend [Fig. 1(a)] up to 60 °C.

The orthopositronium lifetime τ_3, the free-volume size, and τ_2 decrease from 70 °C and change slope suddenly at 90 °C. Even the intensity I_2, which is constant up to 90 °C, also changes slope [see Fig. 2(a)], indicating that 90 °C is the glass transition temperature (T_g) for this polymer. This agrees well with the value of T_g obtained from differential-scanning-calorimetry measurements as well as the value reported in the literature. Experimental results on polystyrene,[25] epoxy resin,[26] poly(methyl methacrylate), and other methacrylates[27] do show an abrupt change in the slope of the τ_3 versus temperature curve at T_g. According to Kindl and Reiter,[28] the glass transition of the polymer is characterized by the onset of a cooperative motion of large segments of the molecules (micro-Brownian motion) in the amorphous region. Below the glass transition temperature, only limited local motions of a small fraction of the molecules are possible. In the present case, it appears that this type of motion actually starts from 70 °C and, at each annealing temperature, some free-volume sites are trapped in the sample. This excess free volume allows molecular segments to diffuse, leading therefore to a reduction in the free-volume size. On the other hand, in the crystalline region, because of this type of motion, trapping centers at the interface between the amorphous and crystalline regions shrink with annealing temperature. This is very well reflected in the intensity of the second lifetime component, which is almost constant up to the glass transition temperature [see Fig. 2(a)], demonstrating that, because of this molecular motion, no additional trapping centers were created in the crystalline region or even at the interface between the amorphous and crystalline regions. After 90 °C, there is an increase in the motion of longer segments of molecules characteristic of the rubbery state. This motion requires more free volume than the short-range excursions of atoms in the glassy state. The increase in free-volume size with increasing temperature leads to an increase of the volume-expansion coefficient in this region. This increase of the volume-expansion coefficient is the result of the increase in the amplitude of molecular vibrations with increasing temperature; hence, there is an increase in the free-volume size from 90 to 100 °C.

From 100 °C onward, all the annihilation parameters once again start to decrease. A possible explanation for this is the following: This decrease may be due to the breakoff of macromolecular entanglements, which starts at a temperature higher than 100 °C. Even thermal degradation of the polymer can also be involved. Consequently, the free volume starts to decrease. On the other hand, throughout the annealing temperature range studied, the free-volume number density remains almost constant, as reflected in the constancy of I_3. In the crystalline region, positron-trapping centers are initially constant up to the glass transition temperature T_g and vary slightly at temperatures higher than T_g, as is evident from the τ_2 and I_2 variations. On the whole, it is the free-volume size (and hence τ_3) which is the only changing parameter. On the basis of this study of free-volume size as a function of annealing temperature, it is clear that only in the amorphous regions of the polymer matrix does much of the structural change occur during annealing.

B. Doped sample

τ_2 and τ_3 data of (0.8 wt %) iodine-doped sample, are shown in Figs. 1(b) and 3(b) and the corresponding intensities in Figs. 2(b) and 6(b), respectively. By comparing Figs. 1(a) and 1(b), 2(a) and 2(b), and 3(a) and 3(b), it is evident that there is a considerable change in the annihilation parameters upon doping with iodine. The results seem to suggest that, as soon as iodine is added to the polymer, the iodine atoms diffuse into the amorphous region of the polymer,[10] mainly into the free-volume sites. These iodine atoms form complexes with the side chain group which contain π bonds which are loosely bound and therefore there is a reduction in the positronium-trapping centers as well as the interface between the crystalline and the amorphous regions. This change is noticeable in the plot of τ_3 as a function of annealing temperature displayed in Fig. 3(b).

By comparing the plots of the annihilation parameters of the undoped sample with those of the doped sample, one can notice somewhat different trends of the change in τ_3 in these two cases. In the undoped sample, initially τ_3 shows an increasing trend, whereas in the doped sample it is almost constant. After 70 °C, τ_3 decreases up to the glass transition temperature (T_g) in the undoped sample and in the doped sample it decreases suddenly at the glass transition. Also, the glass transition temperature in the doped sample is shifted toward lower temperatures, from 90 to 60 °C. After T_g, τ_3 increases abruptly and then decreases monotonically in the undoped state, but in the doped state it is constant up to 100 °C before decreasing.

The variation of τ_3 with annealing temperature in the doped state can be explained as follows: The value of τ_3 in the doped state is smaller than that of the undoped state at room temperature. Since iodine is a good quencher of o-Ps, the reduced value of τ_3 is understandable. Because of chemical quenching, one cannot use Eq. (1) to evaluate the free-volume size in the case of the doped sample. As discussed earlier, in the case of the undoped sample, here also the ordering of the polymer is still present in the lateral direction, but not in the longitudinal direction of the polymer main chains. In the doped sample, iodine atoms form complexes only with the bulky group (the π electrons are present only in this bulky group). Therefore one could not expect much chain folding as has been observed in the undoped sample, which is the major process involved during heat treatment which enhances τ_3 at lower temperature. In the doped sample, because of complex formation, chain folding is less at lower annealing temperatures and hence there is an observed constancy in τ_3 at the initial stages of annealing. At the glass transition temperature in the case of the undoped sample, the cooperative motion is spread over a temperature interval of about 30 °C (60–90 °C), but in the doped sample the spread is much smaller. Even after T_g (the polymer in the rubbery state), because of the presence of complexes, the motion of longer molecules is hindered and hence there is a constancy in τ_3 up to 100 °C. Here, also, there is not much structural change occurring in the crystalline region, as evidenced by the annealing results (from the variation of the second component). After 100 °C, similar macromolecular breakoff and degradation of the polymer take place, as is reflected in the decrease of τ_3 with annealing temperature.

IV. CONCLUSIONS

This study shows that the positron-lifetime technique is a very useful method in determining free-volume-related microstructural changes in a polymer. In polyacrylonitrile, lifetime measurements as a function of annealing temperature in the undoped state as well as the (0.8 wt % iodine) doped state yields the following information: At lower annealing temperatures, the molecular-chain-folding process is more prevalent in the undoped sample, which is hindered by the presence of complexes formed by iodine with the side chains, than in the case of the doped sample. After 100 °C, in both states the polymer degrades. This study also gives the T_g of PAN as 90 °C, which is shifted by 30 °C, in the doped sample.

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