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TRANSPORT OF IODINE IN POLY(ETHYLENETEREPHTHALATE)

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Abstract—Iodine sorption characteristics of poly(ethyleneterephthalate) have been studied through free volume changes by the positron annihilation lifetime (PAL) technique. The results show swelling of the polymer, charge transfer complex (CTC) formation in the initial stages and precipitation of iodine in the final stages of sorption. Additionally, the results suggest a conformational transformation in the amorphous region of the polymer in the final stages of sorption which is in agreement with the earlier predictions. It is also revealed that iodine acts more as an inhibitor than a quencher of the o-Ps. The average free volume size suggests that the predominant species which fills the free volume holes during iodine sorption is I_3^-. The sorption in PET obeys Case II diffusion. Furthermore, the study shows that Fujita's free volume theory, which relates the fractional free volume and diffusion coefficient, deviates. © 1997 Elsevier Science Ltd

INTRODUCTION

Doped polymers have recently been the subject of intensive studies. According to the type of additive and its concentration, technologically interesting properties can be obtained from the known structure of doped materials and conditions of preparation [1]. Thus, complete information about the effect of additives on a specific polymer helps in tailoring that polymer for a particular application. Although, polymers have traditionally been considered as good electrical insulators, researchers have shown that a certain class of polymers which are conjugated (extended π-conjugation along the polymer back bone), exhibits increased conductivity on doping [2].

The introduction of a dopant can considerably modify the charge storage property of a polymer [3] or it can improve the charge carrier mobility [4]. In addition, the presence of a dopant can have an unwanted effect on the physical properties such as tensile strength and fatigue resistance [5]. Sorption is the process in which a foreign species can be added into the polymer by diffusion and leads to changes in the physical state of the polymer, such as swelling, plasticization and induced crystallization [5]. The specific features observed during the diffusion process vary greatly depending on whether the polymer is in the rubbery, glassy or semicrystalline state at the imposed conditions of temperature and pressure [5]. The presence of additives/dopants influence the transport properties of the material as well [6]. When a dopant such as iodine is introduced into a polymer matrix, it is important to understand its ability to form charge transfer complexes (CTCs), the mechanism of charge production and site of localization inside the polymer matrix. The improved conducting behaviour of polymers on iodine doping is generally attributed to the formation of CTCs [7].

Fujita, in an attempt to understand the transport of small molecules in polymers extended the free volume theory of diffusion to account for the dependence of the diffusion coefficient on the concentration of diffusing molecules in polymeric films. The proposed model is based on an oversimplified view of molecular processes which do not take into account the detailed molecular structure of the polymer–penetrant system but relate the diffusion coefficient to the free volume fraction of the system [8–10]. This has been found to describe satisfactorily the diffusion of a number of organic liquids and vapours in polymers.

In the case of diffusion, the diffusate always moves in the direction of diminishing concentration and Fick's law relates the flux of the diffusing particles to the concentration gradient [11]. The diffusion characteristics represent the extreme response of polymers to the solvent and have substantially different characteristics. Generally, all rubbery polymers obey Fick's law (Case I diffusion) and glassy polymers show non-Fickian behaviour (Case II diffusion) [5].

Poly(ethyleneterephthalate) (PET) is considered to be an excellent material for making good quality films for specific application. But, a few disadvantages exist, mostly originating from its low water wettability and poor antistatic properties. Therefore, a large number of experiments have been performed to improve these undesirable properties of PET, for instance by acid–alkaline treatment, irradiation with ionizing radiation and plasma discharge [12]. Although, PET has a very poor crystallizability, organic liquids like acetone have been shown to induce crystallization in them [13]. On account of the donating nature of the conjugate pair of π electrons from the carbonyl groups of PET, doping with iodine is expected to allow CTC formation at these sites because of the strong affinity of iodine towards these electrons. Also, depending on the environment, the macromolecules of a solid polymer may change their conformations in order to minimize the interfacial energy. It has been reported that PET, when sorbed in an aqueous media like water, shows some conformational changes [14]. The pioneering work by Pennings and Bosman [15] shows that activation energies of relaxation at the surface are very closely related to the activation energies of bulk relaxations, which seems to indicate that the molecular mobility at the surface and in the bulk are more or less the same. Prompted by these interesting aspects of PET, we thought it worthwhile to study iodine sorption in PET using the positron annihilation lifetime (PAL) technique. We also intended to find the existence of any conformational changes upon sorption. We have used this "nano hole probe" (PAL) technique to evaluate the fractional free volume and the method of the single free phase model of absorption for diffusion coefficient measurements. The PAL technique used in this study is briefly outlined below.

After entering a condensed medium, the positrons rapidly lose almost all their energy by collisions with molecules. They continue to do so until they eventually annihilate with an electron (free or bound to an atom in the medium) or they may form a Positronium atom (Ps) and annihilate from this state. Ps can exist in two spin states. Positrons bound in the *para* state (p-Ps) annihilate with a lifetime of 125 psec; those bound in the *ortho* state (o-Ps) annihilate predominantly via a pick-off process in which the Ps positron picks up an electron of opposite spin from the surroundings and its lifetime gets reduced to a few nsec from 140 nsec. The o-Ps pick-off lifetime (τ_3) depends on the overlap of the Ps wave function with that of the molecules forming free volume holes. Hence, the larger the hole size, the smaller is the overlap and the longer the lifetime. The o-Ps lifetime (τ_3) and its intensity I_3 are representatives of free volume size and their number density, respectively [16, 17]. PAL also provides information with regard to regions of the polymers with densified structure (crystalline regions) through τ_2 and I_2. A lucid explanation about the formation of Ps and its trapping in free volume holes can be obtained from ref. [16].

EXPERIMENTAL

PET of molecular weight of 20,000 was obtained from commercial sources in the form of a 0.1 mm thick film. The results from the XRD data shows this polymer to be semicrystalline with approximately 80% crystallinity. Iodine sorption was carried out by soaking the sample in an aqueous KI/iodine solution for different time intervals. After each experimental interval of immersion, the samples were removed and blotted free of surplus iodine. Then using a Mettler digital balance, its mass was determined to a good accuracy. The samples were then used in the lifetime measurement. This was carried out using a 15 μCi positron source (^{22}Na) which was prepared on a kapton foil of 0.5 mil thick. Ten films of PET on either side of the source were used in a sandwich configuration. The experiment was performed with a fast–fast coincidence system with a time resolution of 340 psec obtained with ^{60}Co radiation for 40% ^{22}Na energy gating. More details of the experiment can be found elsewhere [17]. All these measurements were carried out at room temperature. Two to three lifetime spectra with at least one million events were accumulated for each sorption level. The instrumental time resolution and source correction terms were obtained from the measured spectrum of a medium of known lifetime fitted with the use of a computer program, RESOLUTION [18]. Consistently good spectra were analyzed using the program PATFIT-88 [18].

RESULTS AND DISCUSSION

Positron lifetime results

As is the situation in many polymers [17, 19], we have resolved the PAL spectra into three lifetime components which gave a very good fit and χ^2 values. Among the three lifetime components, the shorter component τ_1 with intensity I_1 is attributed to the free annihilation of the positrons with an unresolvable contribution from the decay of p-Ps. The origin of the intermediate component is still under discussion and different researchers follow slightly different approaches. We follow the approach of Goldanskii *et al.*, [20] according to which the second lifetime component τ_2 with intensity I_2 is attributed to the annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline–amorphous interface. The long lifetime component (τ_3) with intensity I_3 is attributed to the pick-off annihilation of the o-Ps in the free volume sites present in the amorphous regions of the polymer matrix [19].

The relation between the free volume size and the o-Ps lifetime was developed by Tao [21] for molecular liquids. This was later modified by Nakanishi *et al.*, [19] and this simple relation connecting the free volume radius (R) and the o-Ps lifetime (τ_3) is

$$\tau_3^{-1} = 2[(1 - R/R_o) + 0.159\ \{\sin(2\pi R/R_o)\}]\ \text{nsec}^{-1} \tag{1}$$

where $R_o = R + \Delta R$, and ΔR is the thickness of the electron layer and its fitted value is 0.1656 nm [19]. The free volume size is calculated as $V_{f3} = (4/3)\pi R^3$. From this, the fractional free volume can be calculated as

$$F_v = C\ V_{f3}\ I_3 \tag{2}$$

where C is the structural constant. For PET it is experimentally determined to be 0.0017 Å^{-3} using the value of the coefficient of thermal expansion obtained from a separate isochronal annealing study.

Iodine in free volume holes

Figure 1 shows a plot of τ_3, V_{f3} and I_3 as a function of sorption time. When introduced into a polymer matrix, iodine can act as a positron "scavenger" forming different positronium/iodine complexes. If this process were to occur, then it should have resulted in abrupt changes in the lifetime values since the annihilation lifetime of the formed Ps-iodine compound (PsI$_2$ or PsI) is estimated to be 0.4 nsec [22]. Contrary to this, the present results show a gradual variation in τ_3. Even the second lifetime component whose value is around 480 psec does not show any variation as a function of sorption time. Hence the possibility of the above process is completely ruled out.

Based on the variation of the lifetime parameters, the initial stage of sorption can be divided into two phases. Phase I (where the o-Ps lifetime and free volume size shows constancy) and Phase II (where o-Ps lifetime shows a rising trend). In both of these two phases the o-Ps intensity falls linearly. In the later stages of sorption, the τ_3 and V_{f3} decreases in which period the I_3 value levels-off. Their variation can be explained in the following way: iodine is known to be a quencher of o-Ps and hence a reduction in its lifetime is expected. In contradiction to this, the o-Ps lifetime and hence the free volume size remains unaltered during the I phase and increases in the II phase of the initial stages of sorption. In both of these two phases, the o-Ps intensity decreases continuously indicating the filling of the free volume holes by iodine and hence a reduction in their number density.

We can explain the initial constancy of τ_3 as due to the combined effect of swelling and CTC formation in the following way: the PET surface has been shown to exhibit a swelling nature in liquid media like water on sorption [14]. On extending this argument to the bulk of the polymer as discussed in reference [15], the swelling should result in an increase in the free volume size and hence an increase in τ_3. On the other hand, the presence of iodine could lead to CTC formation. Iodine is shown to form complexes with carbonyl [23] and phenyl groups [24]. Since PET contains both of these two groups, it is suggested that these are the possible sites for iodine for form CTC. Poly(ethylenenaphthalene-2,6-dicarboxylate) (PEN), an homologous polymer of PET in which the benzyl ring is substituted by naphthalene, has been shown to have 26% large sorption ability than PET [25]. Moreover, it has been reported that the addition of an arylate group to PET will increase the crystallizability compared to PET homopolymer [26]. The above two works show that the benzyl group found in the polymer backbone of PET is not an active site. Hence, the carbonyl groups are the only available sites for iodine to form a CTC. These CTCs provide conducting pathways through the amorphous regions of the polymer and would result in an enhancement of the conductivity. The iodine species having accepted the electrons gets a negative charge and thus becomes the attractive centre for positrons. As the number of such CTCs increases, the annihilation rate increases leading to a decrease in the o-Ps lifetime. In the present case, it appears that increase in τ_3 due to swelling almost counterbalances the decrease in τ_3 due to CTC formation and hence a constancy in the value of o-Ps lifetime and the free volume size is observed.

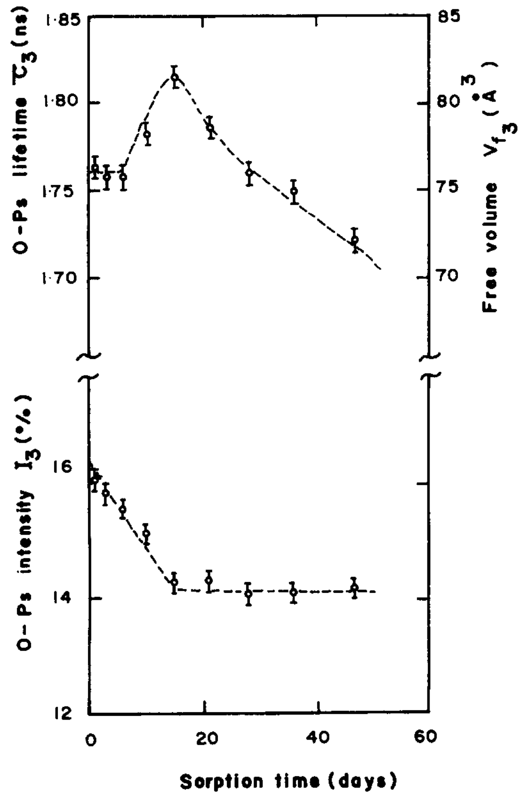

Fig. 1. Variation of o-Ps lifetime τ_3, its intensity I_3 and free volume size V_{f3} as a function of sorption time. Dashed line is to guide the eye.

In the II phase of the initial stage of sorption, since the carbonyl groups are the only sites where the iodine can form CTCs, the swelling process dominates the effect of CTC formation. The phenomenon of swelling depends on the forces of interaction between the solvent molecules and the polymer segments. When the swelling increases, more and more of the polymer molecules loosen [27]. Hence the free volume size increases from this sorption level onwards leading to an increase in o-Ps lifetime. By analogy from gas sorption experiments in polymers [28] we can say that, even though the swelling starts initially, it is prominent only after a particular solvent concentration is reached. Even the swelling in case of water sorption of PET is shown to occur more strongly after a sufficient interval of time [14].

In the final stages of sorption, the results are still interesting. τ_3 decreases and I_3 remains constant. In a very recent study, it has been shown that PET, after a certain period of water sorption, shows a conformational change [14]. The different conformations of the monomer units are due to the motion of the flexible parts. Based on molecular modelling calculations, PET in the untreated state exists more in a coiled conformation than in the stretched state and the ratio of these two states is reported to be 74:26 [14]. This ratio changes to 26:74 when it is sorbed in water as the O-CH_2-CH_2-O group which is highly flexible makes the molecule spread out to expose its ester groups to water and to maximize the possibility of hydrogen bond formation. In the present case, since I_3 remains constant suggests that the filling of the iodine is complete and the iodine gets precipitated. This also indicates that the CTC formation too is complete. At this stage, the molecules with carbonyl groups together with benzyl group will be bulky and because of the flexibility of the O-CH_2-CH_2-O group, they may spread out to stretched conformation. Due to this change in conformation, the free volume size might decrease resulting in a decrease in τ_3. Observed results support this. Since this is a sudden change, the free volume size decreases continuously, even though there is a counteracting effect in the form of swelling which tends to increase the size of the free volume. Interestingly, this coiled to stretched conformational

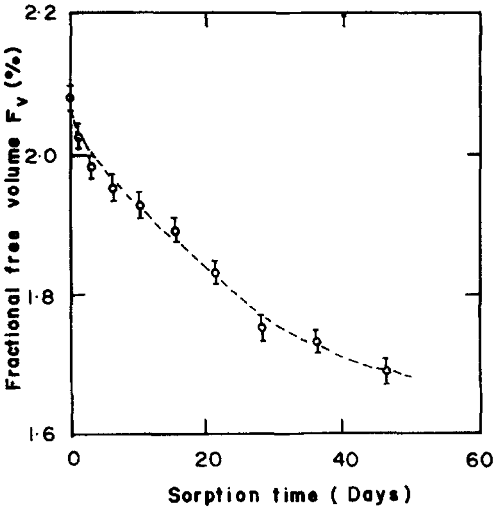

Fig. 2. Variation of fractional free volume F_v as a function of sorption time. Dashed line is to guide the eye.

change has no effect on the number density of free volume sites as evidenced by the constancy in I_3 (Fig. 1). The gradual decrease of the fractional free volume (F_v) which is a measure of the free volume content also supports the explanation that these free volume holes get filled by the iodine molecules during the process of sorption as shown in Fig. 2.

In any given sample, all the free volume holes are not of the same size and the fact that one observes a well defined lifetime τ_3 does not mean that all the positrons are annihilating in holes of the same size. So, in practice the concept of average free volume is used. Kobayashi *et al.*, [29] have defined a lower and upper limit for the distribution of free volume sizes. Following this, we have estimated the lower and upper limit for the free volume sizes in the present case to be 49 and 105 Å^3. Various techniques have been used [30, 31] to study the nature of iodine species entering the polymer matrix when it is iodinated. These results guided us to match the size of different iodine species that can fit into the free volume holes in PET which has an average free volume size of 77 Å^3. The size of the I_3^- species (104 Å^3) fits well within the obtained size limits. The Mössbauer result of iodine doped polyacetylene gives the ratio of I_5^-/I_3^- to be 0.33 [32]. This suggests that I_3^- is the most predominant species which gets into the polymer matrix during iodination and the present results support this.

Effect of iodine on the crystalline and crystalline/amorphous interface regions

The intermediate lifetime component τ_2 and its intensity I_2 as a function of sorption time are depicted in Fig. 3. It is clear from this figure that τ_2 remains constant in the entire sorption period, whereas I_2 shows an initial increase (Phase I) and then decreases (Phase II) throughout the sorption period. The explanations for these variations are as follows: the crystalline regions usually have a rigid structure when compared to the amorphous regions. When the dopant forms CTCs in the crystalline regions, during the early stages of sorption, the number of annihilation sites increases which should result in an increase in I_2, but the CTCs are of the same kind and hence τ_2 should have a constant value. That is what we observe in τ_2 and I_2.

In Phase II, the swelling will be dominant and the polymer coils become loosened, and they may be diffused into these microvoid type defects. This may result in the observed decrease of the I_2. Surprisingly, the average size of these defects is not affected by this process as can be evidenced by the constancy in lifetime τ_2. Thus, the present results show that the conformational change from "coil to stretch form" has an effect only on the amorphous regions, and has no effect on the crystalline regions. The overall variation of the annihilation parameters in the crystalline regions is also not much which may be due to the highly crystalline nature (80% crystallinity) of the sample.

Diffusion coefficient measurements

We have used Fick's law of diffusion to understand the sorption mechanism of iodine in PET. Stefan on modifying the theoretical equation of Fick's law of diffusion in a plane sheet [33] gives an approximate

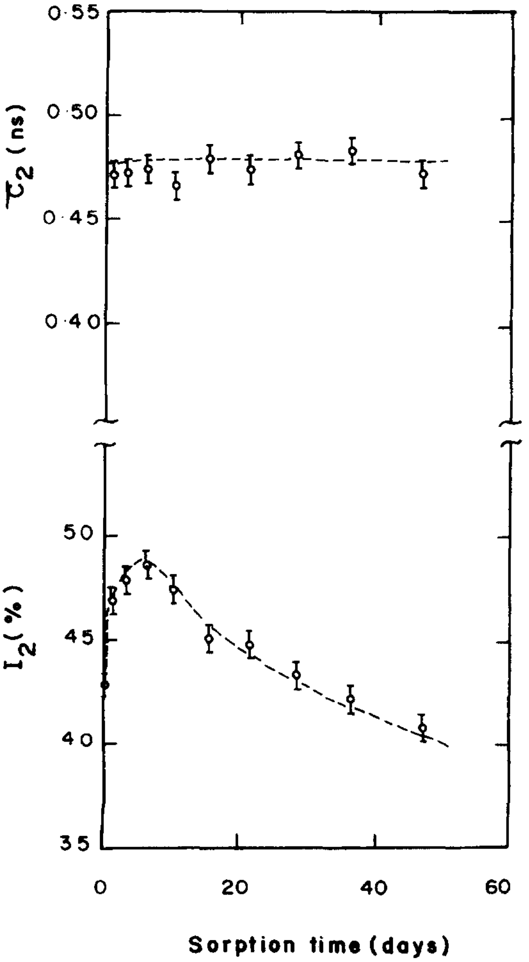

Fig. 3. Variation of second lifetime component τ_2 and its intensity I_2 as a function of sorption time. Dashed line is to guide the eye.

Table 1. Iodine mass uptake as a function of sorption time

Sorption time (days)	Mass uptake (mg)
Sorption time	Mass uptake
1.25	0.8
3.25	1.5
6.25	1.9
10.25	3.2
15.25	4.1
21.25	5.3
28.25	5.8
36.25	7.1
46.75	8.0

relation for the diffusion coefficient as

$$M_t/M_m = 4\,(Dt/\pi l^2)^{1/2} \qquad (3)$$

where M_t and M_m are the masses of the penetrant taken up or lost at time t and m (time when the sample has reached the equilibrium weight). D is the diffusion coefficient and l is the thickness of the sheet. The iodine uptake at any time t (M_t) is calculated as

$$M_t = (W_s - W_d)/W_d \qquad (4)$$

where W_d is the weight of the dry sample and W_s is the weight of the sample which has been soaked for a time t. M_m is calculated as

$$M_m = (W_m - W_d)/W_d \qquad (5)$$

where W_m is the weight of the sample in the final stage of the sorption. Table 1 shows the iodine mass uptake as a function of sorption time. A plot of M_t/M_m vs $\sqrt{t}$ is shown in Fig. 4. It is evident from this figure that, throughout the period of sorption the ratio of M_t/M_m varies linearly with $\sqrt{t}$. From the linear portion of the line in the interval $0 < M_t/M_m < 0.5$, the apparent diffusion coefficient D has been calculated and its value is found to be 9×10^{-10} cm^2/sec.

If the given system exhibits a classical Fickian behaviour, (Case I diffusion) then the ratio M_t/M_m should level off after the initial linear rise. Additionally, the Fickian behaviour is characterized by a rate of diffusion much less than that of polymer segmental relaxation. This law applies generally to all rubbery polymers. In the case of polymers of non-Fickian behaviour (Case II diffusion), the diffusion is much faster than that of the polymer segmental relaxation. This is generally applicable to all glassy polymers. PET, which is in glassy state at room temperature also shows Case II diffusion. But, interestingly, the variation of M_t/M_m vs $\sqrt{t}$ is linear throughout which fits to a relation of the type

$$M_t/M_m = 0.033\,\sqrt{t} + (-0.12) \qquad (6)$$

Such a linear variation type has been found for the case of ethanol transport in poly(methyl methacrylate) and the diffusion type has been attributed to Case II [34]. So, in the present case of an inorganic sorbate the diffusion is also of non-Fickian (Case II) type.

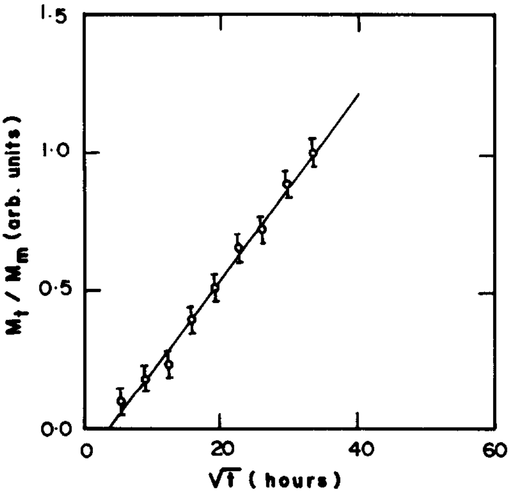

Fig. 4. Variation of M_t/M_m as a function of the square root of sorption time. Solid line is the linear fit to the experimental value.

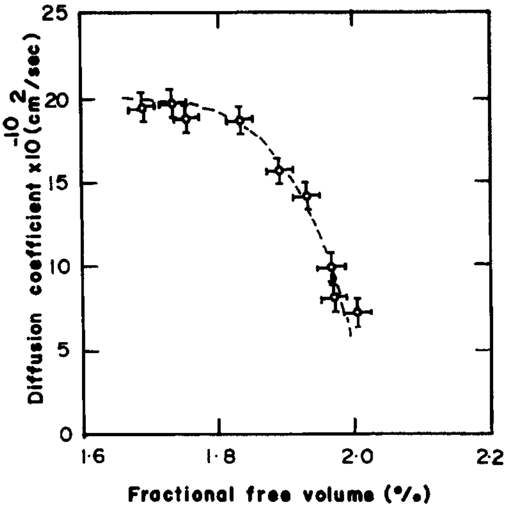

Fig. 5. Variation of diffusion coefficient D with fractional free volume F_v. Dashed line is to guide the eye.

Free volume and diffusion coefficient

We have used the results of the present study to test the correlation between F_v and diffusion coefficient (D) as per Fujita's theory. The solvent diffusion coefficient follows a simple exponential dependence on the total fractional free volume [10, 11]. As mentioned earlier, this theory satisfactorily explains the diffusion of organic liquids and vapours in polymers. As we have used an inorganic solvent such as aqueous iodine solution, we investigated whether the fractional free volume bears the same relation to diffusion coefficient (D). The D has been calculated for each sorption level using equation (3). A plot of D vs F_v is presented in Fig. 5. It is evident from this figure that the variation of D vs F_v neither fits an exponential trend nor a power regression relation. In comparison to our earlier study on polycarbonate [35], where the sorption of iodine in polycarbonate follows a normal Fickian behaviour and Fujita's exponential relation between F_v and D holds good, the present results deviate from this. These results indicate that a deviation from Fick's law means deviation from Fujita's free volume concept. More investigations of this kind are needed to arrive at a definite conclusion in this regard.

CONCLUSIONS

Using the PAL technique, we have studied the free volume changes in PET in the presence of iodine dopant. Sorbate iodine acts as an inhibitor rather than a quencher of o-Ps. The variation of o-Ps intensity suggests that the free volume holes are filled by iodine molecules during the initial stages of sorption.

The measured size of the free volume holes indicate that I_3^- is the most predominant species filling the free volume holes. The positron results also indicate that the carbonyl groups of the PET are the active sites for CTC formation.

The changes in the amorphous region at the later stages of sorption confirms the presence of a conformational change from coiled to stretched state. Diffusion of iodine in PET is of non-Fickian type. The variation of fractional free volume with diffusion coefficient does not follow Fujita's concept of free volume.

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