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Influence of ion-irradiation on the free volume controlled diffusion process in polycarbonate—a positron lifetime study

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Abstract

Iodine sorption in un-irradiated and ion-irradiated polycarbonate (PC) has been investigated using positron lifetime spectroscopy. The decrease in positron lifetime parameters of ion-irradiated sample is attributed to the free volume modifications, and the formation of more stable free radicals on cross-linking. The difference UV absorption spectrum shows a strong absorption peak at 384 nm which is due to 2,2′-dihydroxybenzophenone; this depicts the possibility of photo stabilisation of polycarbonate on ion-irradiation. A comparative study of sorption process is explained in terms of iodine diffusion in free volume holes in un-irradiated and ion-irradiated polycarbonates. The experimental results on iodine diffusion shows an early saturation of positron parameters in irradiated PC, which is due to an increase in the rate of diffusion as small number of bigger size free volume holes are formed on irradiation. The diffusion process follows Fick's law and, an exponential type of correlation has been observed between fractional free volume and diffusion coefficient which indicates that Fujita's free volume theory is valid before and after ion-irradiation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Ion-irradiation; *ortho*-Positronium lifetime

1. Introduction

In polymers, the desired physical and chemical properties needed for some specific applications may be obtained by their exposure to high energy radiation or ion-irradiation. Polymers undergo a change in molecular weight on irradiation due to chain-scission and cross-linking. Some polymers like poly(methyl methacrylate) (PMMA) [1] undergo chain-scission on exposure to radiation while cross-linking is observed in the case of poly(tetra fluroethylene) (PTFE) [2]. In certain cases like polycaprolactone irradiation results in both cross-linking and chain-scission [3] Recently, ion-irradiation which induced physico-chemical modifications in polymeric materials have been reported [4], and therefore it is expected that more complex effects and new phenomena can be created in the polymeric materials by ion-irradiation. The different ways by which the gross properties of polymeric materials are affected by environmental conditions are innumerable [1,2]. The exact effect produced depends on the structure of the polymer and the nature of radiations [5]. A good number of reviews are available dealing with the variations in polymeric properties from fundamental photo physics studies to investigations of molecular weight changes upon irradiation [1,6].

The diffusion of solvents in amorphous glassy polymers had been the subject of much attention in polymer technology including packaging of foods, drugs, cosmetics, and controlled release of dissolved materials. In amorphous domains of the polymer, there exist low electron density regions called free volume holes or cavities. The amount of free volume holes in a polymer is called the fractional free volume (F_v) or free volume content. Over the years there have been several developments in the free volume theory [7–9]. In polymers, diffusion of molecules is somewhat complex, to a large extent it depends on the magnitude of the non-equilibrium free volume available in the polymer matrix [10]. Solvent diffusivity can be influenced significantly by small changes in the chemical structure of the diffusant molecule or the polymer. For molecules of low solubility, the physical state of the polymer is unaffected by the diffusant, so that the diffusion is expected to follow Fick's law [11]. If the rate of diffusion is lesser than the polymer segmental relaxation, it is termed as Fickian

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behaviour and if the rate of diffusion is much greater than the polymer segmental relaxation, it is termed as non-Fickian behaviour.

The rate of diffusion in amorphous domains of the polymer will depend to a large extent on size of the diffusing molecules and size of the gaps available [12]. In this respect, the simplest theory of free volume is the one by Fujita [13], which owes its origin to the free volume theory of Cohen and Turnbull [8]. This theory assumes that the rate of diffusion of molecules depends on the amount of free volume in the polymer matrix and thus relates the diffusion coefficient (D) to the fractional free volume (F_v) of the system. According to this theory the diffusion coefficient varies exponentially with the fractional free volume of a polymer at constant temperature, which can mathematically be expressed as

$$D = A_{\mathrm{d}} \exp(-B_{\mathrm{d}}/F_v) \tag{1}$$

where, the parameter A_{d} depends mainly on the size and shape of the diffusive molecules and B_{d} on the minimum volume required for the displacement of diffusive molecules in the polymer, Schneider et al. [14] have shown that the diffusion of toluene in butyl rubber follows the predictions of Fujita's free volume theory. Even though Fujita's free volume theory satisfactorily describes the diffusion of a number of organic liquids and vapors in polymer solutions, there have been no or only a few attempts to verify this theory in solid polymers. Secondly, in the case of polymer solutions, only D was measured directly and the free volume was derived indirectly. Now-a-days, a sophisticated tool like positron lifetime spectroscopy (PLS) is available for determining directly the angstrom-sized free volume holes and their concentration in polymers [15,16].

A brief description of PLS technique is as follows. When an energetic positron from a radioactive source enters a condensed medium like polymer, it thermalizes by losing its energy in a very short time, then annihilates with the electron of the medium. Annihilation usually takes place from different positron states viz. free annihilation process, or from a localised state (trapped state) or from a bound state called positronium (Ps). Ps can exist in two spin states, a *para*-positronium (*p*-Ps, spin anti-parallel), which annihilates with a lifetime of 0.125 ns and *ortho*-positronium (*o*-Ps, spin parallel), which annihilates with a lifetime of 140 ns in free space. In condensed matter, the *o*-Ps annihilates predominantly via a fast channel with an electron of the surrounding medium possessing an opposite spin; a process called pick-off annihilation and the *o*-Ps lifetime gets reduced to a few nanoseconds. Each of these annihilation processes has a characteristic annihilation lifetime. In polymers, the *o*-Ps lifetime is an important parameter since positronium is trapped and annihilated in free volume sites and hence it is related to the mean size of free volume holes in the polymer matrix [17].

Polymeric materials find use in a variety of commercial and technological applications. When such materials are used in applications such as protective barriers in chemical industries or in radiation environments, etc. their resistivity towards solvents or to energetic radiation such as gamma rays and ions, etc. is an important factor to be understood. Furthermore, the diffusion of gas molecules and solvents in irradiated polymeric materials are different compared to unexposed polymers and are necessary to decide their end application in a hostile environment. To this end one generally uses the sorption method, which is one of the simplest methods used to measure the diffusivity in polymer–solvent system [18]. A recent sorption study on irradiated polymer shows changes in both physical and chemical properties [19] testifying the need for such studies. Further, PLS is a very sensitive technique and it gives direct information on free volume holes and their concentration upon irradiation. With this point in view we have carried out iodine sorption in both unirradiated and ion-irradiated polycarbonates. We have used the PLS technique to measure the free volume size and its content and the sorption method to determine the transport of iodine diffusion in polycarbonate before and after ion irradiation. From literature survey we observe that there has been no report on the iodine transport studies in ion-irradiated polycarbonate so far.

2. Experimental

2.1. Sample and its treatment

Polycarbonate (PC) was obtained from M/s. Goodfellow, England in the form of a sheet of 1 mm thick, having a molecular weight of 28 000 is used in the present experiments. Rectangular sample of dimension $20 \times 12\ \mathrm{mm}^2$ was cut and carbon ion-irradiation was carried out utilising the 15 MV Pelletron facility at the Nuclear Science Center (NSC), New Delhi. The sample was mounted on the sample holder and placed in the path of the ion beam of 84 Mev $^{12}\mathrm{C}^{6+}$ in vacuum, with a fluence of 1×10^{12} ions cm^{-2}. The ion beam was scanned vertically covering the entire area of the sample for a known period of time. In order to suppress thermal decomposition of the sample during irradiation, the current density was maintained well below 10 nA during irradiation.

The irradiated PC samples were cut into two identical halves $10 \times 12\ \mathrm{mm}^2$ for use in lifetime measurements and sorption. Sorption of iodine was carried out by soaking the sample in 15–20 ml of aqueous KI/iodine solution taken in an airtight test bottle. The samples were removed after a known interval of soaking time and the surface-adhered iodine drops were washed and dried carefully by pressing the samples in between filter paper wraps and then weighed. The samples were weighed on a digital Sortorious balance Model BP 210 D (Germany) with the precision of ±0.01 mg before and after soaking. Sorption was done for different intervals of soaking and after each sorption time the samples were washed, dried, and weighed.

2.2. Positron annihilation lifetime measurement

The samples so treated were used in lifetime measurements using Positron Lifetime Spectrometer. The Positron Lifetime Spectrometer consists of a fast–fast coincidence system with KL-236 plastic scintillators coupled to RCA-8575 photo multipliers as detectors and has a time resolution of 340 ps. The two identical halves of PC samples are placed on either side of a 10 μCi ^{22}Na positron source deposited on a pure Kapton foil of 0.0127 mm thickness. This sample–source sandwich was placed between the two detectors of PLS to acquire lifetime spectrum. A detailed description of PLS and data collection procedure is reported elsewhere [20]. All lifetime measurements were performed at room temperature and two to three positron lifetime spectra with more than a million counts under each spectrum were recorded for each sorption time. The consistently reproducible spectra were analyzed into three components with the help of the computer program PATFIT-88 [21] with source and background corrections. Proper source correction term and resolution function were estimated from a lifetime of well annealed aluminium using the program RESOLUTION [21]. The UV absorption spectra for un-irradiated and irradiated PC samples were taken on a HP Model 8452A diode-array UV/VIS spectrometer.

3. Results and discussion

The lifetime spectra of the present polymer (PC) were resolved into three lifetime components τ_1, τ_2, and, τ_3 with their intensities as I_1, I_2, and I_3, respectively. The shortest lifetime component τ_1 with intensity I_1 is attributed to *p*-Ps and free positron annihilations. The intermediate lifetime component τ_2 with intensity I_2 is considered to be mainly due to annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline–amorphous interface regions. The longest-lived component τ_3 with intensity I_3 is due to pick-off annihilation of the *o*-Ps in the free volume sites present in the amorphous regions of the polymer matrix [22]. The *o*-Ps lifetime (τ_3) is related to the free volume hole size by a simple relation given by Nakanashi et al. [23] which was developed on the basis of theoretical models originally proposed by Tao [24] for molecular liquids and later by Eldrup et al. [25]. In this model, positronium is assumed to be localised in a spherical potential well having an infinite potential barrier of radius R_0 with an electron layer in the region $R < r < R_0$. The relation between τ_3 and the radius R of the free volume cavity is

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

where $R_0 = R + \delta R$ and the δR is an adjustable parameter. By fitting Eq. (2) with τ_3 values for known hole sizes in porous materials such as zeolites, a value of $\delta R = 0.1657$ nm was obtained. With this value of δR, the free volume radius R is calculated from Eq. (2) and the average size of the free volume hole V_{f3} is calculated as $V_{f3} = (4/3)\pi R^3$. The fractional free volume F_v can be estimated as

$$F_v = CV_{f3}I_3 \tag{3}$$

where C is the structural constant derived from the coefficient of thermal expansion of the free volume of the polymer (PC) which was determined from a separate isochronal annealing study.

The irradiation of polymer has a direct influence on the free volume and diffusion of dopants in such systems is controlled by the free volume and its content. So, it is appropriate that we consider only *o*-Ps lifetime and its intensity in understanding the influence of irradiation on free volume i.e. free volume modification and how this will influence diffusion process. Therefore, we discuss only these two parameters in this study.

3.1. Positron lifetime results

The analysed results of the positron spectra and the UV absorption results for un-irradiated and irradiated PC are listed in Table 1. The chemical structure of polycarbonate and the final radicals after the irradiation are shown in Fig. 1. As we can see from Table 1, a decrease in τ_3 (1.87–1.82 ns) and V_{f3} (87–82 Å^3) is observed for irradiated PC compared to un-irradiated sample. This can be explained in the following way. An early investigation by Zimmermann et al. [26] reports that the C–O bonds adjacent to the carbonyl group in the PC chain are the vulnerable bonds, lacking the resonance stabilisation of the phenyl group. The most important volatile product during PC degradation is CO_2 and hence the carbonyl linkage is the most reactive group in the polymer [27]. On irradiation, the decrease in τ_3 and V_{f3}, may be due to cross-linking process, before this, chain scissions must have occurred mainly at the C–O bonds adjacent to the carbonyl group. Thus, on irradiation, the carbonate group absorbs energy selectively, and as such PC undergoes chain scission with the formation of free radicals such as phenoxy-type and phenyl radicals initially and thereafter cross-linking of the free radicals may occur. The evolutions

Table 1

Poly-carbonate (PC)	τ_3 (ns)	V_{f3} (Å)^3	I_3 (%)	F_v (%)	UV absorption band 384 (nm)	UV absorption band 328 (nm)	Cross-link density ν_d ($\times 10^{-5}$ g mol cm^{-3})
Un-irradiated	1.87	87	35	2.9	Present	Present	2.77
Ion-irradiated	1.82	82	24	1.8	Present	Absent	4.33

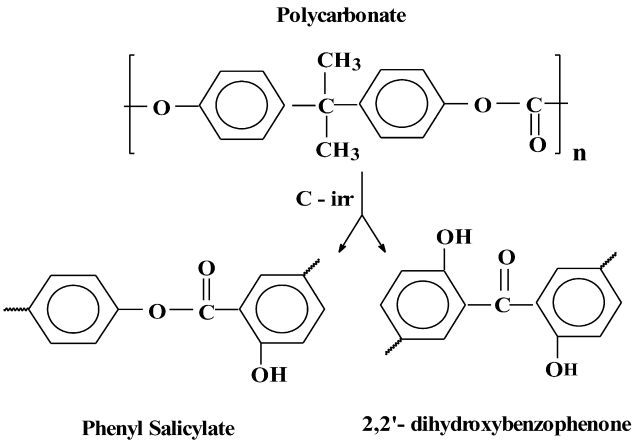

Fig. 1. Structures of polycarbonate and the radicals phenyl salicylate and 2,2′-dihydroxybenzophenone.

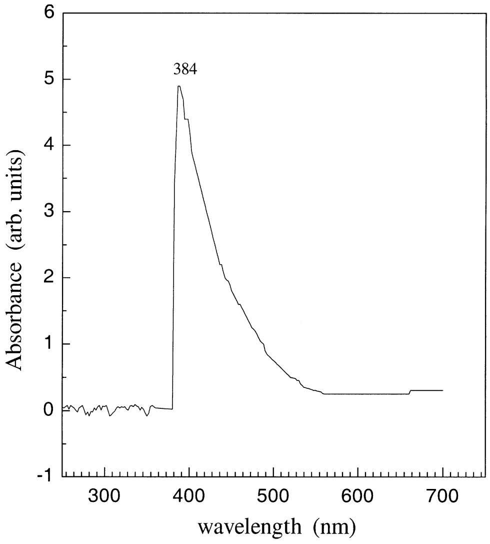

Fig. 2. UV absorption difference spectrum between un-irradiated and C^{6+} ion-irradiated polycarbonate.

of CO and CO_2 which are the byproducts of the chain scission have been observed by the mass spectroscopic analysis. Earlier studies on viscosity of UV irradiated PC [28] is a supportive evidence to the earlier description. Here the authors attribute the change in molecular weight (M_w) to chain-scission and partial cross-linking. It has been shown for polystyrene (PS) that mainly cross-linking occurs under light ion-irradiation [29]. Experimental studies of photo-irradiation of polymers [30] reveals that an increase in viscosity is due to cross-linking. Hama and Shinohara [31] reported that photolysis of C–O bonds in PC yields phenyl and phenoxy-type radicals and the more stable free radicals of polyenyl-type are produced, which are thought to be associated with conjugated double bonds and formed by cross-linking of the phenyl radicals. In the cross-linked state the polymer chains are expected to have a closer packing, thereby the sizes of the free volume holes decreases, hence upon irradiation, a decrease in o-Ps lifetime τ_3 and free volume V_{f3} is on the expected lines.

From Table 1 it can also be noted that, a decrease in o-Ps intensity I_3 (35–24%) and fractional free volume F_v (2.9–1.8%) similar to τ_3 and V_{f3} is observed for the irradiated PC. As explained earlier, due to ion irradiation cross-linking occurs and the average free volume size decreases. The cross-linking also results in close packing of the polymer chains. This close packing may result in the decrease of the number density of free volume sites and hence I_3 decrease is observed. It is also known that, most of the aryl esters and carbonates on photolysis undergo Photo-Fries rearrangement [32], the products formed are due to the rearrangement of oxygen atoms. If PC undergoes such a rearrangement on irradiation, it results in the formation of photostablisers such as phenyl salicylate and 2,2′-dihydroxybenzophenone (Fig. 1). To provide evidence, the UV absorption spectra of PC were taken before and after ion-irradiation and the difference spectrum of the two is shown in Fig. 2. From the figure it is evident that the spectrum shows a strong absorption peak at 384 nm which is due to 2,2′-dihydroxybenzophenone [28,33], confirms that the Photo-Fries rearrangement has indeed occurred in PC upon ion-irradiation. The UV irradiation of PC [34] shows a weak absorption band at 328 nm, which is due to phenyl salicylate, and interestingly it is absent in the present spectrum. The absence of the weak absorption peak at 328 nm is an indication that most of the oxygen atoms of phenyl salicylate have completely undergone further rearrangement to form more stable 2,2′-dihydroxybenzophenone [35,36]. The more stable photostabliser so produced, also prevents the formation of o-Ps. Thus the decrease in o-Ps intensity I_3 is observed with irradiated PC. The decrease in fractional free volume F_v can be attributed to the increase in cross-link density in PC on irradiation. Cross-link density ν_d has been calculated making use of the kinetic theory of rubber elasticity [37] and the empirical relation between ν_d and free volume size V_{f3} [38]. The results of this calculation are given in the last column of the Table 1. This clearly shows that there is an increase in cross-link density upon irradiation. Kaplan and Guner [39] observed that the cross-link density of poly(N-vinyl-2-pyrrolidone) (PVP) increased with irradiation dose. A recent PAL study on polyisoprene [40] showed that a decrease in the fractional free volume with an increase in cross-link density and a decrease in the average hole size. In this context the decrease in the fractional free volume F_v as well as o-Ps lifetime τ_3 can be ascribed to an increase in cross-link density.

3.2. Iodine sorption in free volume holes

A comparative study of iodine sorption in un-irradiated and C^{6+} ion-irradiated PC is done in this paper. These data are shown in Figs. 3(a), (b) and 4. It is observed that for un-irradiated PC all the positron parameters decrease slowly in the initial sorption stages (up to 29 days) of sorption and remains constant on further increase in sorption time. A similar behaviour is found of course in ion-irradiated PC except for the distinct difference, that is a sharp decrease is noted in the initial stages (up to 5.25 days) and reaches a plateau or saturation on further sorption. This change in the sorption behavior can be explained as follows. During the initial stages of sorption (up to 29 days) in un-irradiated PC, the iodine molecules generally seem to diffuse into the free volume cavities present in the amorphous regions, hence diffusion of iodine molecules involves the transport of these into the pre-existing free volume holes [41]. The slow decrease in iodine diffusion further suggests that in un-irradiated PC there is a large number of free volume holes of smaller size and hence more time is required to fill such a large number of holes [42]. In the final stages of sorption (above 29 days) the value of τ_3 and V_{f3} remains constant, indicating that the filling of free volume holes by iodine is complete. Figs. 3(b) and 4 show a decrease in *o*-Ps intensity I_3 and fractional free volume F_v, respectively, similar to the decrease in τ_3 and V_{f3} for un-irradiated sample. Since I_3 is a relative measure of free volume sites, filling of the sites by iodine shall result in decrease in these sites. This decrease is observed in I_3. Since, F_v is roughly the product of V_{f3} and I_3 (Eq. (3)) it is expected F_v should also exhibit similar behaviour. The observed results are in conformity with this.

In the case of C^{6+} ion-irradiated sample, a sharp decrease in *o*-Ps lifetime τ_3, intensity I_3 and fractional free volume F_v as a function of sorption time is observed (Figs. 3(a), (b) and 4) respectively. Upon ion-irradiation the free volume content of the PC gets modified due to the processes discussed earlier in Section 1. As a result, the polymer chains will be less flexible due to cross-linking that might result in less number of bigger size free volume holes. Only this prescription can support the observed sorption, which is faster i.e. within 5.25 days it reaches saturation unlike 29 days in un-irradiated PC. So iodine diffuses more easily through the modified free volume configuration of larger size holes and filling will be faster.

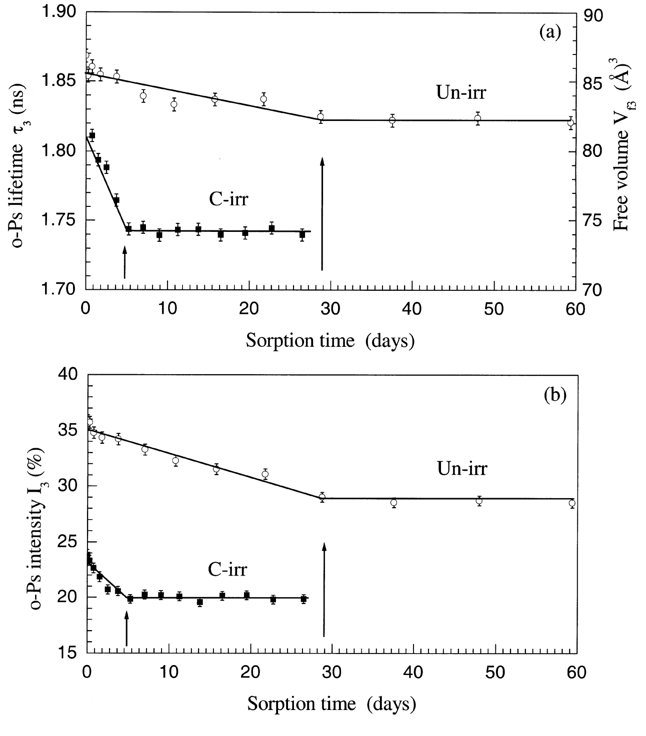

Fig. 3. Variation of (a) *o*-Ps lifetime τ_3 and free volume V_{f3} and (b) *o*-Ps intensity I_3 as a function of sorption time. The solid lines drawn guide the eye.

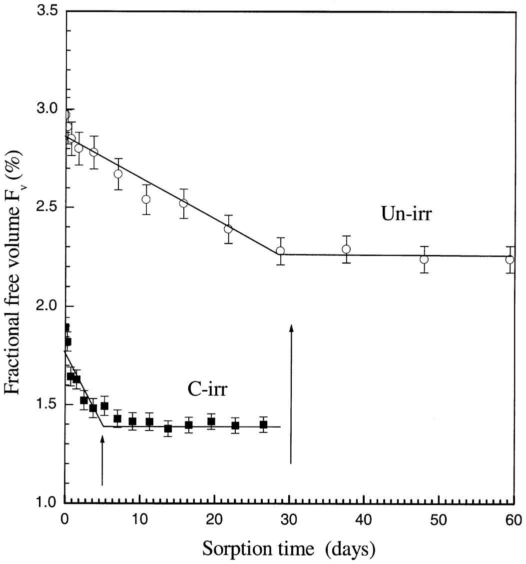

Fig. 4. Variation of fractional free volume (F_v) as a function of sorption time. The solid lines drawn guide the eye.

3.3. Sorption kinetics

In order to understand the sorption mechanism of iodine in un-irradiated and ion-irradiated PC, we have used Fick's law of diffusion [43]. For a diffusion process in a plane sheet with surfaces maintained at a constant concentration is represented by the equation according to Crank [18]

$$(M_t/M_\infty) = 1 - \sum_{n=0}^{\infty} \{8/\pi^2(2n+1)^2\}\exp[-D(2n+1)^2\pi^2 t/L^2] \tag{4}$$

where L is the thickness of the sheet, M_t and M_∞ are the masses of the penetrant sorbed at times t and ∞ (this is the time corresponding to final stages of sorption). The ratio (M_t/M_∞) in Eq. (4) can be expressed as

$$(M_t/M_\infty) = (W_t - W_d)/(W_\infty - W_d) \tag{5}$$

where W_d is the weight of the dry sample, W_t is the weight of the sample that has been soaked for a time t and W_∞ is the weight of the sample in the final stages of sorption. The ratio (M_t/M_∞) was calculated according to Eq. (5) with the measured values of W_d, W_t and W_∞. According to Stefan's approximation [44] the amount of substance diffused is proportional to square root of time ($t^{1/2}$), which is given by:

$$(M_t/M_\infty) = 4(Dt/\pi L^2)^{1/2} \tag{6}$$

Eq. (6) is derived under the assumption that D the diffusion coefficient is a constant. The diffusion coefficient was also calculated from the late-time approximation [45] of Eq. (4) taking $n = 0$ which results in:

$$(M_t/M_\infty) = 1 - [(8/\pi^2)\exp(-D\pi^2 t/L^2)] \tag{7}$$

A plot of this ratio (M_t/M_∞) versus square root of sorption time ($t^{1/2}$) is generally termed as the sorption curve. Fig. 5 shows the sorption curves for un-irradiated and irradiated PCs. The sorption curve illustrates whether the sorption mechanism is of Fickian type or non-Fickian. As we can see, the ratio (M_t/M_∞) varies linearly with $t^{1/2}$ up to a value of approximately (M_t/M_∞) = 0.5 in both un-irradiated and irradiated PCs and levels off at the final stages of sorption. This shows that the sorption is Fickian before and after irradiation. Fickian type diffusion is characterised by the rate of diffusion being much less than that of the polymer segmental relaxation.

To understand clearly the mechanism of iodine transport in irradiated and un-irradiated polymer matrices, the sorption results have been further fitted to a relation of the type [46]

$$(M_t/M_\infty) = Kt^n \tag{8}$$

where K is a constant, which depends on the structural characteristics of the polymer. The value of the exponent n indicates the type of transport mechanism. A value of $n = 0.5$ is suggestive of normal Fickian behaviour and $n = 1$ refers to non-Fickian. A value of n between 0.5 and 1, refers to the diffusion process of anomalous type. From the least squares fit of Eq. (8), the values of n for un-irradiated and irradiated PC are found to be 0.49 and 0.54, respectively, and the k values are found to be of the same order as that of diffusion of organic liquids studied in polymers [47]. In accordance with the description of these sorption modes, we can arrive at the plausible conclusion that the iodine diffusion in both un-irradiated and irradiated PCs (Fig. 5) is Fickian. The values of D obtained from the best fit of Eq. (4) to the data up to (M_t/M_∞) = 0.5 are 57 and 97×10^{-10} cm^2 s^{-1} for un-irradiated and irradiated PCs, respectively. The diffusion coefficient is approximately 1.7 times greater in ion-irradiated PC than in the un-irradiated sample. The increase in diffusion coefficient may be attributed to the formation of large size free volume holes on irradiation. The solid curve in Fig. 5 is a fit to Crank's diffusion expression (Eq. (4)) with the above values of diffusion coefficients for un-irradiated and irradiated PCs. A comparison of diffusion processes in un-irradiated and irradiated PCs as can be seen from Fig. 5, shows that although the sorption curves seems to be similar, there is a distinct difference in the final stages of sorption, i.e. an early equilibrium saturation is attained in irradiated PC when compared to un-irradiated case. This can be explained as follows. In case of un-irradiated sample the absence of the long chain flexible groups and the presence of two strong phenyl groups in the chain backbone prevent it from swelling. Hence, the rate of iodine diffusion is much less than that of the polymer segmental relaxation and the sorption is Fickian. The reported work on the transport of organic solvents such as carbon tetrachloride, acetone, and methanol [48] in PC are found to be of Fickian type. The mass uptake in irradiated PC is identical to un-irradiated PC up to (M_t/M_∞) = 0.5, but thereafter, it reaches saturation quickly than the other case. This is due to the fact that free radicals formed during irradiation results in cross-linking and this seems to ease the rigidity in the chain backbone, so the structure is somewhat flexible and hence iodine uptake is fast in the irradiated sample.

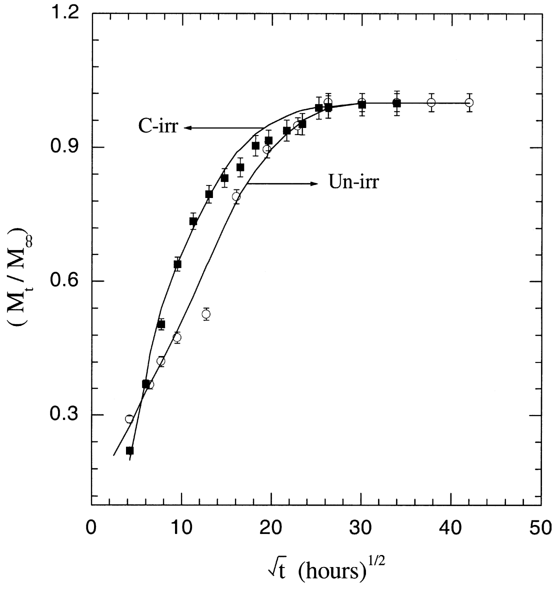

Fig. 5. Variation of (M_t/M_∞) as a function of square root of sorption time. Symbols are experimental points: the solid lines are fits to Eq. (4) (Fickian diffusion).

In order to verify the D values obtained from Eq. (6), the plots of $\ln[1 - (M_t/M_\infty)]$ as a function of sorption time using long-time sorption (M_t/M_∞) > 0.5 for un-irradiated and irradiated PCs were made. The D values are estimated using the slopes of this plot and their values are found to be 59 and 96×10^{-10} cm^2 s^{-1} for un-irradiated and ion-irradiated PCs, respectively. It is clear that the D values are not altered very much indicating that even at the later stages of sorption, PC exhibits Fickian diffusion before and after ion-irradiation. To test whether the diffusion process follows the predictions of Fujita's theory of free volume [13], the measured fractional free volume F_v from the positron results (Eq. (3)) and the diffusion coefficients D from sorption measurements (Eq. (6)) are used, and a plot of $\ln D$ versus $(1/F_v)$ for un-irradiated and irradiated PCs are made and shown in Fig. 6. For a diffusion process obeying Fujita's free volume theory, this plot should result in a

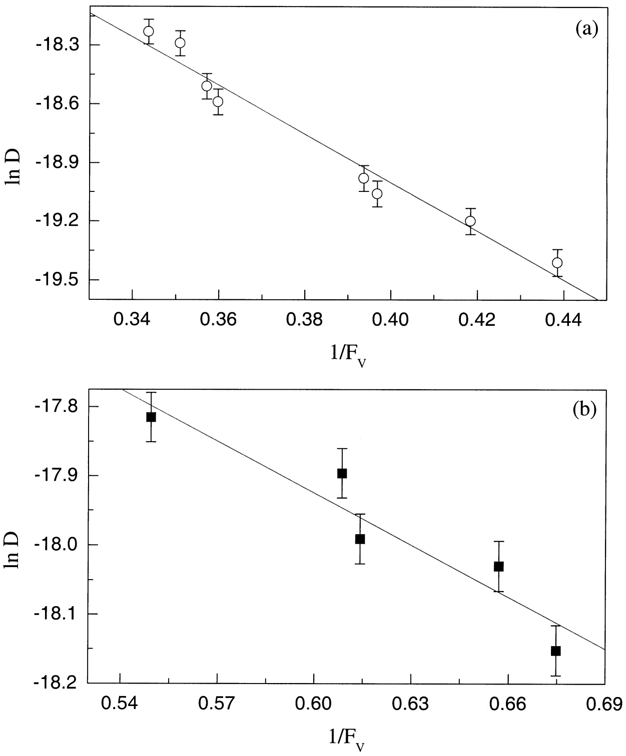

Fig. 6. Variation of ln D as a function of inverse of Fractional free volume ($1/F_v$) for (a) un-irradiated and (b) ion-irradiated polycarbonate. The solid lines are the linear fits to the data points.

straight line with a negative slope. The intercept and slope of this line will give the respective values of the constants A_d and B_d in Eq. (1). It is clear from the figure that the ln D decreases linearly with ($1/F_v$) in both un-irradiated and irradiated PCs. This means D increases as F_v increases, and this correlation between D and F_v is in consonance with Fujita's theory [13]. Now the question with regard to this correlation is that, how is the sorption behaviour not changed after ion-irradiation although the D has changed drastically? At present we do not find any plausible explanation for this.

4. Conclusions

A comparison study of iodine diffusion in un-irradiated polycarbonate and C^{6+} ion-irradiated polycarbonate is made using PLS technique and the following observations are made.

The decrease in all the positron parameters (τ_3, V_{f3}, I_3, and F_v) on ion-irradiation suggest that more stable polyenyl-type free radicals are formed due to cross-linking of phenyl radicals. The formation of more stable free radical leads to the development of a small number of large size free volume holes. The absorption spectrum of the irradiated PC shows a peak at 384 nm suggesting the formation of 2,2′-dihydroxybenzophenone and hence the Photo-Fries rearrangement has occurred. The radicals inhibit the Ps formation and free volume stability is attained due to Photo-Fries rearrangement, which leads to a decrease in number density and fractional free volume. The decrease in fractional free volume shows that there is an increase in the cross-link density and as such polymer chain mobility hinders.

The iodine sorption in un-irradiated and irradiated PCs suggest that more sorption time (29 days) is required for un-irradiated PC to reach equilibrium whereas it takes only 5.25 days in the case of irradiated sample. The diffusion of iodine is Fickian in both the cases. Furthermore, the correlation between diffusion coefficient and fractional free volume is in accordance with Fujita's free volume theory in both the cases.

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