

Positron Annihilation Study of Iodine Sorption in Acrylonitrile–Butadiene–Styrene

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ABSTRACT: The influence of iodine on the free volume of acrylonitrile–butadiene–styrene (ABS) was investigated by positron annihilation lifetime spectroscopy (PALS). The results indicate the filling of free-volume holes, formation of a positronium–iodine compound (PsI_2/PsI), and possible charge-transfer complexes (CTCs) in the initial stages and the swelling of iodine in the final stages of sorption. The present study also revealed that iodine acts as a chemical quencher of *o*-Ps. The average size of the free volume suggests that I_3^- is the predominant species that fills up the free-volume holes during iodination. The diffusion process in the present case shows non-Fickian behavior and deviates from Fujita's free-volume concept as far as the fractional free volume and diffusion coefficient are concerned. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2077–2085, 1998

Key words: acrylonitrile–butadiene–styrene; positron lifetime; free volume; iodine sorption

INTRODUCTION

The diffusion of small molecules in a polymer matrix is interesting in many ways. The resistance of polymeric materials toward organic and inorganic solvents is an important factor in chemical industries. The sorption properties of polymeric materials are a prerequisite in relation to their end applications.¹ So, complete information about the effect of additives on a specific polymer helps in tailoring that polymer for a specific application. Presently, polymeric sorbents are widely employed for the isolation and purification of organic substances, treatment of waste waters, chromatographic analysis, solid-phase extraction, absorption of organic vapors, and so on. Very recently, it has been reported that the styrene-based hyper-

crosslinked sorbents, “styrosorbs,” absorb large amounts of various organic vapors from the air and molecular iodine from their aqueous solutions.² Among the manifold adsorbents as viable candidates for scientific investigation or in absorption technology, copolymers of styrene are of great importance due to their high hydrolytic stability and simplicity of synthesis.

The introduction of a dopant into a polymer matrix can considerably modify the charge storage property of the polymer³ or it can improve the charge carrier mobility.⁴ Also, the presence of a dopant can lead to an unwanted effect on their physical properties such as tensile strength and fatigue resistance. Sorption is the process in which a foreign species is introduced into the polymer by diffusion and can lead to physical changes in the state of the polymer like 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

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pressure.⁵ When iodine is used as a dopant/diffusant, it is important to understand its ability to form charge-transfer complexes (CTCs), its mechanism of charge production, and its site of localization in the polymer matrix. Improved conducting behavior has been observed for polymers doped with iodine which is generally attributed to the formation of CTCs.⁶

On the theoretical front, there are a number of theories to explain the diffusion process in polymers. We are specifically interested in theories which are mainly free volume-based and molecular shape- and size-dependent. In this category, we have Fujita's free-volume theory^{7,8} which owes its origin to Cohen and Turnbull.⁹ Fujita's theory explains the diffusion process based on free volume and accounts for the dependence of the diffusion coefficient on the concentration of the diffusing molecules in polymeric films. This theory assumes that^{7,10} the rate of diffusion of a molecule depends primarily on the ease with which the polymer chains exchange their positions with the penetrant molecules. The mobility of the polymer, in turn, depends on the amount of free volume in the matrix and thus relates the diffusion coefficient to the fractional free volume of the system. This simple theory has been tested and found to describe the diffusion of a number of organic liquids and vapors in polymers satisfactorily.⁸ More recent theory on these lines is the one due to Mauritz et al.¹¹ This is also mainly a free volume-based, molecular shape-dependent diffusion theory for large molecules in rubbery polymers. In the rubbery state, polymers can be viewed as being in a dynamic fluidlike state and the penetrant molecule can be envisioned as "swimming" through its liquidlike medium.¹² Furthermore, this theory dwells upon the concept of combining free volume and energy-activated diffusion which was addressed earlier by the Mearers model.¹³ Nevertheless, this theory is not suitable for glassy polymers as it was developed mainly for rubbery polymers.

Although diffusion in the case of glassy polymers is somewhat complex, to a large extent, it depends on the magnitude of the nonequilibrium free volume available in the polymer matrix.^{14,15} The success of Fujita's theory prompted us to use this to understand the transport phenomenon of iodine diffusion in the glassy acrylonitrile-butadiene-styrene (ABS).

In the process of diffusion, the penetrant always moves in the direction of diminishing concentration and Fick's law relates the flux of diffus-

ing particles to the concentration gradient.¹⁶ However, the diffusion process in systems of almost similar character cannot always follow Fick's law. In this context, it is interesting to note that carbon tetrachloride diffusion in glassy polycarbonate obeys Fick's law,¹⁷ whereas water sorption by glassy polymers departs from Fick's law.¹⁸

The above-mentioned aspects motivated us to study iodine sorption in ABS. To our knowledge, there are no investigations on ABS, particularly diffusion studies. Moreover, this is the first positron annihilation study of ABS. This polymer is of particular interest because it is a two-phase system having the styrene-acrylonitrile copolymer as the continuous phase with a dispersed phase of butadiene-derived rubber. Depending on the method of polymerization, rubber particles may be solid or of the occluded variety, which contains the subinclusions of the glassy matrix.¹⁹ If doped with iodine, the phenyl group in the ABS structure, which is an electron donor, becomes a possible site for CTC formation because of the strong affinity of iodine toward these electrons. However, the exact nature of the complex formation in ABS with iodine is still to be understood. In this study, we used positron annihilation lifetime spectroscopy (PALS), which is a nondestructive microprobe for the evaluation of the fractional free volume. The method of the single free-phase model of absorption was used for the diffusion coefficient measurement.

In brief, the positron lifetime method can be explained as follows: When an energetic positron enters a condensed medium, it thermalizes quickly and thereafter annihilates with the electrons of the medium via free annihilation or forms a bound state with an electron called a positronium (Ps). Ps can exist in two spin states. The *para* state (*p*-Ps) (particle spins antiparallel) annihilates with a lifetime of 125 ps. The *ortho* state (*o*-Ps) (particle spins parallel) annihilates with a lifetime of 140 ns. In condensed matter, *o*-Ps annihilates mainly into two photons by a pick-off mechanism in which the positron of *o*-Ps annihilates with an electron of opposite spin from the surrounding molecules; thereby, its lifetime is reduced to a few nanoseconds. The lifetime of *o*-Ps depends on the overlap of the Ps wave function with the electron wave function of the free-volume cavity. Hence, the larger is the hole size, the smaller is the overlap and, hence, the longer the lifetime. So, the *o*-Ps pick-off lifetime (τ_3) and its intensity (I_3) are a measure of the free-volume size and their number density, respectively.^{20,21}

The formation of Ps and its trapping in free-volume holes is very well explained in the literature.^{20,22}

EXPERIMENTAL

ABS samples with a molecular weight of 1,20,000 was obtained from Goodfellow (Cambridge, England) in the form of a sheet of 1.5-mm thickness. The results from an XRD study shows this polymer to be semicrystalline with 52% crystallinity. Iodine sorption was carried out by soaking the sample in an aqueous KI/iodine solution for different intervals of time. The insertion of iodine in a polymer can lead to perturbation of the local molecular environment. The forces of attraction or dispersion start acting between the polymer chains and the iodine molecule depending on their chemical nature. The slow penetration of the iodine molecules into the interstices of the polymer coil can make the polymer swell. During the swelling process, the volume of the polymer matrix increases and the iodine molecules can diffuse into it. When the solvent (iodine)–solute (polymer) interaction becomes stronger than the solute–solute attraction, the forces holding the polymer segments together become weak and the solvent molecules can force their way between the segments, break the segment–segment contacts, surround individual segments, and establish contact with them. In this process, the segments can unfold, leading to a change in their conformation.²³

After each sorption period, the sample was dried with a blotting paper and weighed in a Mettler digital balance to a good accuracy. Then, these samples were used in the lifetime measurements. For lifetime measurements, a 15 μ Ci positron source (²²Na) was prepared on a Kapton foil $\frac{1}{2}$ -mil thick. This was sandwiched between two identical samples of a 15 \times 15 mm area. The experiment was performed using a fast–fast coincidence system with a time resolution of 340 ps. The details of the experimental technique can be found in an earlier publication.²¹ Two to three lifetime spectra, each having more than 1 million counts under the spectrum, were collected at each sorption level and consistently reproducible spectra were analyzed into three components with the help of the computer program PATFIT-88 (ref. 24) after subtracting the measured source term and background contribution.

RESULTS AND DISCUSSION

Positron Lifetime Results

As in many polymers,^{21,25} the resolved three lifetime components are attributed to various states of positron annihilation, namely, the shortest lifetime component τ_1 with intensity I_1 is attributed to free annihilation of the positrons with a contribution from the decay of *p*-Ps. The origin of the second lifetime component is still not very clear and different research groups follow slightly different approaches. We follow the prescription outlined by Goldanskii et al.,²⁶ according to which the second lifetime component τ_2 with intensity I_2 is considered to be caused due to the annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline–amorphous interfaces. The longest 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 mainly in the amorphous regions of the polymer matrix.²⁵

The annihilation of *o*-Ps in the spherical free-volume cavities can be described by a simple quantum mechanical model^{22,27} which assumes the Ps atom to be localized in a spherical potential well with an electron layer of thickness ΔR . This model provides the relationship between the radius R of the free-volume hole and the *o*-Ps lifetime (τ_3) as

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

where $R_0 = R + \Delta R$. Parameter ΔR was determined by fitting the experimental values of τ_3 obtained for materials of known hole size such as zeolites. The value of $\Delta R = 0.1656$ nm was obtained in this way. The above relation is successful in many ways in determining the average size of free-volume holes. Surprisingly, more extensive theoretical treatments lead to almost similar results.²⁸ A point to be noted here is that a recent work on stretched PEEK and PMMA reports that the free-volume holes are of ellipsoidal shape rather than spherical.²⁹ But this proposition is still to be convincingly investigated for its usage. Assuming the free-volume holes to be spherical,^{20,30} its average size is then calculated as $V_{f3} = (4/3)\pi R^3$ using the value of R derived from eq. (1). Since the measured size of the free-volume holes is an average of many such holes, it is obvi-

ous that there is a distribution of free-volume holes.^{31,32} From the average free-volume size, the fractional free volume or the free-volume content can be calculated as

$$F_v = CV_{f3}I_3 \quad (2)$$

where C is the structural constant. One way of calculating C is from a measurement of the thermal expansion coefficient of the free volume (α_0). This α_0 is calculated using the value of V_{f3} obtained through eq. (1) as follows:

$$\alpha_0 = (V_{f3T} - V_{f30})/V_{f30}(T - T_0) \text{ K}^{-1} \quad (3)$$

where V_{f30} and V_{f3T} are the sizes of the free volume at room temperature and at a temperature where the free-volume expansion is maximum (this was done in a separate isochronal annealing experiment in which the free-volume radius and its size were calculated at each annealing temperature. These results are not reported here). T_0 and T are the corresponding temperatures. The value of α_0 for the ABS sample turns out to be $1.27 \times 10^{-4} \text{ K}^{-1}$, which is in agreement with the polymer data available. Based on the Williams, Landel, and Ferry (WLF) theory,³³ the fractional free volume (F_v) can be represented as^{34,35}

$$F_v = 0.025 + \alpha_0 (T - T_g) \quad (4)$$

Now, using the value of α_0 obtained as described above, eq. (4) is fitted for temperatures from T_g to $(T_g + 100 \text{ K})$. The value of F_v so obtained at each temperature is used in eq. (2) to calculate the value of C since we know V_{f3} and I_3 at these temperatures. In this way, we obtain the value of C as 0.619 nm^{-3} . We have estimated the C value in the range $(T_g \text{ to } T_g + 100 \text{ K})$, where the WLF theory and, hence, the temperature dependence of the fractional free volume [eq. (4)] are valid.^{35,36} This value of C is used in the present experiment to calculate F_v under the assumption that C will not change very much on iodination.³⁷

Iodine in Free-Volume Holes

From the obtained results, a plot of τ_3 , I_3 , V_{f3} , and F_v as a function of sorption time is made and

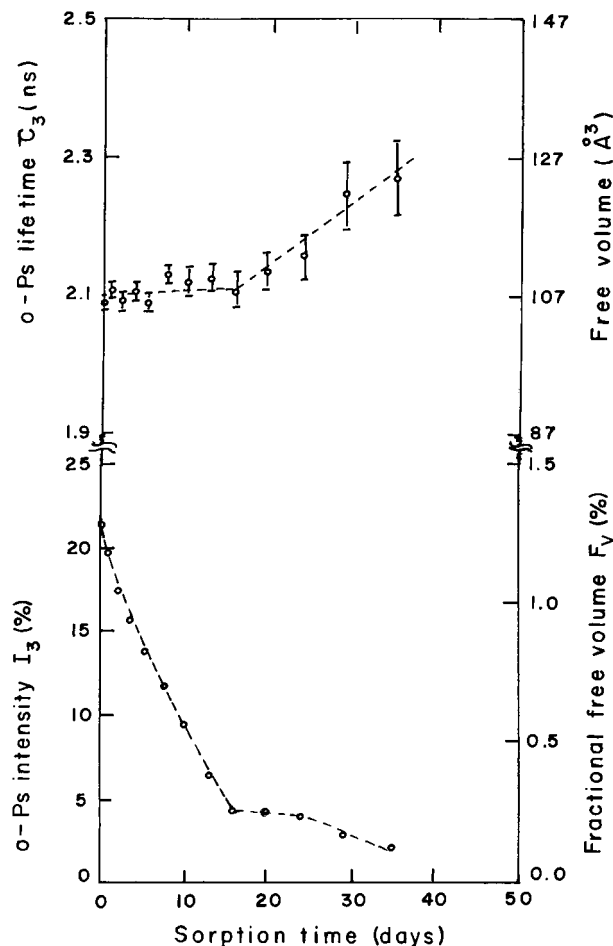


Figure 1 Variation of *o*-Ps lifetime τ_3 , its intensity I_3 , free volume V_{f3} , and fractional free volume F_v as a function of sorption time. Dashed lines are to guide the eye.

shown in Figure 1. As can be seen, the *o*-Ps lifetime and, hence, the free-volume size remains constant in the initial stages of sorption (up to $t = 16$ days). During the same interval, the *o*-Ps intensity and the fractional free volume decrease linearly. In the later stages of sorption, τ_3 and V_{f3} increase while I_3 and F_v remain constant for some period and then decrease slightly. These variations can be explained in the following way: The decrease in the *o*-Ps intensity in the early stages of sorption seems to indicate the filling of the free-volume holes by iodine and, hence, reduction in their number density. Since free-volume holes are not of the same size throughout the matrix, iodine seems to fill in the free-volume holes of a certain dimension enough to accommodate them but without affecting the average size of the free-volume holes. This might be the reason for the constancy of τ_3 in the early stages of sorption.

In the next stage of sorption (beyond $t = 16$ days), the iodine atoms seem to have filled most of the free-volume holes of the right size and no more filling is possible; a constancy in the value of I_3 is observed on further sorption. Correspondingly, during the same period, the increase in τ_3 may be interpreted as due to swelling. Polymers are known to undergo swelling in the presence of liquid media.^{2,23,38} The literature provides evidence that hypercrosslinked styrene-based polymers like polystyrene are characterized by a very low packing density of polymer chains in space due to the number of rigid spacers holding the polymer chains apart.² In spite of the high crosslinking density, the network exhibits the ability to swell, that is, increase in volume when the polymer is put in contact with the sorbate species.² Moreover, in the dry state, the polymer is strongly strained because of the rigidity of the network. The inner strains relax on expansion of the network, which strongly facilitates its swelling in any liquid media.²

The system under investigation is a two-phase one and the diffusion profile is not simple. It is of interest to know which part of ABS gets diffusant iodine first. Experiments conducted on ABS rubber CKC-30 (ref. 16) do provide some evidence on this aspect. In this experiment, the distribution of iodine over the surface of a section of a styrene-butadiene copolymer whose side surface was radiation-grafted with acrylonitrile shows a maximum in the region of acrylonitrile. Since styrene-acrylonitrile in the present ABS sample forms a continuous phase and butadiene forms a dispersed phase, the probability of iodine entering the dispersed phase is less.

The phenomenon of swelling depends on the forces of interaction between the solvent molecules and the polymer segments. In the case of a gas-sorption experiment, Ito et al.³⁹ reported that, at longer contact times, the polymer will be close to a swelled condition due to substantial gas sorption. By analogy, for the present case, swelling seems to occur at later stages of sorption. When the swelling increases, more and more segments of the polymer molecules loosen.²³ Hence, an increase in free-volume size is expected. This is what we observe in Figure 1 (after $t = 16$ days). The swelling may also lead to coagulation of small-size free-volume holes and, hence, the number density of the free volume decreases in the final stages of sorption.

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 Ps atoms are annihilating from holes of the same size. Therefore, there is a distribution of holes of different sizes and the *o*-Ps atom can sample a number of such holes during its lifetime. So, the measured lifetime is the sum of contributions from all the holes. As such, the concept of the average free volume is used.³¹ To understand the effect of the sum, let us consider two free-volume holes of sizes "a" and "b." The probability of finding Ps in either of these holes is proportional to the volume of the hole. Therefore, the average lifetime according to Kobayashi et al.³¹ is

$$\tau_{\text{ave}} = [(V_a/\tau_a) + (V_b/\tau_b)]^{-1} (V_a + V_b) \quad \text{ns} \quad (5)$$

Using this relation, Kobayashi et al.³¹ evaluated the lower and upper limits for free-volume sizes with an average size of 105 \AA^3 as 70 and 140 \AA^3 . Details of the calculation can be found in ref. 31. Following this, we estimated the lower and upper limits for the ABS sample whose average free-volume size is 106 \AA^3 and this turns out to be 71 and 141 \AA^3 , respectively. To understand the nature of the iodine species entering the polymer matrix when it is iodinated, various techniques have been used in the past.^{40,41} Now, with the positron data, we have made an attempt to match the sizes of different iodine species that can fit into the free-volume holes in ABS. From the list of different iodine species, the size of the I_3^- species (104 \AA^3) fits the free-volume size within the obtained size limits. The Mössbauer results of iodine-doped polyacetylene give the ratio of I_5^-/I_3^- to be 0.33 .⁴² This suggests that I_3^- is the most predominant species compared to I_5^- . Since the I_5^- size does not fit into the size limits of the present case, we conclude that I_3^- is the predominant species which fills the free-volume holes.

Influence of Iodine on Crystalline and Crystalline/Amorphous Interface Regions

The variation of the second lifetime τ_2 and its intensity I_2 as a function of sorption is shown in Figure 2. It is clear from this that the second lifetime decreases while its intensity increases during the initial stages of sorption and both remain unaltered at the final stages of sorption.

It is well known that the quenching of Ps can take place in three different ways and one among them is chemical quenching.⁴³ If the molecules of the medium react strongly with Ps, a Ps compound is formed. As a result, the lifetime of the

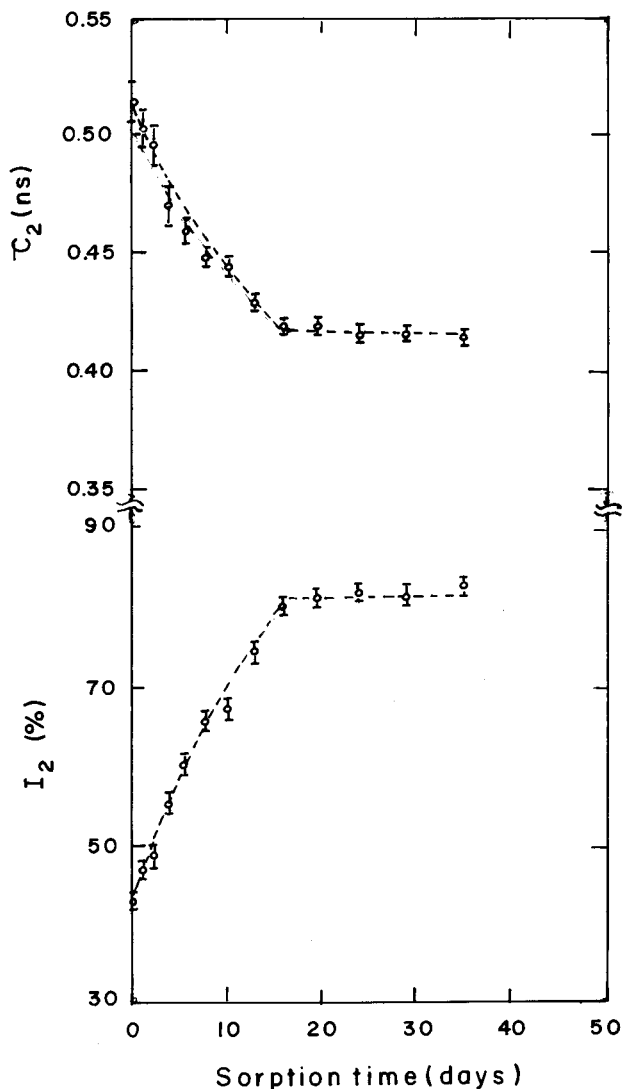


Figure 2 Variation of second lifetime component τ_2 and its intensity I_2 as a function of sorption time. Dashed lines are to guide the eye.

o-Ps will be reduced due to the fact that the positron in a Ps compound has an opportunity to meet the "paired" electrons with mixed spins. Iodine has been shown to form Ps-iodine compounds, PsI_2 or PsI .⁴³ The lifetime of these Ps-iodine compounds was estimated to be 0.4 ns (ref. 43) in iodine solutions of organic solvents. Since the value of τ_2 in the present case is around this value and it changes upon iodination, we propose that there is PsI/PsI_2 formation.

Also, iodine is known to form CTCs with polymers like polyvinylpyrrolidone,⁴⁴ poly(vinylidene fluoride)⁴⁵ polyacetylene,⁴⁰ and polystyrene.⁴⁶ The phenyl group of styrene acting as a donor variety and the cyano group of acrylonitrile acting

as an acceptor variety to form a weak CTC has been reported.⁴⁷ In the case of iodine-doped polystyrene,⁴⁶ the authors explained the interaction between polystyrene and iodine, giving electron-donor characteristics to the π bond centers of the phenyl group and electron-acceptor characteristics to iodine. These results indicate that the phenyl group in ABS can act as an electron donor in forming a complex with the acceptor iodine. The formation of the phenyl-iodine complex has been reported even in a carbon disulfide solution.⁴⁸ The formed CTC will provide conducting pathways, resulting in enhancement of the conductivity,⁴⁵ and also become attractive sites for positrons/positronium. So, the number of annihilation sites increases and, hence, I_2 should increase. For iodine transport in polythene, Davies⁴ showed that the iodine dopant affects the *c*-*a* interface regions also.

Based on the above-mentioned discussions, we explain that the decreasing trend of τ_2 during the early stages of sorption is due to the combined effect of chemical quenching, resulting in a Ps-iodine compound and CTC formation. CTCs may form either in the crystalline or in the *c*-*a* interface regions which makes the annihilation rate fast. The increase of I_2 in Figure 2 is a clear indication of this effect.

During the later stages of sorption, the constancy in the values of I_2 and τ_2 suggests that the further addition of iodine atoms has no effect on the crystalline and *c*-*a* interface regions. This constancy also suggests that the swelling seems to have no significant influence on the crystalline and *c*-*a* interface regions in the later stages of sorption.

Diffusion Coefficient Measurements

To understand the sorption mechanism of iodine in ABS, we used Fick's law of diffusion. Stefan, on modifying the theoretical equation of Fick's law of diffusion in a plane sheet,⁴⁹ arrived at a relation for the diffusion coefficient as

$$M_t/M_m = 4(Dt/\pi L^2)^{1/2} \quad (6)$$

where M_t and M_m are the masses of the penetrant taken up or lost at times t and m (time when the equilibrium sample weight has been reached). D is the diffusion coefficient and L is the thickness of the sheet. The ratio (M_t/M_m) in eq. (6) can be determined from

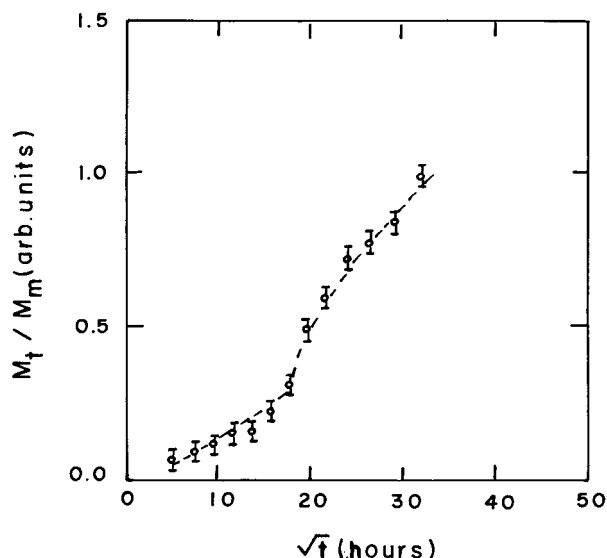


Figure 3 Variation of M_t/M_m as a function of square root of sorption time. Dashed lines are to guide the eye.

$$M_t/M_m = (W_s - W_d)/(W_m - W_d) \quad (7)$$

where W_d is the weight of the dry sample, W_s , that of the sample which has been soaked for a time t ; and W_m , the weight of the sample in the final stage of the sorption.

A plot of M_t/M_m versus \sqrt{t} is shown in Figure 3. It is evident from this figure that, in the initial stages of sorption, the ratio of M_t/M_m varies linearly with \sqrt{t} (up to $M_t/M_m = 0.25$) and, thereafter, it changes slope. The change in slope at this sorption period ($\sqrt{t} = 17.6$ h) may be attributed to the onset of plasticization that promotes long-range segmental mobility of the chains as the non-Fickian region is reached. This long-range chain mobility leads to an increased diffusion rate. The evidence for this correlation can be found from ref. 50. Moreover, an increasing diffusion coefficient with increase in the sorption period is generally attributed to plasticization and associated swelling of the amorphous component of the polymer.⁵¹

If the diffusion process in a given system exhibits a classical Fickian behavior, then the ratio of M_t/M_m is linear up to $M_t/M_m = 0.5$ and should level off in the final stages of sorption.⁴⁹ Any deviation from this is termed non-Fickian behavior. Sorption studies in the resin exhibits a non-Fickian behavior wherein a continued increase in the moisture level with time was observed.⁵² A comprehensive review of such studies concerning both Fickian and non-Fickian behaviors can be found

in ref. 53. The first evidence of time-dependent diffusion behavior in glassy polymers under exposure to a constant ambient environment was given by Long and Richman.¹⁸ To characterize the non-Fickian behavior, they separated the absorption into two components: one Fickian and the other due to relaxation. The model including both these effects will be referred to as the "modified Fick's law." If the rate of diffusion is much less than the polymer segmental relaxation, then it is termed Fickian behavior. On the other hand, if the rate of diffusion is much faster than that of the polymer segmental relaxation, it is termed non-Fickian behavior.⁵ The present results (Fig. 3) deviate both from the linear behavior up to $M_t/M_m = 0.5$ and the saturation effect in the final stages, suggesting that the sorption in ABS is of a non-Fickian type. As stated already, the onset of plasticization begins when M_t/M_m exceeds 0.25 and this could be treated as an additional support for the conclusion that the diffusion in ABS is non-Fickian.

Free Volume and Diffusion Coefficient

We used the present positron data to verify whether the diffusion process in ABS follows the prescription of Fujita's theory of free volume.^{7,8} In a simple way, this theory correlates the fractional free volume of the polymer to the diffusion coefficient, that is, the solvent diffusion coefficient follows a simple exponential dependence on the total fractional free volume. Mathematically, this is represented as

$$D = A_d \exp[-B_d/F_v] \quad (8)$$

where A_d is considered to be dependent primarily upon the size and shape of the diffusive molecules and B_d corresponds to the minimum volume required for a displacement of diffusate molecules in the system. As per this expression, D increases as F_v increases.⁵⁴ The diffusion coefficient was calculated for each sorption level from eq. (6). A plot of D versus F_v is presented in Figure 4. It is clear from this figure that the variation of D versus F_v neither follows an exponential trend nor fits a power regression. In an earlier study,³⁷ it was found that iodine sorption in polycarbonate (PC) follows the normal Fickian behavior and the relation between F_v and D is of an exponential type as per Fujita's theory. The present results deviate completely from this. The reason for this may be that PC is an amorphous material and ABS is

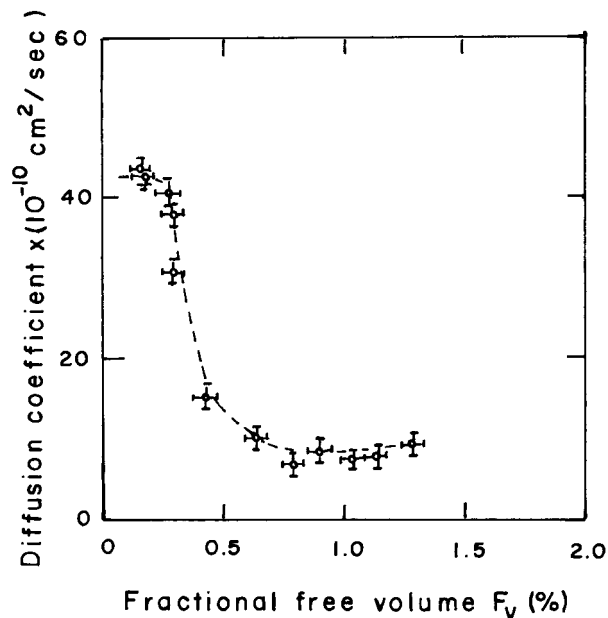


Figure 4 Variation of diffusion coefficient D with fractional free volume F_v . Dashed lines are to guide the eye.

semicrystalline with 52% crystallinity. Another possibility one can think of is that ABS is a two-phase system, and as pointed out earlier, the diffusion in ABS is complex. So, to conclude whether a non-Fickian diffusion process deviates from Fujita's theory or whether a Fickian diffusion follows Fujita's theory, more investigations of this kind are needed.

CONCLUSIONS

We used the PALS technique to study the free-volume changes in ABS in the presence of an iodine dopant and the results can be summarized as follows:

1. The present results show that the iodine species acts as a chemical quenching agent. The variation of the o -Ps intensity suggests that the free-volume holes are filled by the iodine molecules during the initial stages of sorption.
2. The measured average size of the free-volume holes indicate that I_3^- is the most predominant species which fills the free-volume holes. The positron results seem to indicate that the phenyl group of the ABS is the possible site for CTC formation.

3. Diffusion of iodine in ABS is of a non-Fickian type.
4. The relation between the fractional free volume and the diffusion coefficient does not follow the exponential behavior type and, hence, Fujita's free-volume theory of diffusion does not hold.

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