

Water Diffusion in a Soft Contact Lens Polymer and Its Tolerance to UV Radiation Studied by Positron Lifetime Technique

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ABSTRACT: The kinetics of water sorption, the topology or the free-volume changes due to the presence of sorbed water in a soft contact lens polymer, poly(2-hydroxyethyl methacrylate), were investigated by using the positron lifetime technique. It was found that the ortho-positronium lifetime increases in the beginning of sorption because of microstructural swelling of the polymer matrix. After reaching a maximum, the lifetime decreases and becomes constant, maybe because of the filling of the free-volume holes with water molecules. The diffusion process is found to be

non-Fickian. By using the dual-mode sorption model, the Fickian-controlled part and the relaxation-controlled part of diffusion were separated. Further, the positron results seem to indicate the existence of water clusters in the sorbed lens material. The tolerance or stability of the soft lens material to UV radiation seems to be satisfactory as revealed by positron results. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1355–1366, 2004

Key words: diffusion; swelling; visco-elastic properties

INTRODUCTION

From a researcher's perspective, designing a good contact lens polymer is not a trivial task. The contact lens material must satisfy a number of strict requirements. It must be transparent, possess chemical and thermal stability and biocompatibility, and be wettable to tears. It must also have suitable mechanical properties. For hydrogels, this includes low modulus of elasticity (softness) for patient's comfort and good shape memory for handling and proper functioning. Finally, the material must also have good oxygen permeability. Owing to a lack of blood vessels within the corneal framework, the cornea must get oxygen directly from air. When the contact lens comes in the way of the eye and air, it reduces the oxygen supply, which will cause corneal edema. Excessive prolonged levels of edema may lead to a number of physiological responses including microcysts, inflammation, infections, and corneal ulcers.¹ Furthermore, the contact lens is constantly in touch with the lachrymal fluid, which contains not only water but also lipids, sodium, carbon bicarbonate, and enzymes, which tend to form a thin film on the contact lens if the lens is hydrophobic. This reduces the transparency and causes infection and irritation to the eye. If the contact lens has

good wettability or high hydrophilicity, these problems can be overcome.

The dream of realizing such a contact lens came true with the advent of world's first soft contact lens polymer, poly(2-hydroxyethyl methacrylate) (HEMA), in the 1960s. PHEMA has proven itself to be a promising material, even today, despite the entry of very many new materials to the contact lens industry. It is a transparent hydrogel, which, when hydrated, absorbs up to 40% water but is insoluble in water because of the presence of crosslinkers that form a three-dimensional network.¹ Under equilibrium water content conditions, it has glass transition temperature (T_g) below the room temperature and, hence, it has appreciable softness.² Hydrogels have high polymer-polymer segment interactions. This provides stability of the gel from collapsing on swelling.³ The polarity of the segments is responsible for the hydrophilicity of the gel. In a hydrogel, polymer-solvent interactions are stronger than the polymer-polymer interactions. However, there exists a balance between the two at equilibrium sorption to control the swelling. PHEMA is prepared by free-radical polymerization of HEMA monomer by using either a thermal or a UV initiation system. It is also prepared by a spin-cast process, which involves polymerizing HEMA monomer in a spinning concave mold where the lens power is controlled by the spin rate and mold optics. The degree of swelling is characteristic of its composition and crosslink density. The gel tends to absorb or expel fluid efficiently with changes in the environmental conditions such as os-

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motric pressure on the gel. This helps in controlled drug release to the eye in some specific cases.

Oxygen transport from air to the eye takes place via the water present in the contact lens. Oxygen slips into pockets that exist in the loose hydrogen-bonded network of water molecules without forcing them apart. The oxygen is then caged by water molecules, which weakly pin it in place. Thus, the oxygen permeability of a soft lens is proportional to the water content of the lens. The ability of a hydrogel to absorb water depends mainly on the topology (or nanopores or free-volume cavities)⁴ and the presence of hydrophilic or polar groups such as OH.² The topology or free volume in a hydrogel has connect structure. Water traverses the polymer through the network of nanopores, which are also coincident with polar hydroxyls. In this way, the topology provides direct access to the hydrophilic sites for the water molecule.⁴ Also, the larger the free-volume hole volume fraction, the larger will be the moisture uptake. Regardless of the exact nature of the bonds, it is sufficient to note that the hydroxyl group is involved in hydrogen bonding, even in the dry polymer. Soles et al.⁵ found that there is a slight exponential dependence of the diffusion coefficient on the average nanopore size at room temperature. In their work, they found no correlation between nanopore content and transport kinetics because the polar trapping sites act as a rate-limiting factor.⁵

Free-volume cavities or nanopores are low electron-density regions located mainly in the amorphous domains of the polymer matrix.⁶ The rate of diffusion in the amorphous polymer will depend on the size of the diffusing molecules and the open volume available. Over the years, there have been several developments in the free-volume theory. One of the simple theories, the simpler theory of free volume is by Fujita,⁷ which owes its origin to the free-volume theory of Cohen and Turnbull.⁸ A simple picture of Fujita's theory can be visualized through the correlation of the diffusion coefficient and the free-volume fraction of the polymer. This can be mathematically expressed as

$$D = A_d \exp[-B_d/F_v] \quad (1)$$

where the parameters A_d and B_d are constants. The parameter A_d depends mainly on the size of the diffusant, whereas B_d depends on the minimum volume required for the displacement of the diffusant. Because diffusion depends on the chemical structure of the polymer and the size of the diffusant molecules, understanding of the diffusion mechanism is usually done through the application of Fick's laws and its modified versions, from which one can obtain information on the rate of diffusion and the polymer segmental relaxation.^{9,10} So, diffusion kinetics of water

and its influence on the microstructure of contact lens polymer are an important aspect of research.

Radiation-induced changes in a polymer are important from the view point of its applications. The different means by which the properties of the polymeric materials are affected by environmental conditions are innumerable.^{11,12} The exact effect produced depends on the structure of the polymer and the nature of radiation.¹³ Radiation-induced changes are mainly caused by chain scission and crosslinking, resulting sometimes in the degradation of the polymer. The diffusion of gas molecules and solvents in irradiated polymers are considerably different from those of unirradiated polymers. In reference to contact lens polymers, it is important to know how its transport properties are affected under the influence of UV irradiation in particular. To accomplish this, one needs to measure the nanopores of the lens material. One of the most versatile methods available nowadays for this purpose is the positron lifetime technique (PLT). A brief outline of this technique is given in the following paragraph.

When an energetic positron from a radioactive source enters a condensed medium such as a polymer, it gets thermalized by losing its energy in a very short time; then it annihilates with an electron of the medium. Annihilation usually takes place from different positron states (viz., free annihilation process), or from a localized state (trapped state), or from a bound state called positronium (Ps). Ps can exist in two spin states: para-positronium (p-Ps, particle spins antiparallel), which annihilates with a lifetime of 0.125 ns and the other spin state called ortho-positronium (o-Ps, particle spins 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 because positronium is trapped and annihilated in free-volume sites and, hence, it provides information on the mean size of the free-volume holes in the polymer matrix.⁶

In view of the above-mentioned aspects of the diffusion and its relation to nanopores, we have studied the diffusion kinetics of water and how its presence modifies the topology in PHEMA. For this, we used the combination of two methods, namely, sorption method and PLT.

EXPERIMENTAL

Sample details

PHEMA samples were procured from a commercial source. Several companies, such as Paragon Optical

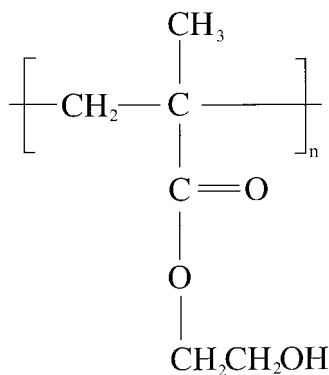


Figure 1 Chemical Structure of PHEMA.

(Damascus, Syria), Bausch & Lomb (US), Ciba-Vision (US), Cooper Vision (US), produce PHEMA. The samples were in the form of circular discs of thickness of about 1.5 mm and of diameter 13.5 mm. Pure PHEMA gel is colorless with index of refraction of 1.44 and specific gravity of $\sim 1.17 \text{ g mL}^{-1}$. The T_g is about 70°C in the dry state. The molecular formula of the monomer HEMA is $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OH}$. The chemical structure of PHEMA is given in Figure 1.

Water sorption

Well-polished samples of PHEMA were dried for several hours in a vacuum desiccator before sorption measurements started. The dry weight of the samples was recorded on a digital balance (Sartorius BP210 D, Germany), with a precision of $\pm 0.01 \text{ mg}$. Then, the samples were soaked in distilled water for a known interval of sorption time. After this, the samples were removed from water, blotted off to remove excess moisture from the surface, and weighed again. Then, the samples were used in positron lifetime measurements. This cycle of experimentation was continued until the weight gain of the samples reached a plateau value, which was taken as the equilibrium moisture uptake. Contact lenses are continuously in contact with the fluid [i.e., human tears (lachrymal fluid), which consists of 98.2% of water alone, and the remaining 1.8% constitutes other chemical species such as bicarbonates and chlorides of sodium, calcium, etc. and biomolecules such as protein, albumin, enzymes, etc.]. Nevertheless, water as the sorbant used in this study can be very nearly approximated as human tears. The results can be treated as approximately equivalent to that obtainable for actual tears.

Positron lifetime measurements

Positron lifetime measurements were carried out by using a fast-fast coincidence system consisting of KL-236 plastic scintillators coupled with RCA-8575 pho-

tomultipliers as detectors. A $10 \mu\text{Ci } ^{22}\text{Na}$ deposited on a pure kapton foil of thickness 0.0127 mm was used as the positron source. The source-sample sandwich geometry (sample on either side of ^{22}Na positron source) was used for the positron lifetime measurements. More details of the experimental procedures are reported elsewhere.^{6,14} Positron lifetime spectra with more than 1×10^6 counts under each spectrum were recorded for each sorption time. The instrumental time resolution and source correction terms were obtained from the measured spectrum of a medium of known lifetime (well-annealed aluminum) fitted with the computer program RESOLUTION.¹⁵ A time resolution of 340 ps was obtained with 40% ^{22}Na energy gating. All lifetime experiments were performed at room temperature. Care was taken to check periodically the effects of electronic drifts, if any, although the experimental arrangement was housed in an air-conditioned room. For each sorption time, several runs of the lifetime spectra were taken to check the reproducibility of the measurements. The lifetime spectra were analyzed by using the computer program PATFIT-88¹⁵ with proper source and background corrections. All spectra were resolved into three lifetime components, as it gave better χ^2 values and standard deviations. Four-component constrained analysis was also used to separate the o-Ps annihilations in sorbed water.

UV irradiation

A 125-W mercury vapor lamp without optical filter was used as UV source to irradiate the contact lens sample. The UV lamp was positioned at a distance of 15 cm from the sample so that the light flux was normal to the surface of the sample. Air flow at a low rate from an electric fan was used to maintain the sample at room temperature during irradiation. The sample was irradiated for known intervals of time. After each irradiation, the positron lifetime measurements were conducted on the irradiated sample and analysis was made as described above.

RESULTS AND DISCUSSION

Positron lifetime results

The general way of interpreting the three resolved positron lifetime components to various states of positron annihilation is as follows: The first short-lived 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 caused mainly by the annihilation of positrons trapped at defects present in the crystalline and crystalline-amorphous (c-a) 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.^{6,16}

In polymers, of the three lifetime components, the o-Ps pick-off lifetime τ_3 with intensity I_3 is important because τ_3 is related to the average free-volume hole size and I_3 is considered as a measure of the number density of free-volume holes. I_3 also represents the probability of o-Ps formation.¹⁷ Because diffusion in polymers has a direct bearing on the free-volume content of the polymer [eq. (1)], for an understanding of the diffusion kinetics in terms of free volume, we need to look at τ_3 and I_3 only. These two parameters are independent of the first two lifetime components. Therefore, τ_3 and I_3 are the focus of this investigation. The o-Ps lifetime τ_3 is related to the free-volume size by a simple relation given by Nakanishi et al.,¹⁸ which was developed on the basis of the theoretical models originally proposed by Tao¹⁹ for molecular liquids and later by Eldrup et al.²⁰ In this model, positronium is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R_0 with an electron layer in the region $R < r < R_0$ and predicts the connection between τ_3 and the free-volume size (spherical). By using this semiempirical approach, we can determine the average radius of the free-volume hole (R) from the relation¹⁸

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

where $R_0 = R + \Delta R$ and the reasonable assumption is that lifetime of the o-Ps in the electron layer of thickness ΔR is the spin-averaged Ps lifetime of 0.5 ns. The value of $\Delta R = 0.1657$ nm was determined by fitting eq. (2) with experimental values of τ_3 obtained for molecular materials with known hole sizes such as zeolites.¹⁶ This equation is used to calculate free-volume radius (R) of the polymer sample at each sorption time. Then, the average free-volume size is evaluated as $V_f = (4/3)\pi R^3$. The fractional free volume F_v can be estimated as

$$F_v = CI_3V_f \quad (3)$$

where C is termed as the structural constant which may be calculated in the following way: according to one of the methods,²¹ C can be calculated by equating F_v in the above equation to the volume percentage of sorbed water under equilibrium conditions, which, in the present case, turns out to be 38%. It means that the fractional free volume in HEMA is on the order of 38%, which is very large to be in agreement with free-volume theory as applied to polymers and eq. (3) is the off-short theory. So, this method of C evaluation is not suitable at least for the present case. Hence, to

evaluate C , we assumed the value for F_v below and up to T_g to be 2.5% in accordance with the free-volume theory.²² The values of I_3 and V_f are 25.5% and 63.4 \AA^3 , respectively, for the present sample in as received state. By putting these values in eq. (3), the value of C was calculated and this turns out to be 0.00154 \AA^{-3} , which is comparable with the values reported elsewhere.²² This value of C is used in the evaluation of F_v by using eq. (3) and the measured values of V_f and I_3 .

Polymers are known to undergo swelling in the presence of liquid media.^{23–25} When water enters the polymer, it leads to perturbation of the local molecular environment. The phenomenon of swelling depends on the forces of interaction between the solvent molecules and the polymer segments. Water, being a good plasticizer with molecular kinetic diameter of 3 \AA , penetrates into the polymer (PHEMA) matrix with an average free-volume diameter about 6 \AA . The penetrated water molecules establish polar attractive forces with the polymer chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility,²⁴ which leads to swelling. During the swelling process, the volume of the polymer matrix changes, thereby increasing the pathways for water molecules to diffuse. In the present case, the macroscopic dimension of the sample changes. That is, the thickness of the sample increases from 1.26 to 1.74 mm at equilibrium water uptake. When the sorbate (water)–sorbent (polymer) interaction becomes stronger than the sorbent–sorbent attraction, the forces holding the polymer segments together become weak and the sorbate molecules can force their way between the segments, break the segment–segment contacts, surround the individual segments, and establish contact with them. In the dry state, the polymer is strongly strained because of the rigidity of the network. The inner strains relax when the network expands, and this strongly facilitates its swelling in any liquid media.^{25,26}

The swelling ratio measurement shows that PHEMA absorbs a large amount of water. The uptake is relatively quick at the beginning but saturation occurs only after 10 h of soaking at 38% swelling ratio. There are significant changes in the lifetime and the intensity of o-Ps as a function of sorption time (Fig. 2). In the beginning of the sorption (up to 60 min), the o-Ps lifetime increases by about 500 ps. Later, it decreases to a constant value, supposedly an equilibrium value, suggesting that all possible sites of free-volume cavities being occupied by water or OH water interaction saturates. On the other hand, the o-Ps intensity variation is interesting. It decreases by 7% (from 25.5 to 18.5%) in 45 min of sorption. This decrease can be attributed to the reordering of PHEMA chains as a result of swelling process, which might result in the coalescence of small free-volume holes into comparatively larger ones. Thus, the number of free-volume

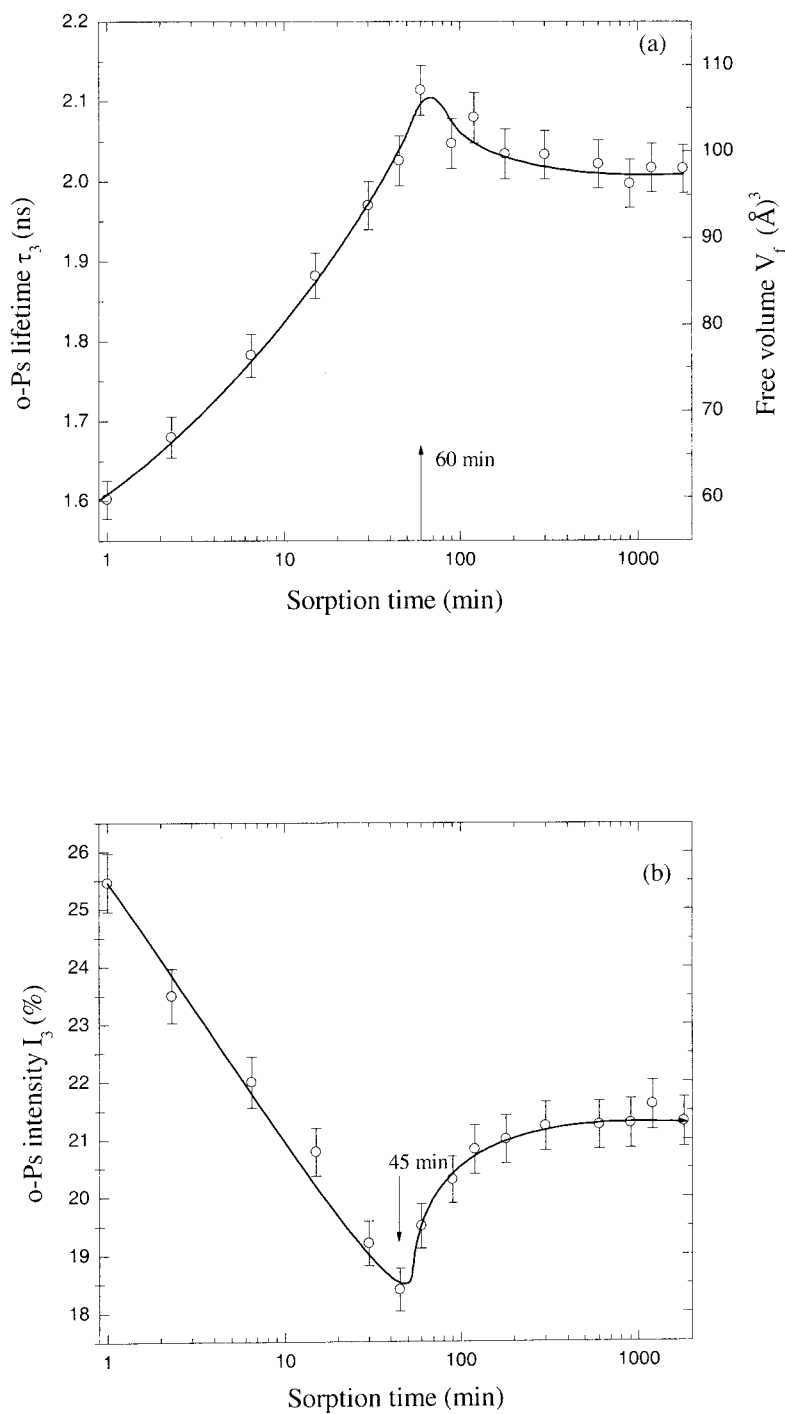


Figure 2 (a) Variation of τ_3 and V_f as a function of sorption time. (b) Variation of I_3 as a function of sorption time. Solid lines drawn are to guide the eye.

holes are expected to decrease. These results also shed some light on the topology of PHEMA. Because water uptake is large in the initial stages, it seems that water molecules very easily reach every HEMA unit quickly. If this is the case, then the PHEMA should be composed of interconnected channels or interconnected pores, which allow rapid diffusion of water rather than isolated pores. If the free-volume holes were

composed of independent pores, the decrease would be a slow process.²⁷

On careful examination, it becomes quite evident that the large increase (500 ps) and decrease of τ_3 to a constant value of 2003 ps suggests that o-Ps annihilates not only in the free volume of PHEMA but also in the sorbed water present in it. This expectation is mainly due to a large intake of water (initial mass of

the sample = 447.68 mg; final mass of the sample = 705.00 mg; initial thickness of the sample = 1.26 mm; final thickness = 1.74 mm). There is good supporting evidence from Suvegh et al.,²⁷ who report o-Ps annihilation in a water–monomer mixture. To explore this possibility, we resolved the positron lifetime spectrum into four components by assigning the third component τ_3 to lifetime of o-Ps in water (1800 ps) and I_3 to the corresponding intensity. In this analysis, the component τ_4 is prescribed to the lifetime of o-Ps in the polymer (i.e., o-Ps annihilating in free-volume cavities of the polymer and I_4 is the corresponding intensity). As the free analysis did not result in good convolution, we had to go for constrained analysis of the positron lifetime spectra. In this attempt, τ_3 was fixed at the lifetime of o-Ps in pure water (i.e., 1800 ps). To observe the variations in τ_4 and I_4 only, I_3 was also fixed on the basis of the percentage of water present at the respective sorption time, and the results of this analysis are shown in Figure 3. The parameters τ_4 and I_4 exhibit the same tendency of variation as in three-component analysis but their peaking and saturation points are at higher values of sorption time. This shift certainly points to the role of sorbed water as far as o-Ps annihilation is concerned.

We further made another constrained analysis just to see the variations of I_3 and I_4 only. For this, τ_3 was fixed at 1.8 ns and τ_4 at different values obtained from the previous analysis for respective sorption times. The variations are shown in Figure 4. The variation of I_3 is on the expected line (i.e., because τ_3 is o-Ps lifetime in water, increase of I_3 is an indication that as the water content increases, the fraction of o-Ps annihilating in water also increases) [Fig. 4(a)]. Because τ_4 is prescribed to o-Ps lifetime in free volume of PHEMA, as more and more water gets in, the free-volume cavities of PHEMA gets filled up with water and hence I_4 should decrease, which is what we observe in Figure 4(b). At the later stages of sorption (after 900 min) (M_t/M_∞), for instance, mass uptake becomes unity or swelling ratio becomes practically constant at 38%. In this region of sorption time, we notice the constancy of the two parameters I_3 and I_4 . Thus, this analysis further confirms that o-Ps annihilating in water-filled PHEMA is of two types: one in the nanopores of PHEMA and the other in the filled water itself. The constancy of the lifetime and intensity in the final stages can be interpreted as due to the formation of water clusters that block further entry of water molecules and saturation of the polar sites. Because water is a polar molecule, there are both geometric and energetic reasons for water to take up residence in the unoccupied voids. The aggregation of water in such voids forms clusters. The cluster has its own free-volume cavity or cage.²⁷ Further, there are two types of water molecules in the hydrated HEMA: the free and the bound water molecules. The water molecules

attached to the hydroxyl group OH are bound and they produce polymer chain relaxation resulting in the swelling. The water molecules away from these sites are free and are responsible for oxygen transport through their cage.⁴

Sorption kinetics

To understand the sorption mechanism of water sorption in PHEMA and to determine the diffusion coefficient D , we have invoked Fick's second law of diffusion,²⁸ which is mathematically represented as

$$(\delta C_d / \delta t) = D(\delta^2 C_d / \delta x^2) \quad (4)$$

where C_d is the concentration of the diffusant species, t is the sorption time, and $(\delta C_d / \delta x)$ is the concentration gradient. Crank's solution^{23,29} for this equation in a plane sheet of the sample of thickness L with surfaces maintained at constant concentration is given by

$$(M_t / M_\infty) = 1 - (8 / \pi^2) \sum_{n=0}^{\infty} \{1 / (2n + 1)^2\} \times \exp\{-D(2n + 1)^2 \pi^2 t / L^2\} \quad (5)$$

where 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). In eqs. (4) and (5), the diffusion coefficient D is independent of the concentration of the diffusing molecules. The ratio (M_t / M_∞) in eq. (5) can be experimentally determined as

$$(M_t / M_\infty) = (W_t - W_d) / (W_\infty - W_d) \quad (6)$$

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 (equilibrium mass uptake). The ratio (M_t / M_∞) was calculated by using eq. (6) with the measured values of W_d , W_t , and W_∞ . A widely used approximation is that, at short times (up to $M_t / M_\infty = 0.5$), the amount of substance diffused is proportional to $(t^{1/2})$, which is known as Stefan's approximation^{29,30} and is given by

$$(M_t / M_\infty) = 4(Dt / \pi L^2)^{1/2} \quad (7)$$

This equation is derived under the assumption that D , the diffusion coefficient, is a constant. A plot of this ratio (M_t / M_∞) versus square root of sorption time ($t^{1/2}$) is generally termed as the sorption curve, which is shown in Figure 5 for the present case, and D can be calculated from the slope of the initial linear portion of the curve. The ratio (M_t / M_∞), as can be seen from Figure 5, varies linearly with $t^{1/2}$ up to (M_t / M_∞)

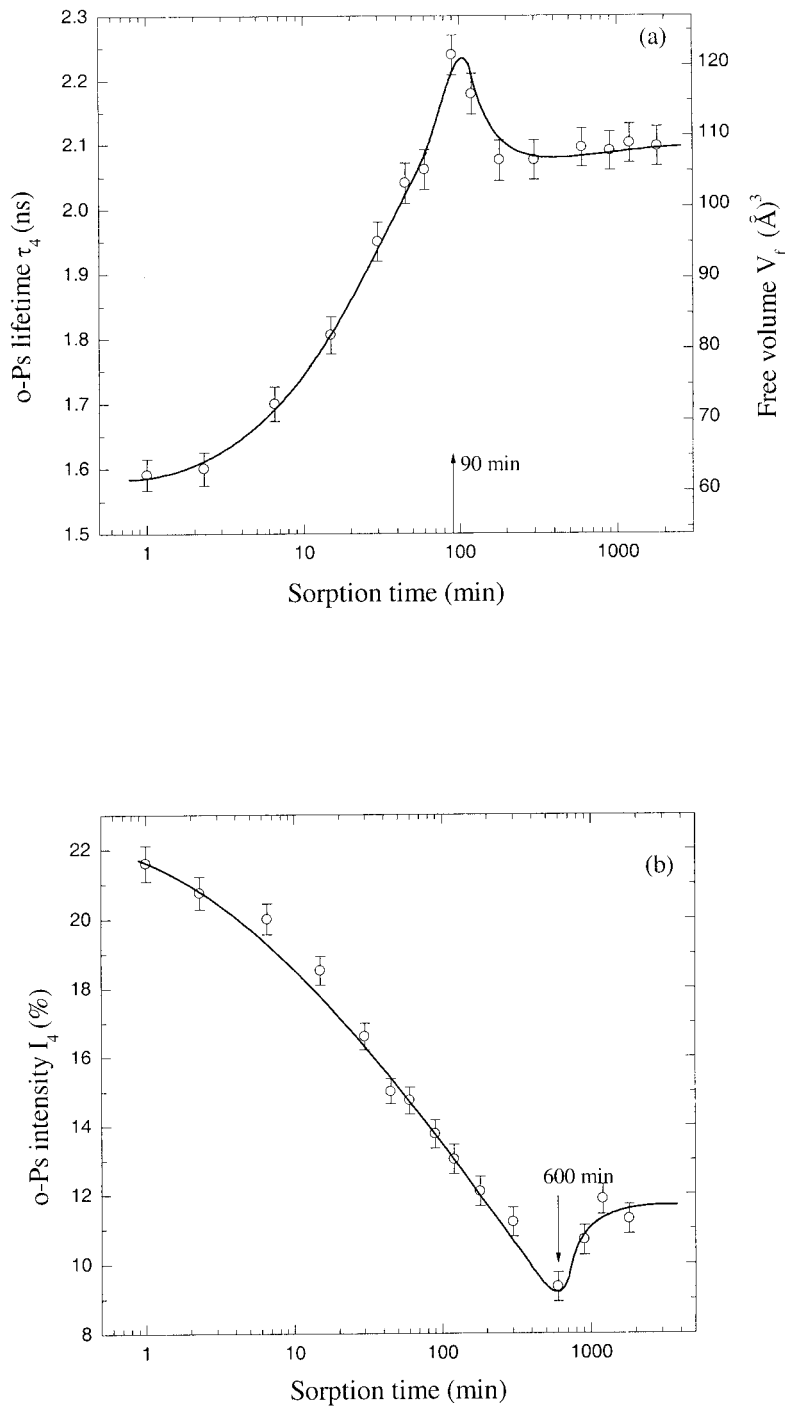


Figure 3 (a) Variation of τ_4 and V_f as a function of sorption time. (b) Variation of I_4 as a function of sorption time [four-component analysis]. Solid lines drawn are to guide the eye.

= 0.48; thereafter it changes slope showing an upward curvature. By taking $n = 0$, eq. (5) reduces to the form

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

This is known as the late time approximation from which also D can be calculated.

For a clear understanding of the diffusion mechanism of water transport in this polymer matrix, the sorption results have been further fitted to a relation of the type³¹

$$M_t/M_\infty = Kt^n \quad (9)$$

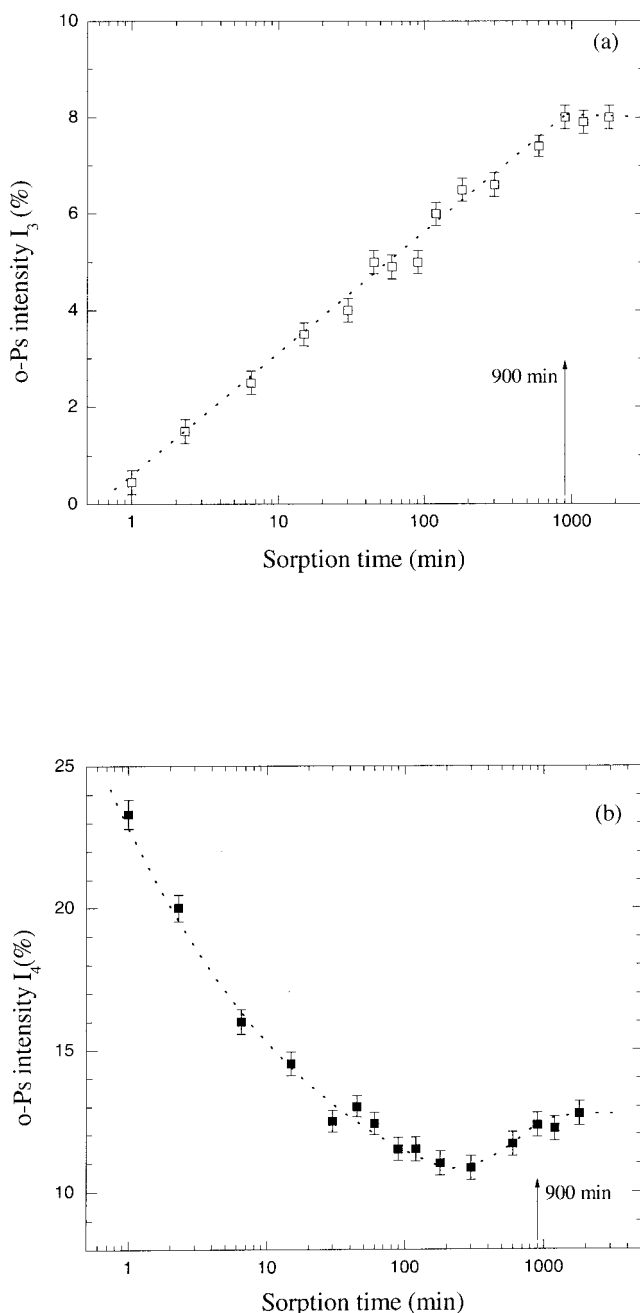


Figure 4 (a) Variation of I_3 as a function of sorption time. (b) Variation of I_4 as a function of sorption time [four-component analysis]. Dotted lines drawn are to guide the eye.

Here, K is a constant, which depends on the structural characteristics of the polymer network. The exponent n is an indicator of the diffusion mechanism. Normally if $n = 0.5$, diffusion is termed as Fickian. A value of $n = 1$ refers to non-Fickian diffusion. A value of n between 0.5 and 1 labels diffusion as anomalous. For the anomalous type, diffusion and relaxation rates are almost comparable. From the linear fit of eq. (9), we get $n = 0.73$ and $K = 0.018$ for the present case of

PHEMA [Fig. 6(a)]. The K value is comparable to the values reported in literature.³² The value of 0.73 for n suggests that the sorption of water in PHEMA is anomalous and deviates from Fickian, because n is greater than 0.5. Based on these results, we tried to fit the experimental results by using eq. (8). It showed us that eq. (8) is not adequate to fit the experimental values of (M_t/M_∞) , further indicating the diffusion is not purely Fickian.

In such situations, sorption kinetics are often described by using the Berens and Hopfenberg model,²³ otherwise called dual-mode sorption model,³³ which incorporates both Fickian diffusion and relaxation controlled diffusion. According to this model, the existence of an upward curvature over an extended period of sorption indicates the presence of a relaxation contribution to the overall sorption²³ (i.e., the diffusion is non-Fickian). For Fickian diffusion, the sorption curve is linear during the initial stages of sorption and reaches a plateau region over an extended period of time.²⁹ From the description of Fickian and non-Fickian sorption processes described above and a careful examination of the sorption curve in Figure 5, we can say that the sorption is definitely anomalous in PHEMA. Fickian-type diffusion is characterized by the rate of diffusion being much less than that of the polymer segmental relaxation due to mechanical, structural, etc., modes of penetrant-polymer system.

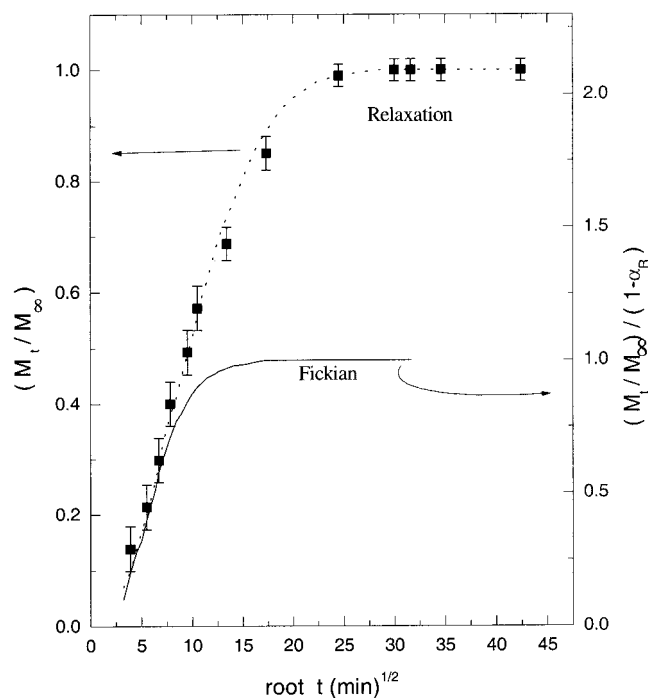


Figure 5 Variation of (M_t/M_∞) and $(M_t/M_\infty)/(1 - \alpha_R)$ as a function of sorption time. The symbols represent the experimental points; the solid line is a fit to part the dotted line and I of eq. (10) (Fickian diffusion) is a fit to part II of eq. (10) (relaxation).

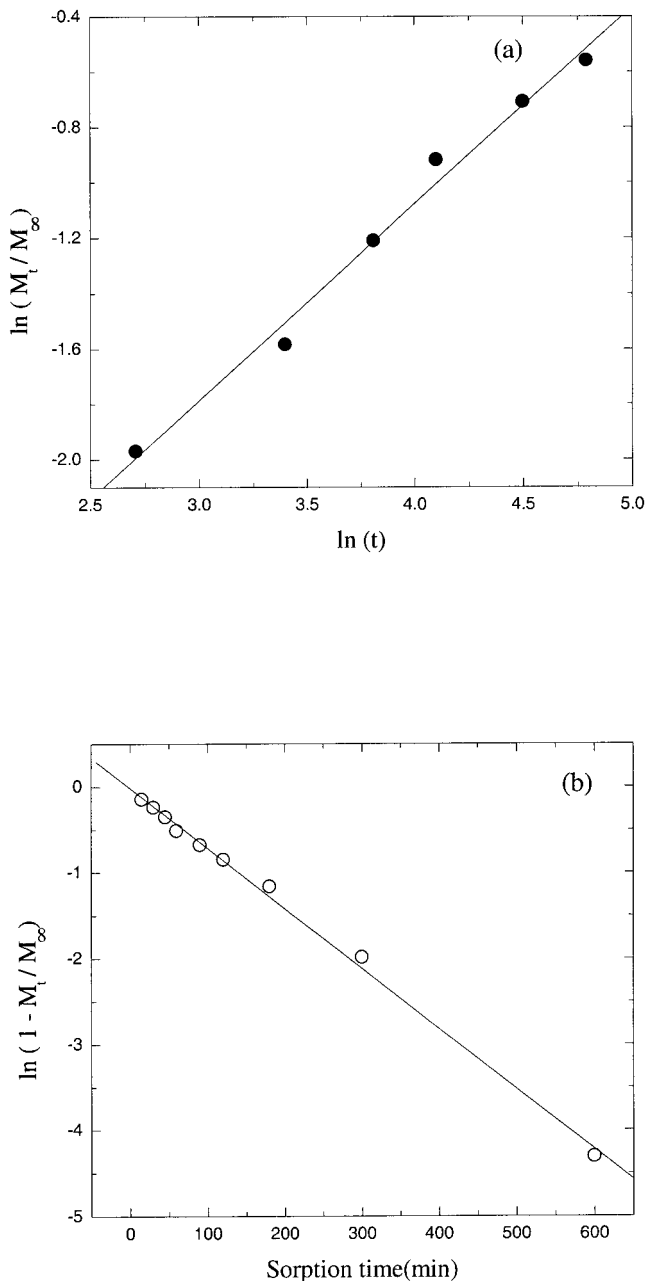


Figure 6 (a) Variation of $\ln(M_t/M_\infty)$ with $\ln(t)$ for the linear portion of the sorption curve. The solid line is a fit to the experimental points. (b) Variation of $\ln(1 - M_t/M_\infty)$ with (t) for the entire sorption period. The solid line is a fit to the experimental points.

Non-Fickian-type diffusion is that for which the diffusion occurs faster than segmental relaxation process.⁹

According to dual-mode sorption model,^{23,29} the sorption at the initial stages in penetrant-free polymer sample is dominated by the rapid Fickian diffusion process, while the incremental sorption shows larger relative contributions from slow relaxation processes. As stated earlier, this model is generally used to explain the contribution of relaxation behavior, which

overshadows the Fickian diffusion at the later stages of sorption. However, this model has been shown to provide a meaningful analysis of several non-Fickian anomalies, including a very slow approach to equilibrium.^{23,33-35} This model is expressed mathematically as

$$(M_t/M_\infty) = (1 - \alpha_R) \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \{1/(2n + 1)^2\} \right. \\ \times \exp\{-D(2n + 1)^2 \pi^2 t/L^2\} \\ \left. + [1 - \{\alpha_R \exp(-t/\tau_R)\}] \right] \quad (10)$$

In this equation, the first term is the contribution from the Fickian diffusion and the second term is the contribution due to polymer relaxation. This model represents diffusion and relaxation as parallel processes and the faster process controls the initial mass uptake.³³ In eq. (10), $(1 - \alpha_R)$ and α_R are the fractions of mass uptake in the overall sorption contributed by the Fickian diffusion and the relaxation, respectively. τ_R is the first-order time constant with the long time drift in the mass uptake. The long time drift in mass uptake is usually ascribed to the mass uptake controlled by the viscoelastic relaxation of polymer chains to accommodate more penetrant.³³ Based on the linearity of initial mass uptake (with $t^{1/2}$) in Figure 5, Fickian diffusion seems to control the initial mass uptake. To separate the pure Fickian contribution in the sorption curve, a plot of $(M_t/M_\infty)/(1 - \alpha_R)$ versus $t^{1/2}$ was made as suggested by McDowell et al.³³ For this plot, the value of $(1 - \alpha_R)$ was chosen to be 0.48 up to which the sorption curve is linear. Because the rate of diffusion in the beginning is controlled by Fickian diffusion, the initial portion of this sorption curve may be used to estimate the true diffusion coefficient even when the total sorption does not follow the Fickian model.³⁶ The best fit value of D is $3.8 \pm 0.28 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Thus, Fickian diffusion is dominated in the initial 48% of mass uptake (represented by the solid line in Fig. 5), while the relaxation process (represented by the dotted line) controls the rest of the diffusion (52%). The solid line in Figure 5 was obtained by fitting the experimental data to the first part of eq. (10) by using the aforementioned value of D .

From the sorption results, the first-order relaxation time constant (τ_R), which characterizes the non-Fickian drift in mass uptake toward equilibrium, was calculated as follows. Relaxation-controlled diffusion is expressed as a single exponential by the second term of eq. (10). This can be written as

$$\ln[1 - (M_t/M_\infty)] = \ln(\alpha_R) - (t/\tau_R) \quad (11)$$

A graph of $\ln[1 - (M_t/M_\infty)]$ versus sorption time t is made for all the values of M_t/M_∞ [Fig. 6(b)]. The value of α_R obtained is close to unity. This value is consistent with the dual-mode sorption model, which prescribes that α_R should be between zero and unity.³⁵ This also suggests that the diffusion process in the present case is non-Fickian and starts at $t = 0$ itself with a characteristic relaxation time τ_R equal to 145 min. The dashed curve in Figure 5 represents the fit to the experimental data with the aforesaid value of τ_R . As we can understand from Figure 5, the contribution from the Fickian part of the curve [i.e., $(1 - \alpha_R)$] is 0.48.

Free volume and permeability

As mentioned in the Introduction, the diffusion of molecules occurs through the free-volume holes, which in the present case may have connect-structure. As water molecules enter the preexisting free-volume sites, they interact with the hydrophilic OH sites forming loose hydrogen bonding.²⁷ This leads to the formation of additional free volume as the polymer chains relax or, in other words, the polymer swells. So, we observe an increase in the average size of the free-volume holes by about 40 \AA^3 (from 64 to 104 \AA^3) in the sorption time regime up to 60 min [Fig. 2(a)].

Although the initial linearity in the sorption curve results in a single averaged D value by using the late time approximation [eq. (8)], varying values of D can be calculated. We know that D is related to the diffusant (water) permeability through the equation

$$P = DS \quad (12)$$

where S is the solubility of the diffusant in the polymer calculated as grams of water per grams of the polymer (PHEMA).³⁷ In the present case, the value of S turns out to be 0.58 g/g . With this value of S and by using eq. (12), the permeability of water in PHEMA is calculated. A plot of P as a function of sorption time is made and shown in Figure 7. From this figure, we see that up to 200 min, P is almost constant. Water intake or permeability of PHEMA is maximum in this initial sorption period. After 200 min, P decreases rapidly, though the free-volume size is sufficient ($\sim 100 \text{ \AA}^3$) to accommodate water molecule ($\sim 14 \text{ \AA}^3$). This decrease may be explained in the following way. By this time, because the polar sites are already saturated with water, the attached water molecules to the polar sites hinder the flow of water (explained earlier). Also, there is evidence that⁵ water molecules at higher uptake levels may be clustered and, hence, their entry is not possible. On clustering, the effective diameter of the water molecule increases, and the diffusion coefficient decreases. It will be difficult for a cluster of several molecules to diffuse through the nanopores than a lone, free-water molecule. This also seems to

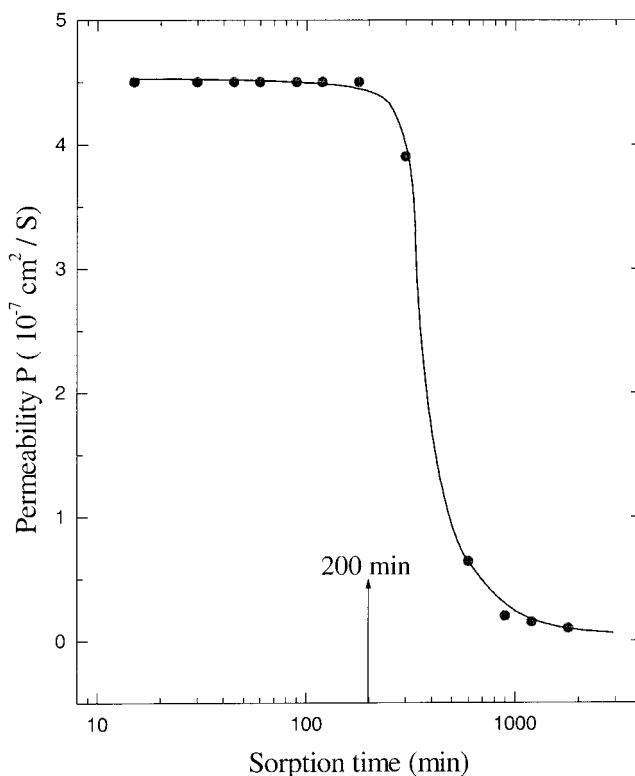


Figure 7 Variation of permeability P with sorption time. The solid line drawn is to guide the eye.

suggest that water be initially absorbed as lone molecule.⁵

UV radiation tolerance

As mentioned in the Introduction, it is important to learn the properties of the contact lens polymers, specifically, the transport properties when they are exposed to UV radiation. From this point of view, the PHEMA samples (dry state) were exposed to UV radiation for different intervals of time and lifetime measurements were made as described earlier. The variations of positron lifetime parameters τ_3 and I_3 (three-component analysis) with UV irradiation time are as shown in Figure 8(a, b). It is interesting to note that τ_3 remains almost constant even up to 200 h of UV irradiation. This infers that no chain scission or crosslinking has taken place to result in changes in V_f [Fig. 8(a)]. However, there is some slight change in the o-Ps intensity (I_3) [Fig. 8(b)] after 140 h of irradiation. This may be attributed to random crosslinking,¹⁴ which also vanishes soon. Thus, the overall effect of UV radiation on the free volume of PHEMA is insignificant, suggesting that after 200 h UV irradiation the PHEMA will have the same transport or sorption characteristics as that of unirradiated PHEMA.

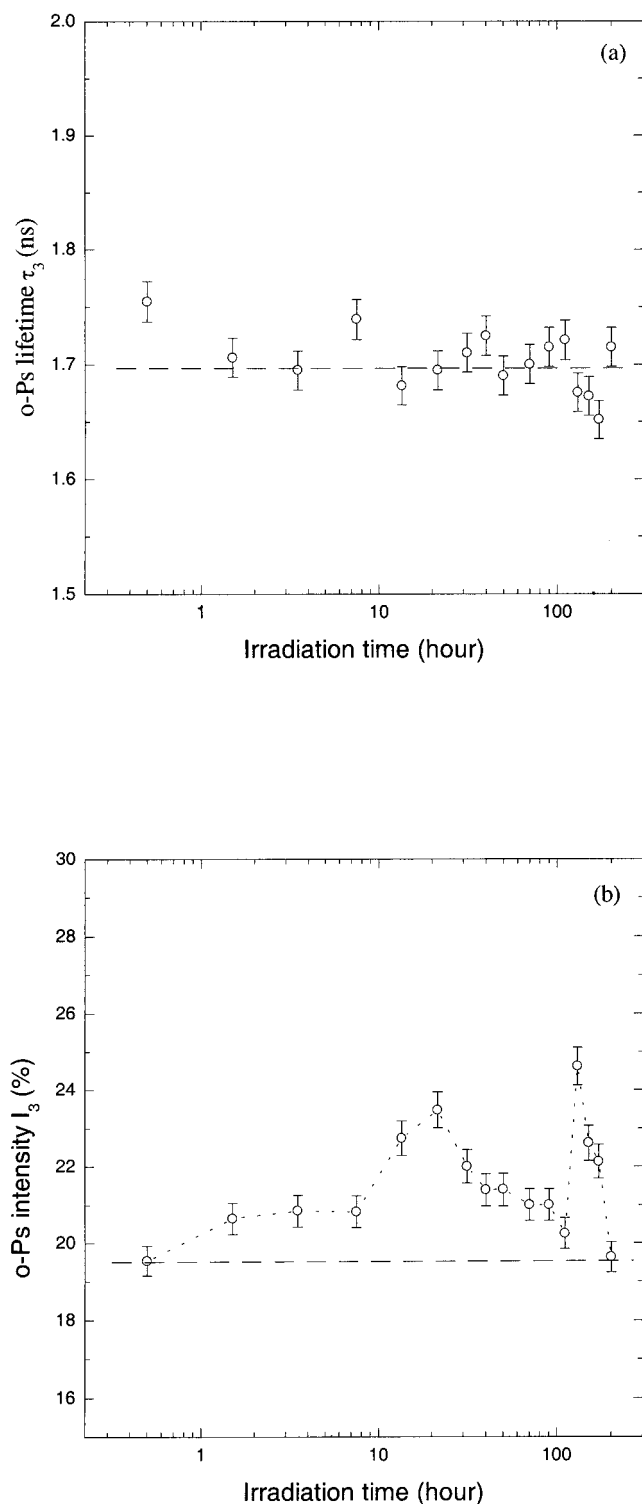


Figure 8 (a) Variation of τ_3 as a function UV irradiation time. The dashed line drawn is to show the constancy in τ_3 value. (b) Variation of I_3 as a function UV irradiation time. The dotted line drawn is to guide the eye. The dashed line drawn is to show that I_3 value returns to its original value after UV irradiation on PHEMA.

CONCLUSIONS

By using positron lifetime technique, we have studied the water sorption in the soft contact lens polymer

PHEMA and the effects of UV irradiation on it: the following are the conclusions drawn.

1. The significant increase in the o-Ps lifetime and, hence, the free volume size in the initial stages of water sorption indicate that the PHEMA swells upon water diffusion. Four-component analysis of positron lifetime spectra clearly shows that o-Ps not only annihilates in the free volume cavities of PHEMA but also in water present in it.
2. The changes in the o-Ps intensity from three-component and four-component analysis further support the above conclusions.
3. Fickian-controlled and relaxation-controlled diffusion of water are separated by using dual sorption method. The results show that the relaxation-controlled diffusion is the dominant process of water uptake in PHEMA.
4. The permeability is more in the initial stages of sorption as indicated positron results.
5. Positron results on UV-irradiated PHEMA clearly demonstrate that sorption characteristics of the contact lens polymer are unaffected.

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