

Oxygen Transport in Crosslinked, Silicon-Containing Copolymers of Methyl Methacrylate

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Synopsis

Copolymers of methyl methacrylate and 1,3-bis(methacryloxy methyl)-1,1,3,3-tetramethyl disiloxane were prepared by chemically induced copolymerization/crosslinking at 60°C and 49 mm Hg. Crosslinked, glassy copolymers were obtained with copolymer mole fraction of the silicon-containing monomer varying from 0.09 to 0.55. Oxygen transport studies were performed with thin films as prepared and after sub- T_g annealing. The results of this study indicated that an enhancement of both the steady state oxygen permeation rate and the oxygen diffusion coefficient was achieved through copolymerization. The oxygen diffusion coefficients through the copolymers were found, within experimental error, to be independent of silicon content and ranged from 0.80×10^{-7} to 1.90×10^{-7} cm²/s vs. oxygen diffusion coefficient for pure poly(methyl methacrylate) of 1.5×10^{-8} cm²/s. Sub- T_g annealing effected a reduction of approximately equal magnitude in both the oxygen diffusion coefficient and the steady state oxygen flux for the copolymers. In addition, the normalized oxygen flux data were predicted with Fick's law, assuming constant boundary conditions and diffusion coefficient. These results were explained in terms of the free volume theory and the combined effects of increased crosslinking density, chain mobility, and oxygen solubility with increased copolymer silicon content.

INTRODUCTION

Copolymers of methyl methacrylate or related esters with disiloxanes and other silicon-containing monomers have attracted considerable interest in recent years due to their potential applications as hard contact lens materials.¹ This is mainly due to the fact that most of these copolymers are glassy with high oxygen permeability.

Copolymers of methyl methacrylate and disiloxane derivatives have been produced by a variety of techniques.²⁻⁶ Recently we discussed the physical, thermodynamic, and morphological characteristics of some of these copolymers.^{7,8} Here we present oxygen transport studies in these copolymers in an effort to understand the increased oxygen permeability of these copolymers over PMMA homopolymers.

EXPERIMENTAL

Monomer Preparation

The silicon-containing monomer, 1,3-bis(methacryloxymethyl)-1,1,3,3-tetramethyldisiloxane (BMTDS), was synthesized via a 3-day, two-step process,

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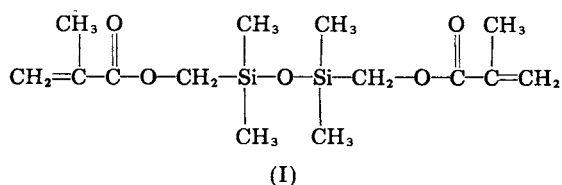
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which has been reported elsewhere.⁷ Briefly, 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane was first prepared by reaction of chloromethyldimethylchlorosilane with water.

In the second step of this preparation procedure 67 g (0.78 mol) methacrylic acid and 2 g hydroquinone were placed in a three-neck flask under a vertical condenser and proper agitation, and heated until refluxing. Sodium methacrylate (37.1 g, 0.34 mol) was added to the stirring refluxing mixture, the rate of addition being slow enough to effect rapid dissolution of the salt. 1,3-Bis(chloromethyl)-1,1,3,3-tetramethyl disiloxane (36.0 g, 0.16 mol) was added dropwise over a period of 1 h, and the entire mixture was refluxed for an additional 3 h. The sodium chloride formed during the reaction was removed via suction filtration, and the filtrate was diluted with an equal volume of benzene. In this solution there were added 200 mL of distilled water, and the two-phase mixture was stirred with gradual addition of sodium bicarbonate (66 g, 0.78 mol). Upon removal of the aqueous layer, the benzene solution was dried overnight over Na_2SO_4 and distilled by vacuum. The fraction with boiling point range 148–150°C/3.3 mm Hg was collected as a yellowish, oily product. Excessive hydroquinone was removed by extraction with a 10% wt aqueous solution of sodium hydroxide until the aqueous layer was colorless. It was not uncommon for the organic phase to emulsify during the extraction; the emulsion was broken after the washing was completed by centrifuging. The product was then dried overnight with anhydrous Na_2SO_4 . The yield of this reaction was 50% (25 g).

The NMR spectral analysis of the silicon-containing monomer was as follows: 0.17 ppm (s, 12H, $-\text{CH}_3$), 1.97 ppm (d, 6H, $\text{C}=\text{C}-\text{CH}_3$), 3.83 ppm (s, 4H, $-\text{CH}_2-$), 5.63 ppm (m, 2H, $-\text{C}=\text{C}-\text{H}$), 6.17 ppm (m, 2 H, $-\text{C}=\text{C}-\text{H}$), suggesting that the product was BMTDS (monomer I):



Copolymer Preparation

Previously distilled methyl methacrylate (MMA) ($\rho_1 = 0.944 \text{ g/cm}^3$) and BMTDS ($\rho_2 = 1 \text{ g/cm}^3$) were added with a syringe to screw-cap plastic vials containing 0.25 wt % of azobis(isobutyronitrile) as initiator. The amounts of MMA and BMTDS used were selected to produce comonomer molar feed ratios, f_1 and f_2 , respectively, covering the whole range of copolymerization. The vials were purged with nitrogen and copolymerization/crosslinking was carried out in a vacuum oven at 49 mm Hg and 60°C for 5 h.

Copolymer cylinders were removed and cut in thin films of diameter 12.70 mm and thickness 0.508 mm using a lathe. The copolymers were hard and transparent. Selected morphological studies and physical properties of these systems are described elsewhere.⁷ Briefly, these copolymers swelled in methylene chloride, chlorobenzene, and ethyl acetate. The glass transition temperature was determined as $122 \pm 2^\circ\text{C}$. Determination of the molecular weight between crosslinks for these highly crosslinked glassy polymers via equilibrium swelling

experiments was not possible due to lack of values of the Flory interaction parameter χ .

Oxygen Transport

An oxygen permeability cell (Oxtran model 100, MoCon Inc., Minneapolis, Minn.) was used to perform transient, one-dimensional diffusion studies. The oxygen flux was determined with a constant current, oxygen-specific detector, with output resistance chosen to provide a simple relationship between the oxygen flux and the output voltage. The oxygen-specific detector operated by combining oxygen, water, and cadmium in an oxidation/reduction reaction with $E_b^0 = 2.40$ V. The measured oxygen flux was independent of carrier gas flow rate as long as the detector efficiency was unaffected.

The carrier gas was a mixture of 3% H₂ and 97% N₂; the hydrogen was necessary to eliminate any O₂ present in this stream, forming water over a platinum catalyst prior to entering the diffusion cell. The carrier gas flow rate was 15 cm³/min for all of the membranes studied, and the relative humidity was maintained at 90%.

The thin copolymer films to be tested were placed between two adhesive-backed stainless steel foil masks, each with a hole diameter of 9.53 mm. The samples were placed in the diffusion cell, and desorbed of oxygen overnight by passing carrier gas over the upstream and downstream sides of the membrane. The oxygen flux curves were acquired by admitting oxygen to the upstream side of the diffusion cell at $t = 0$, and recording the downstream flux of oxygen as a function of time, as well as the oxygen flow rate. All studies were performed at $26 \pm 0.5^\circ\text{C}$. The films were tested at the end of the experiment for pinhole leaks by increasing the flow rate of oxygen, and therefore increasing ΔP_{O_2} across the membrane. A leak was detected simply by a rise in the measured steady state flux of oxygen. Calibration was performed with poly(ethylene terephthalate) films, and a steady state flux of 51.2 ± 0.4 cm³(STP)/m²-day was obtained vs. a literature value of 51.0 cm³(STP)/m²-day.

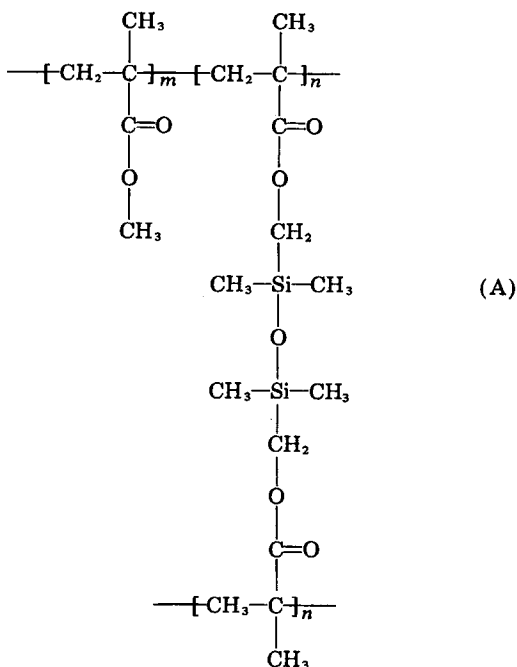
Selected samples of these copolymers were also subjected to sub- T_g annealing at 80°C for 24 h (approximately 42°C below T_g), and tested again for oxygen transport.

RESULTS AND DISCUSSION

Copolymer Structure

In a previous study,⁷ we described some of the thermal, swelling, and morphological characteristics of poly(methyl methacrylate-co-1,3-bis(methacryloxymethyl)-1,1,3,3-tetramethyl disiloxane). These copolymers are indeed crosslinked by short silicon-containing bridges (A) as shown on the following page.

The reaction is similar in nature to typical copolymerization/crosslinking reactions such as reaction of divinyl benzene with styrene¹⁰ or ethyleneglycol dimethacrylate with 2-hydroxyethyl methacrylate.¹ The extent of crosslinking is controlled by the comonomer feed ratio. In general, copolymers with f_2 greater



than 0.2 are highly crosslinked and swell in methylene chloride, ethyl acetate, or chlorobenzene without formation of crazes.

The mole fraction of BMTDS in the final copolymers, F_2 , was determined by elemental analysis of Si, and results for at least six samples of each copolymer composition are shown in Table I. Although there was a difference in the method of copolymerization of these systems versus that of the studies of Yang and Peppas,⁷ the values of F_2 are very similar. Calculation of the reactivity ratios for this system was not undertaken, since the reactions were carried to high extent of reaction. However, Merker and Scott³ have reported $r_1 = 0.93$ and $r_2 = 1.13$ with $r_1 r_2 = 1.05$ for copolymerization of MMA with the structurally similar methacryloxymethyl pentamethyl disiloxane. All samples with $0.09 < F_2 < 0.48$ had glass transition temperatures T_g of $122 \pm 2^\circ\text{C}$.

Oxygen Transport

The transient oxygen transmission study had a threefold purpose: (i) to de-

TABLE I
Analysis of Copolymers of BMTDS and MMA

Feed mole fraction of BMTDS, f_2	Copolymer mole fraction of BMTDS, F_2
0.10	0.09 \pm 0.01
0.20	0.15 \pm 0.02
0.30	0.18 \pm 0.01
0.40	0.32 \pm 0.02
0.50	0.41 \pm 0.01
0.60	0.55 \pm 0.01

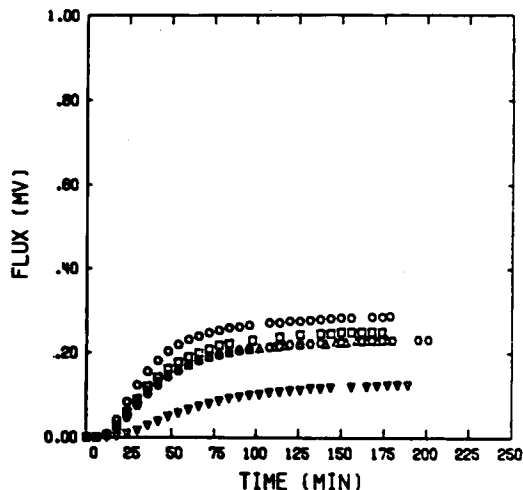


Fig. 1. Transient oxygen transport curves for some copolymers of MMA and BMTDS before annealing. Temperature $26 \pm 0.5^\circ\text{C}$; thickness $L = 0.508$ mm. Composition of samples: (∇) $F_2 = 0.09$; (\circ) $F_2 = 0.15$; (Δ) $F_2 = 0.18$; (\square) $F_2 = 0.42$; (\circ) $F_2 = 0.55$.

termine the effect of silicon content on the oxygen diffusion coefficient and on the steady state oxygen flux; (ii) to determine the effect of sub- T_g annealing on the diffusion coefficient and on the steady state oxygen flux; and (iii) to assess the validity of a Fickian diffusion model for this system.

The results of transient oxygen transport experiments through several copolymers of varying composition are presented in Figures 1 and 2. Figure 1 presents data for films of thickness 0.0508 cm and F_2 varying from 0.09 to 0.55 prior to any annealing process. Figure 2 shows data for the same films after annealing at 80°C for 24 h. All results are given in terms of electrical signal (mV) and can be converted through the conversion factor $1 \text{ mV} = 2020.9 \text{ cm}^3(\text{STP})/\text{m}^2\text{-day}$.

The transient oxygen transmission curves were analyzed by the moment technique introduced by Felder¹¹ to calculate the time lag θ . Provided that the downstream surface concentration is negligible compared to the upstream concentration, as it is the case here, this method requires a normalization of the experimental flux curve of differential permeation studies and subsequent integration employing the following expression:

$$\theta = \lim_{t \rightarrow \infty} \int_0^t \left[1 - \frac{\phi(t)}{\phi(\infty)} \right] dt \quad (1)$$

Here $\phi(t)$ is the flux at time t and $\phi(\infty)$ is the steady state flux. The construction of the permeation cell is such that chamber delay times are minimal and do not affect the calculation of θ .

Equation (1) was evaluated using a second-order numerical integration scheme, allowing the calculation of the diffusion coefficient for a specific penetrant-copolymer system by use of

$$D = L^2/6\theta \quad (2)$$

The results of this analysis are illustrated in Table II. The experimental error

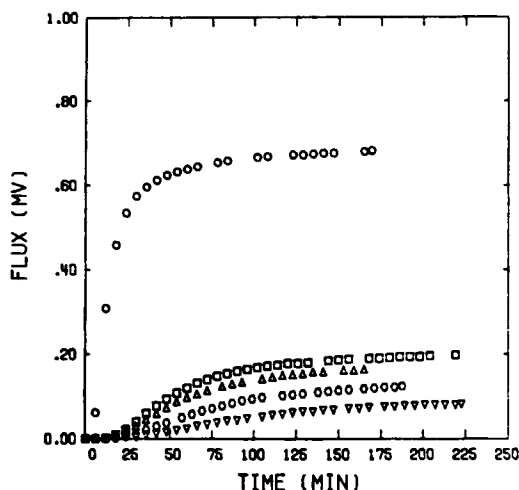


Fig. 2. Transient oxygen transport curves for some copolymers of MMA and BMTDS after annealing at 80°C for 24 h. Sample $F_2 = 0.55$ had thickness $L = 0.254$ mm. All sample compositions as in Figure 1.

associated with this analysis (see the Appendix) is also reported in Table II. The same table includes also data for a pure poly(methyl methacrylate) sample produced by the same preparation technique.

Within experimental error, the calculated diffusion coefficients are equivalent and, therefore, independent of copolymer silicon content. Closer inspection of these two figures indicates that annealing causes a reduction in the diffusion coefficient for a constant F_2 value. Given the magnitude of the relative error in this calculation, one might find this conclusion unfounded; however, for each F_2 value this result is retained, an outcome which is highly unlikely under these circumstances unless the effect is in fact present. Chen¹² has found similar results for methane and propane diffusion into poly(methyl methacrylate), poly(ethylene terephthalate), and polycarbonate.

A plausible explanation regarding the independence of the diffusion coefficient on F_2 is related to the combined effects of increased crosslinking density with increased F_2 , and increased chain flexibility with increased silicon content. The

TABLE II
Transport Properties of Tested Copolymers

Copolymer mole fraction of BMTDS, F_2	Oxygen diffusion coefficient $D \times 10^{+7}$ (cm ² /s)		Oxygen permeation rate at steady state [cm ³ (STP)/m ² -day]	
	Before annealing	After annealing	Before annealing	After annealing
0	0.15 ± 0.30	0.10 ± 0.20	8.1	2.7
0.09 ± 0.01	1.30 ± 0.40	0.80 ± 0.30	260	160
0.15 ± 0.02	1.45 ± 0.40	1.05 ± 0.35	470	250
0.18 ± 0.01	1.50 ± 0.40	1.15 ± 0.35	470	330
0.32 ± 0.02	1.50 ± 0.20	1.20 ± 0.30	500	360
0.41 ± 0.01	1.70 ± 0.40	1.30 ± 0.30	510	400
0.55 ± 0.01	1.90 ± 0.20	1.35 ± 0.25	1070	960

reduction in the diffusion coefficient upon annealing is not as well understood. Quite possibly during annealing (a process which removes most of the internal stresses), a densification of the copolymer occurs by collapsing void volume formed in the polymerization reaction; this void volume is generated by vaporization of methyl methacrylate and through poor polymer chain "packing" from steric strain produced during the polymerization. This concept of void volume removal could account for the observed trend.

The results of the steady state oxygen permeation rate analysis show that the steady state oxygen flux increases with increasing silicon content and decreases upon annealing for constant F_2 (see Table II). This last observation is in agreement with the effect of annealing on the calculated diffusion coefficient.

It is interesting to note that these oxygen transmission rates are slightly higher but of the same order of magnitude as those reported earlier for poly(dimethyl siloxane)-polycarbonate copolymer membranes, widely used for gas separation applications.¹³ Unusually high values of the permeability for glassy polymers have been observed with other silicon-based polymers. For example, Volkov et al.¹⁴ present data for poly(vinyltrimethylsilane) which has a T_g of 170°C. The increase in oxygen flux with silicon content is believed to follow from a parallel increase in oxygen solubility with F_2 . This notion is supported by the data of Stannett and Williams¹⁵ and Yasuda and Rosengren,¹⁶ who have found the solubility of oxygen in poly(ethyl methacrylate) to be $8.6 \times 10^{-2} \text{ cm}^3 \text{ (STP)/cm}^3 \cdot \text{atm}$, while that for vulcanized poly(dimethylsiloxane) containing 10% filler was $31.1 \times 10^{-2} \text{ cm}^3 \text{ (STP)/cm}^3 \cdot \text{atm}$.

It was tacitly assumed in the diffusion coefficients calculation that the oxygen mass transfer was governed by Fick's law. To determine if this assumption is relevant, a selected set of experimental flux curves were compared with the theoretically predicted flux curves (see, e.g., Figs. 3 and 4). The theoretical

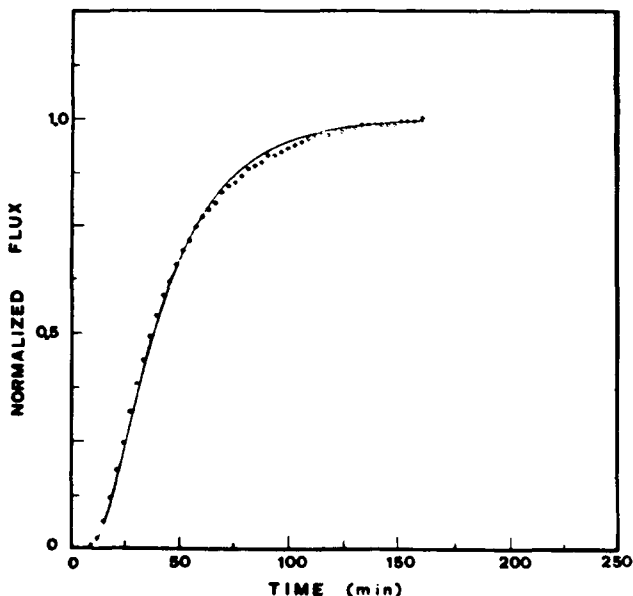


Fig. 3. Comparison of experimental results and theoretical prediction of Fickian normalized oxygen flux curves for the copolymer sample with $F_2 = 0.42$ (prior to annealing).

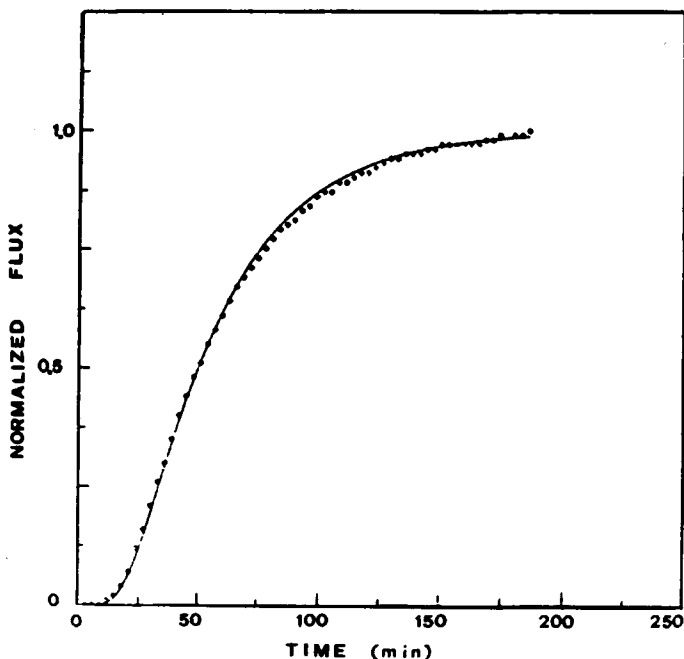


Fig. 4. Comparison of experimental results and theoretical prediction of Fickian normalized oxygen flux curves for the copolymer sample with $F_2 = 0.42$ (after annealing at 80°C for 24 h).

curves were obtained from a solution to Fick's second law derived by Daynes,¹⁷ assuming a constant diffusion coefficient and constant boundary conditions; this solution is presented as follows:

$$\frac{\phi(t)}{\phi(\infty)} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2\pi^2Dt}{L^2}\right) \quad (3)$$

Except for the data for $F_2 = 0.55$, the experimental curves are fitted well with the theoretical curves, confirming the assumption made earlier. Figure 5 ($F_2 = 0.55$) shows a plot which is adequately predicted over the initial portion of the diffusion process, but the predicted and experimental curves diverge during the approach to steady state. This type of behavior is characteristic of diffusion controlled over longer times by the polymer relaxational phenomenon. In an attempt to incorporate this effect into the diffusion model, an additional term corresponding to a first-order relaxation process was included in eq. (3) after Hopfenberg,¹⁸ and a nonlinear regression analysis of the normalized data was performed. The expression used to model this behavior is as follows:

$$\frac{\phi(t)}{\phi(\infty)} = 1 + 2 \cdot B(1) \sum_{n=1}^4 (-1)^n \exp\left(\frac{-n^2\pi^2Dt}{L^2}\right) + B(2) \exp[-B(3) \cdot t] \quad (4)$$

where the $B(i)$ are the regression coefficients. The regression analysis revealed a better statistical fit of the data was obtained with eq. (3) alone [i.e., $B(2) = 0.0$], a further indication that the mass transfer follows Fickian type behavior.

CONCLUSIONS

An oxygen diffusion study of a crosslinked, glassy copolymer containing varied

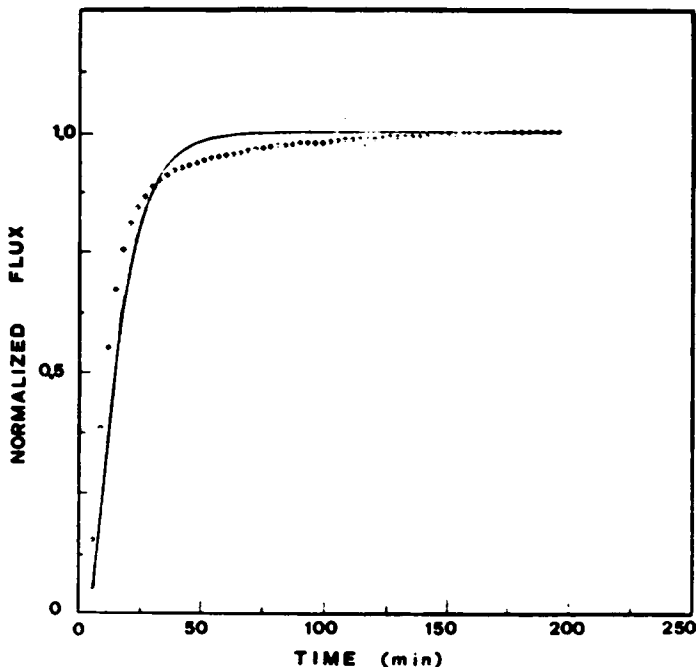


Fig. 5. Comparison of experimental results and theoretical prediction of Fickian normalized oxygen flux curves for the copolymer sample with $F_2 = 0.55$ (prior to annealing).

amounts of two constituents, methyl methacrylate and 1,3-bis(methacryloxy-methyl)-1,1,3,3-tetramethyldisiloxane, was performed. The effects of sub- T_g annealing and increasing silicon content upon the oxygen diffusion coefficient and steady state oxygen permeation rate were analyzed. The experimental results revealed an enhancement of the steady state oxygen flux with an increase in the copolymers over that for pure poly(methyl methacrylate). The calculated diffusion coefficients were found to be independent of silicon content, within experimental error, and the annealing process brought about a significant reduction in both the oxygen diffusion coefficient and steady state flux. Finally, the experimental oxygen permeation curves were theoretically predicted assuming a Fickian model with constant diffusion coefficient and constant boundary conditions.

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APPENDIX: ERROR ANALYSIS OF THE DIFFUSION COEFFICIENT

The diffusion coefficient is calculated with the following expression:

$$D = L^2/6\theta \quad (5)$$

where L is the thickness of the membrane and the error in this measurement, ϵ_L , is $25.4 \mu\text{m}$. The time lag θ in the previous expression is given by

$$\theta = \lim_{t \rightarrow \infty} \int_0^t \left[1 - \frac{\phi(t)}{\phi(\infty)} \right] dt \quad (6)$$

The time lag is calculated numerically using a second-order technique:

$$\theta = \sum_i \alpha_i \left[1 - \frac{\phi_i(t)}{\phi(\infty)} \right] \quad (7)$$

where α_i is the increment of the abscissa (i.e., $\alpha_i = t_i - t_{i-1}$). The error associated with the calculation of the time lag, ϵ_θ , is as follows:

$$\epsilon_\theta = \left[\frac{1}{\phi(\infty)} \sum_i \alpha_i \phi_i(t) \right] \quad (8)$$

Assuming the error in the individual measurements, $\phi_i(t)$, to be normally distributed with mean zero and standard deviation s , i.e.,

$$\epsilon(\phi_i) \sim N(0,s) \quad (9)$$

it can be shown from statistical arguments that

$$\epsilon(\theta) \sim N\left(0, s \left(\sum_i \alpha_i \right)^{1/2}\right) \quad (10)$$

Defining the relative error of X to be $\text{RE}(X)$,

$$\text{RE} \left(\sum_i \alpha_i \phi_i(t) \right) = \frac{\alpha \sqrt{N} \epsilon(\phi_i(t))}{\sum_i \alpha_i \phi_i(t)} \quad (11)$$

then

$$\ln \left[1 + \text{RE} \left(\frac{1}{\phi(\infty)} \sum_i \alpha_i \phi_i(t) \right) \right] = \ln[1 + \text{RE}(\phi(\infty))] + \ln[1 + \text{RE}(\sum_i \alpha_i \phi_i(t))] \quad (12)$$

Therefore,

$$\text{RE}(\theta) = \left[\frac{1}{\phi(\infty)} \sum_i \alpha_i \phi_i(t) \right] \cdot \text{RE} \left(\frac{1}{\phi(\infty)} \sum_i \alpha_i \phi_i(t) \right) / \theta \quad (13)$$

The relative error in the diffusion coefficient, $\text{RE}(D)$, may now be obtained as

$$\ln[1 + \text{RE}(D)] = 2 \ln[1 + \text{RE}(L)] + \ln[1 + \text{RE}(\theta)] \quad (14)$$

The increment α is equal to 3 min, while N , $\phi(\infty)$, and L vary for each individual experiment. The error in the individual measurements, $\phi_i(t)$, is 0.01 mV.

References

1. N. A. Peppas, in *Extended Wear Contact Lenses*, J. Hartstein, Ed., Mosby, St. Louis, 1982, p. 6.
2. R. L. Merker and J. E. Noll, *J. Org. Chem.*, **21**, 1537 (1956).
3. R. L. Merker and M. J. Scott, *J. Polym. Sci.*, **25**, 115 (1957).
4. K. A. Andrianov, N. S. Leznov and A. K. Dabagova, *Izv. Akad. Nauk. SSSR, Otdel. Khim. Nauk*, 459 (1957).
5. L. A. Grigoreva and V. O. Reikhsfel'd, *Vysokomol. Soed.*, **A6**, 988 (1964).
6. N. G. Gaylord, U.S. Pat. 3,808,178 (1974).
7. W. H. M. Yang and N. A. Peppas, *Polym. Bull.*, **9**, 255 (1983).
8. N. A. Peppas, M. W. H. Yang, and S. J. Napp, *Polym. Prepr.*, **24**(1), 5 (1983).
9. W. H. Yang, V. F. Smolen, and N. A. Peppas, *J. Membr. Sci.*, **9**, 53 (1981).
10. G. J. Howard and C. A. Midgley, *J. Appl. Polym. Sci.*, **26**, 3845 (1981).
11. R. M. Felder, *J. Membr. Sci.*, **3**, 15 (1978).
12. S. P. Chen, *Polym. Prepr.*, **15**, 77 (1974).
13. W. J. Ward III, W. R. Browall, and R. M. Saleme, *J. Membr. Sci.*, **1**, 99 (1976).
14. V. V. Volkov, N. S. Nametkin, E. G. Novitskii, and S. G. Durgaryan, *Vysokomol. Soyed.*, **A21**, 920 (1979).
15. V. T. Stannett and J. L. Williams, *J. Polym. Sci.*, **C10**, 45 (1966).
16. H. Yasuda and K. Rosengren, *J. Appl. Polym. Sci.*, **11**, 2839 (1970).

17. H. A. Daynes, *Proc. Roy. Soc. London*, **A97**, 286 (1920).
18. H. B. Hopfenberg, *J. Membr. Sci.*, **3**, 215 (1978).

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