

Synthesis and polymerization of acrylic monomers with hydrophilic long side groups. Oxygen transport through water swollen membranes prepared from these polymers

J. Guzmán*, M. T. Iglesias and E. Riande

Instituto de Ciencia y Tecnología de Polímeros (CSIC), 28006-Madrid, Spain

and V. Compañ and A. Andrio

Departamento de Física, Universidad Jaume I, Castellón, Spain

(Received 24 June 1996; revised 9 January 1997)

The synthesis and characterization of tetraethyleneglycol acrylate (TTEGA) and tetraethyleneglycol diacrylate are described. Radical polymerization reactions of TTEGA were carried out at different temperatures and the curves of conversion against time, obtained by using dilatometric techniques, allowed the determination of $k_p/k_t^{1/2}$, where k_p and k_t are, respectively, the propagation and termination rate constants. The values found for this ratio were comparatively much higher than those reported in the literature for other acrylic monomers. The polymer, poly(tetraethyleneglycol acrylate), is soluble in water, exhibits low glass transition temperature (-45°C) and the percentage of syndiotactic dyads in the chains lies in the vicinity of $65 \pm 5\%$, a value normally found in similar polymers. Both poly(tetraethyleneglycol acrylate-*co*-tetraethyleneglycol diacrylate) and poly(triethyleneglycol acrylate-*co*-triethyleneglycol diacrylate) membranes were prepared by radical polymerization of the corresponding monomers and a small quantity of diacrylic esters. Electrochemical techniques were used to evaluate oxygen transport through these membranes swollen in water. The apparent values of both the permeability and diffusion coefficients are unusually large as a consequence of a high swelling degree of these membranes. Although the solubility coefficient of oxygen in the swollen hydrogels is larger than in water, restrictions in the diffusion path caused by the polymer matrix decrease the diffusion coefficient of the gas to ca one-third of its value in water.
 © 1997 Elsevier Science Ltd.

(Keywords: hydrophilic polymers; oxygen permeability; hydrogel membranes)

INTRODUCTION

Water insoluble hydrophilic polymers, like poly(2-hydroxyethyl methacrylate), are especially suitable for many scientific, biomedical and pharmaceutical applications^{1–5}, such as soft contact lenses, dental materials, optical lenses, materials for encapsulated cells and carriers for controlled drug delivery, whereas water soluble polymers are of great interest for the preparation of superabsorbent hydrogels⁶ with potential applications in agriculture and medicine. Many studies have been reported on the properties of polymers containing hydrophilic groups rigidly attached either to the backbone or to lateral chains, though most of them were performed on polymers prepared from high purity commercial monomers. It is interesting to extend these studies to the synthesis and polymerization of new hydrophilic monomers with the aim of obtaining a better knowledge of the relationship between structure and properties in hydrogels.

Pursuing the objective of preparing hydrosoluble and water-swollen hydrophilic polymers, experimental work

is being done in our laboratories related to the synthesis and characterization of different monomers with either hydroxyl or amino groups in their structure. In this way, the chemical and kinetic aspects of the synthesis of polymers containing hydroxyl groups in the side groups have already been reported^{7–10}. These studies were further extended to the synthesis of water soluble polymers with polar long side groups in their structure¹¹, such as poly(triethyleneglycol acrylate) (PTEGA). In order to obtain more complete information on how the length of the hydrophilic side group of acrylic monomers may affect their polymerization kinetics and the properties of the resulting polymer, the synthesis and polymerization of tetraethyleneglycol acrylate (TTEGA) was undertaken. Another objective of this work was the development of hydrophilic membranes with the potential capability to be used as contact lenses and, for that purpose, membranes of this kind were prepared by radical polymerization of triethyleneglycol acrylate and TTEGA in the presence of crosslinking agents of the same chemical nature as the monofunctional monomers. Thus, new membranes of poly(triethyleneglycol acrylate-*co*-triethyleneglycol diacrylate) and

* To whom correspondence should be addressed

poly(tetraethyleneglycol acrylate-co-tetraethyleneglycol diacrylate) were obtained and their permeability to oxygen in an aqueous medium was studied.

EXPERIMENTAL

Materials

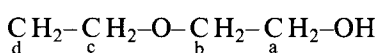
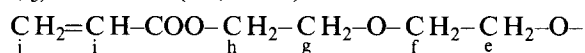
Both triethyleneglycol and tetraethyleneglycol were dried by azeotropic removal of water from a solution of these compounds in benzene. Benzene and dioxane (Merck) were purified by conventional methods whereas acryloyl chloride (Fluka) and triethylamine were used as received. 2,2'-Azobisisobutyronitrile (AIBN) were purified by crystallization from methanol and dried under high vacuum at room temperature.

Synthesis of the acrylic esters of triethyleneglycol and tetraethyleneglycol

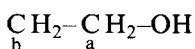
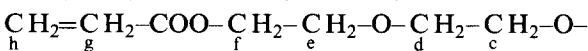
Mixtures of TTEGA (or triethyleneglycol acrylate) and tetraethylene glycol diacrylate (or triethyleneglycol diacrylate) were obtained at 20°C by reaction between tetraethyleneglycol (or triethyleneglycol) and acryloyl chloride in benzene solution and under nitrogen atmosphere, using triethylamine as absorbent of the hydrogen chloride evolved during the reaction. In order to obtain a larger fraction of the monofunctional monomer and an adequate yield, the molar ratio glycol/acid chloride used^{7,8} was 7/3. Acryloyl chloride was slowly added to the mixture for 2 h and the reaction proceeded for a further 10 h, the triethylammonium chloride formed being removed by filtration. The reaction medium was washed several times with distilled water to remove both most of the monofunctional monomer formed during the reaction process and the unreacted glycol. The monoacrylate monomer was then extracted from the aqueous phase with chloroform whereas the diacrylate monomer was isolated from the benzene solution. Finally, both monomers were purified by flash chromatography using a column of silica gel 60 (230–400 mesh ASTM).

Characterization of the monomer

The acrylate esters were characterized by ¹³C nuclear magnetic resonance (n.m.r.) spectroscopy. The resonance spectra were registered with a Varian XL-300 operating at 75.4 MHz, using deuterated chloroform as solvent and tetramethylsilane as internal reference. The ¹³C spectrum of the monoesters showed the absence of the resonance signals corresponding to the diacrylate esters, thus indicating their purity; δ for TTEGA (¹³C, CDCl₃): 61.4 (1C, a), 63.4 (1C, h), 68.9 (1C, g), 70.1–70.42 (4C, c,d,e,f), 72.42 (1C, b), 128.07 (1C, i), 130.8 (1C, j) and 165.9 (1C, C=O).



The glycol residue of the diacrylate ester showed only three signals at 63.5, 68.97 and 70.5 ppm assigned to the carbons h, g and f + e, respectively; δ for triethyleneglycol acrylate (¹³C, CDCl₃): 61.4 (1C, a), 63.4 (1C, f), 68.9 (1C, e), 70.1–70.4 (2C, c,d), 72.39 (1C, b), 128.01 (1C, g), 130.95 (1C, h) and 165.99 (1C, C=O).



The glycol residue of the triethyleneglycol diacrylate showed only three signals at 63.5, 69.1 and 70.5 ppm assigned to the carbons f, e and d, respectively.

Polymerization of TTEGA

The polymerization kinetics of triethyleneglycol acrylate has already been reported¹¹. The polymerization of TTEGA was carried out in dioxane solution at several temperatures between 50 and 65°C, using AIBN as initiator. The progress of the polymerization at each temperature of interest was measured with a double branch dilatometer of 6 ml volume and 1.036 mm capillary diameter. The polymer, PTTEGA, was isolated from the reaction medium by several precipitations in n-hexane and finally was dried in high vacuum at 80°C.

Characterization of the polymer

The characterization of PTTEGA was performed by ¹H and ¹³C n.m.r. spectroscopy. The spectra obtained with a Varian XL-300 spectrometer, using deuterated chloroform as solvent and tetramethylsilane as internal standard, showed the purity of the polymer. The stereochemical composition of the polymer was determined by ¹³C n.m.r. spectroscopy. The stereoregularity of acrylic polymers^{12–16} is more difficult to measure than that of methacrylic chains due to the fact that the chemical shifts of the carbons and protons in acrylics are only slightly influenced by the stereochemical configuration of nearby units. In this sense, only the carbonyl carbons of the side chain and the methine carbons of the main chain give signals which suggest a tacticity effect. In particular, the peaks corresponding to the C=O carbons show a complicated spectral pattern with overlapping of almost all the signals. Nevertheless, by deconvolution of the different peaks, the signals were separated and the tacticity of the polymers calculated, obtaining values for the isotactic diads in the region of 0.35 ± 0.05. The ¹³C n.m.r. spectrum of PTTEGA with the corresponding assignment of the resonance signals is shown in Figure 1.

As a consequence of the relatively large number of oxyethylene units in the side groups, PTTEGA is soluble in water. The glass transition temperature of the dried polymer, determined with a Perkin Elmer DSC8 calorimeter at a heating rate of 10°C min⁻¹, was

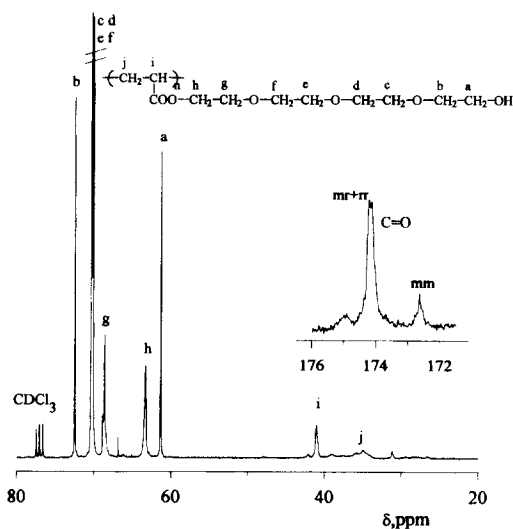


Figure 1 ¹³C (¹H) n.m.r. spectra of PTTEGA

Table 1 Characteristics of the polymer networks

Polymer	T_g (°C)	% Cross-linking Agent	w
PTEGA	-48	2	0.70
PTTEGA	-45	1	0.77

-45°C. The comparison with other acrylic polymers with short pendent chains such as poly(methyl acrylate), poly(ethyl acrylate)¹⁷ and poly(3-hydroxyneopentyl acrylate)⁷ shows, as expected, that the glass transition temperature of PTTEGA is lower than those of the other polymers due to the higher flexibility of its pendent chain. However, the T_g of PTTEGA is similar to that of poly(triethyleneglycol acrylate) (PTEGA)¹¹, indicating that the presence of one additional oxyethylene unit does not change the glass transition temperature of the polymer.

Preparation of the membranes

Membranes of PTEGA/PTTEGA were obtained at 50°C by radical polymerization of triethylene/tetraethyleneglycol acrylates, using 1% of triethyleneglycol/tetraethyleneglycol diacrylates as crosslinking agents and AIBN as initiator. The polymerization was carried out in a Teflon mould under nitrogen atmosphere.

Permeation measurements

Prior to the measurements, PTEGA and PTTEGA membranes were swollen in water until equilibrium attained in approximately 30 min. The water weight fractions (w) in the swollen networks were 0.70 and 0.77 for PTEGA and PTTEGA, respectively, corresponding to swelling degrees of 233 and 348%, respectively. Some characteristics of the membranes prepared with these polymers are shown in *Table 1*. The diffusional characteristics of the membranes were determined utilizing the experimental assembly commonly used to measure the permeability of oxygen through contact lenses. It comprises a permeometer model 201T (Rheder Development Co.) in which the polarographic cell is a solid cylindrical cathode of 24 carat gold (4.25 mm diameter and 6 mm long). The anode is a silver hollow cylinder 7 mm long, the inner and outer diameters being 5 and 10 mm, respectively. A thermistor is installed into the anode to monitor the temperature of the cell and the membrane. The temperature was controlled by a thermostat bath of water, which was adjusted so as not to permit changes in this parameter higher than 0.1°C. More details and a sketch of the experimental assembly are given elsewhere¹⁸.

RESULTS AND DISCUSSION

Kinetics of polymerization

By assuming that the decomposition of the initiator is a first order reaction, the rate of radical initiated polymerization can be written as

$$-\frac{dM}{dt} = k_p \left(\frac{2fk_d[I_0]}{k_t} \right)^{1/2} [M] \exp\left(\frac{-k_d t}{2}\right) \quad (1)$$

where k_d , k_p and k_t are the rate constants for initiator decomposition, propagation and termination reactions, respectively, $[M]$ is the instantaneous concentration of

monomer, $[I_0]$ is the initial concentration of initiator, and f is the efficiency of the initiator. Moreover, in the development of equation (1) both depropagation reactions and the thermal polymerization are assumed to be negligible. Integration of equation (1) gives

$$\ln \frac{[M_0]}{[M]} = 2k_p \left(\frac{2f[I_0]}{k_t k_d} \right)^{1/2} \left[1 - \exp\left(\frac{-k_d t}{2}\right) \right] \quad (2)$$

In dilatometric experiments it is useful to transform equation (2) into

$$-\ln \left[\left(1 - \frac{\Delta h}{\Delta h_{100}} \right) \frac{V_0}{V_0 - \Delta V} \right] = 2k_p \left(\frac{2f[I_0]}{k_t k_d} \right)^{1/2} \times \left[1 - \exp\left(\frac{-k_d t}{2}\right) \right] \quad (3)$$

which can also be expressed in a more convenient form by

$$\Delta h = \Delta h_{100} \left\{ 1 - \frac{V_0 - \Delta V}{V_0} \exp \left\{ -2k_p \left(\frac{2f[I_0]}{k_t k_d} \right)^{1/2} \times \left[1 - \exp\left(\frac{-k_d t}{2}\right) \right] \right\} \right\} \quad (4)$$

where Δh and Δh_{100} are the changes of dilatometric height at time t and at 100% of conversion, respectively, V_0 is the initial volume of monomer and solvent in the dilatometer, and ΔV is the change of volume at time t .

Values of $k_p/k_t^{1/2}$ and Δh_{100} were obtained from the dilatometric measurements by a non-linear least squares procedure described in detail elsewhere^{7,8}. The values of k_d were taken from the literature^{19,20}. Curves showing the time dependence of conversion are given in *Figure 2*. From semi-logarithmic plots of the conversion against $1 - \exp(k_d t/2)$ straight lines were obtained whose slopes ($= 2k_p(2f[I_0]/k_t k_d)^{1/2}$) allowed the determination of $k_p/k_t^{1/2}$. Results for this ratio at different temperatures, calculated by assuming that $f = 0.6$, are given in *Table 2*. It is noteworthy that the results shown in this table for $k_p/k_t^{1/2}$ are much higher than those reported for other acrylates^{8,13,17}, particularly triethyleneglycol acrylate (TEGA)¹¹, a monomer that shows great similarity to TTEGA. In most monomers and at the temperatures used in this work, $k_p/k_t^{1/2}$ lies in the interval²¹ 0.1–1, the highest values being obtained for acrylic monomers. Even assuming $f = 1$ instead of 0.6 in equation (3), the values of $k_p/k_t^{1/2}$ are only reduced by a factor of about 1.3, so that the differences with similar monomers still remain significantly large. To elucidate the cause of this apparent inconsistency would require one to measure the absolute rate constants of TEGA and TTEGA.

The temperature dependence of the ratio $k_p/k_t^{1/2}$ may

Table 2 Kinetic constants for the polymerization of TTEGA in 1,4-dioxane. $[M_0] = 0.57 \text{ mol l}^{-1}$; $[I_0] = 5.6 \times 10^{-3} \text{ mol l}^{-1}$

T (°C)	$k_p/k_t^{1/2}$ ($l^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$)
50	1.10
55	1.20
60	1.24
65	1.46

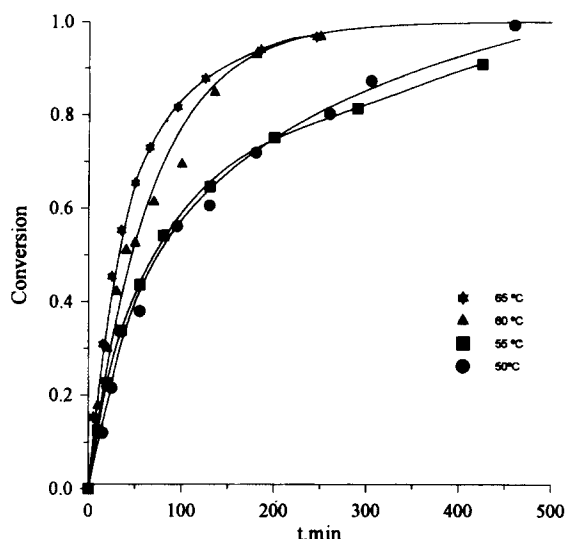


Figure 2 Variation of conversion with time for the polymerization of TTEGA in 1,4-dioxane at several temperatures

be expressed in terms of the Arrhenius equation by

$$\frac{k_p}{k_t^{1/2}} = A \exp\left(-\frac{\Delta E^\ddagger}{RT}\right) \quad (5)$$

where A is a combination of the frequency factors for the two rate constants; $\Delta E^\ddagger = \Delta E_p^\ddagger - \Delta E_t^\ddagger/2$, ΔE_p^\ddagger and ΔE_t^\ddagger are, respectively, the activation energies of propagation and termination, T the absolute temperature, and R the gas constant. By using the values of $k_p/k_t^{1/2}$ shown in Table 2 an Arrhenius fit for the polymerization of TTEGA in dioxane is obtained (Figure 3). The straight line allows the determination of the activation energy for the polymerization of this monomer under the conditions described in the experimental part; the value was $3.8 \text{ kcal mol}^{-1}$.

Oxygen permeation through swollen PTEGA and PTTEGA membranes

In the apparatus used in this study, the oxygen permeates from one side of the membrane where the partial pressure of the gas is kept constant ($p = p_0 = 155 \text{ mm Hg}$) to the other side facing the cathode of the polarographic cell where the partial pressure is $p_L \cong 0$. Under steady state conditions the transport of gas in the membrane involves the motion of the molecules of oxygen with velocity u_x under the driving force of the gradient of chemical potential, $\partial\mu/\partial x$, against the resistance of the matrix defined by the friction coefficient ζ . The flux at the position x ($0 \leq x \leq l$), (where l is the thickness of the membrane), can be written as

$$J_x = cu_x = -\frac{c}{\zeta} \frac{\partial\mu}{\partial x} = -D \frac{\partial \ln c}{\partial x} \quad (6)$$

where at low concentrations the chemical potential is given by

$$\mu = \mu_0 + RT \ln a \cong \mu_0 + RT \ln c \quad (7)$$

The gas concentration at a point x in the membrane, $c(x)$, is at equilibrium with its partial pressure at the same point, $p(x)$, and both magnitudes are related by Henry's law, i.e. $c(x) = Sp(x)$, where S is the gas solubility coefficient in the membrane. Consequently the flux of gas can be written as

$$J_x = -\frac{RT}{\zeta} \frac{\partial p}{\partial x} = -DS \frac{\partial p}{\partial x} = -P \frac{\partial p}{\partial x} \quad (8)$$

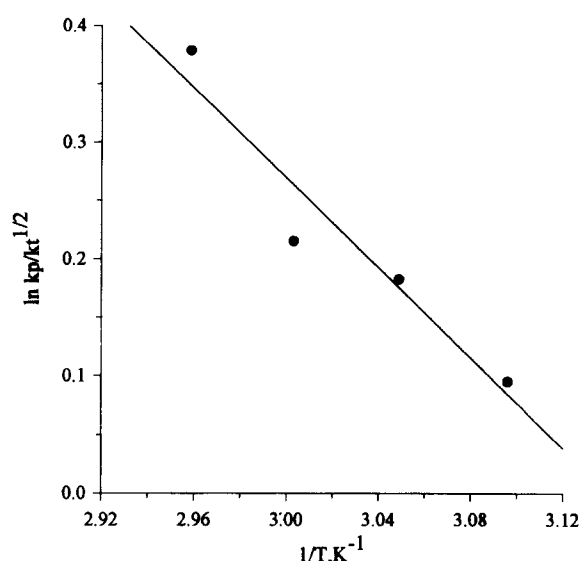
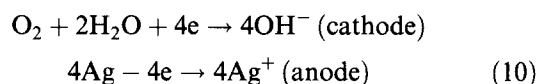


Figure 3 Arrhenius plot for the polymerization of TTEGA in 1,4-dioxane

where $P(= DS)$ and $D(= RT/\zeta)$ are, respectively, the permeability coefficient and the diffusion coefficient. Integration of this equation gives

$$J_x = P \frac{p_0 - p_L}{L} \cong P \frac{p_0}{L} \quad (9)$$

where the pressure at the side of the membrane facing the electrodes is considered to be negligible. The transport of oxygen through the swollen membranes was monitored by the following electrochemical reactions taking place at the electrodes:



Equations (9) and (10) indicate that once steady state conditions are reached, the intensity of current necessary to reduce the oxygen diffusing through the membranes can be written as

$$I(t \rightarrow \infty) = -nFAJ_x = nFAP \frac{p_0}{L} \quad (11)$$

where A is the area of the membrane (area of the cathode = $14.24 \pm 0.13 \times 10^{-2} \text{ cm}^2$), F is Faraday's constant ($= 96490 \text{ C mol}^{-1}$) and $n(= 4)$ is the number of electrons transferred from the anode to the cathode to reduce each molecule of oxygen.

Under non-steady state conditions, gas transport across the membranes is governed by Fick's second law:

$$\frac{\partial p(x, t)}{\partial t} = D \frac{\partial^2 p(x, t)}{\partial x^2} \quad (12)$$

By using the boundary conditions,

$$\begin{aligned} p(x = -0, t < 0) &= 0 & p(x = L, t < 0) &= 0 \\ p(x = 0, t \geq 0) &= p_0 & p(x = L, t \geq 0) &= p_L \cong 0 \end{aligned} \quad (13)$$

(the solution of equation (12) in terms of current intensities gives^{18,22,23})

$$\frac{I(t)}{I(t \rightarrow \infty)} = 1 - \exp\left(-\frac{6Dt}{L^2}\right) \quad (14)$$

By measuring $I(t)$ as a function of time, the values of both the permeability and diffusion coefficients can be

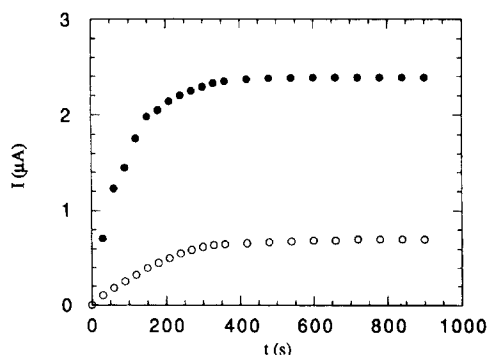


Figure 4 Dependence of the current intensity on time at 25°C for (●) PTTEGA and (○) PTEGA

Table 3 Values of the asymptotic current $I(t \rightarrow \infty)$, permeability (P) and diffusion coefficients (D) at different temperatures for PTTEGA

$T(^{\circ}\text{C})$	$I(t \rightarrow \infty) (\mu\text{A})$	P (barrers)	$10^6 \times D$ ($\text{cm}^2 \text{s}^{-1}$)
20	2.19	46.42	9.30
25	2.39	50.66	11.50
30	2.58	54.68	15.10
35	2.66	56.38	15.90
40	2.73	57.86	16.70
45	2.78	58.92	16.90
50	2.85	60.41	17.30

1 barrer = $10^{-10} \text{ cm}^3 \text{ O}_2$ (STP) $\text{cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}$

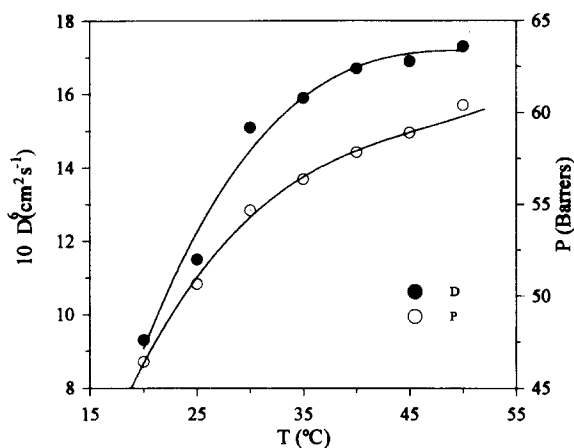


Figure 5 Influence of the temperature on the diffusion and permeability coefficients for PTTEGA

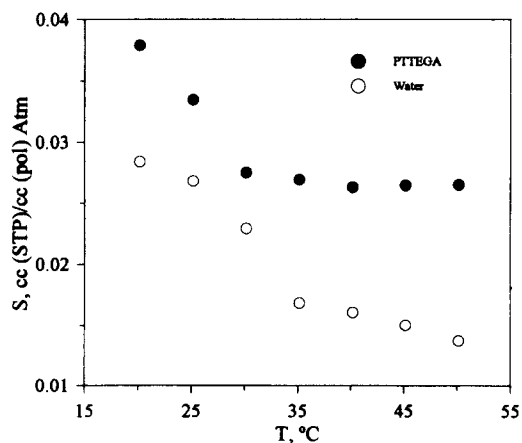


Figure 6 Solubility coefficients of oxygen for the PTTEGA hydrogel and pure water

readily determined, respectively, by means of equation (11) and from the slope ($6D/L^2$) of the plots $\ln[I_{\infty}-I(t)/I_{\infty}]$ against t , as equation (14) suggests. It should be pointed out, however, that, as a consequence of the liquid-membrane interfaces, the partial pressure difference between the two faces of the membrane could differ slightly from $p_0 - p_L$. On the other hand, the diffusion resistance of the solution layer separating the membrane from the electrode has not been considered, so that the permeation measurements embody the assembly comprising the membrane and the thin solution layer. For this reason, the results obtained for P and D with the experimental device used in this study are apparent values. The difference between apparent and true values of the diffusive parameters decreases with decreasing water content of the hydrogels, decreasing thickness of the solution layer between membrane and cathode and with increasing thickness of the membrane itself. It should be stressed, however, that the thickness of the water layer between the membrane and the cathode in the apparatus used in this work is only a few micrometres and, consequently, the uncertainty involved in the diffusive parameters due to the resistance of the layer is a minor one. Studies carried out on hydrogels used as contact lenses have shown that the mechanism of absorption-diffusion is basically controlled by the hydrogel²⁴.

Prior to each electrochemical experiment, nitrogen was bubbled in the high pressure chamber and the deoxygenation was monitored by following the evolution of the electrical current. Once the intensity reached a minimum, as a consequence of the total consumption of oxygen, nitrogen bubbling was stopped and the atmospheric oxygen was dissolved in the high pressure compartment. Oxygen started to diffuse through the membrane producing an increase in $I(t)$ with time until the current intensity reached an asymptotic value, I_{∞} . Illustrative plots showing the evolution of the intensity with time are presented in Figure 4. The apparent values of P and D can be obtained from $I(t)$ and I_{∞} by using the procedures outlined above, and average results of these quantities are given in Table 3. In the case of PTEGA, the measurements were only carried out at 25°C, the values of P and D being 34.3 barrers and $7.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively, which are lower than the results obtained for the same parameters, 50.66 barrers and $11.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively, found for PTTEGA membranes at the same temperature.

The temperature dependencies of both the apparent diffusion and permeability coefficients for the PTTEGA network are shown in Figure 5 where, below ca 45°C, a sharp increase in the values of these parameters with temperature are observed, each of them approaching a nearly asymptotic value for $T > 45^{\circ}\text{C}$. Values of the solubility coefficient, S , calculated from the results for P and D , are represented as a function of temperature in Figure 6. In the same figure, for comparative purposes, the variation of the solubility coefficient of oxygen in pure water is plotted. It is noteworthy that the curves depicting the temperature dependence of the solubility coefficient in the swollen hydrogels and in water follow similar trends. The values of S decrease rapidly with increasing temperature until a temperature is reached ($T \approx 30^{\circ}\text{C}$ for the hydrogel and $T \approx 35^{\circ}$ for water) above which the solubility coefficient decreases slowly with increasing temperature for water and remains

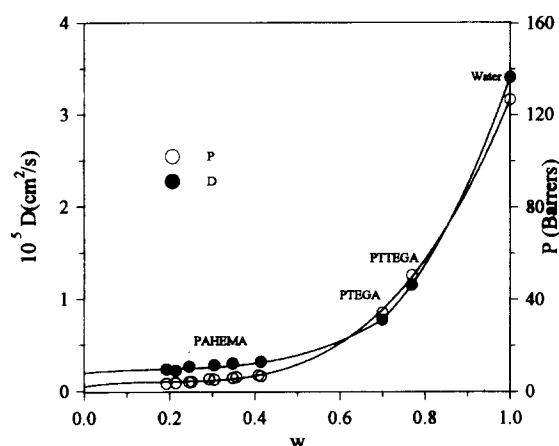


Figure 7 Permeability and diffusion coefficients for different hydrogels as a function of the degree of swelling (see text)

nearly constant for the hydrogel. Moreover, the results plotted in Figure 6 suggest that a high degree of swelling causes an anomalous enhancement of the solubility of the gas in the hydrogels.

It is tempting to compare the values of permeability and diffusion coefficients of oxygen through different hydrogels, with different degrees of swelling, with those reported for pure water²⁵. Results represented in Figure 7 show that, for hydrogels with relatively low water content, both the diffusion and permeability coefficients increase slightly with the weight fraction of water, w . For example, the apparent values of both P and D for oxygen through hydrogels prepared from 2-hydroxyethyl methacrylate-*p*-methacryloyl-oxyacetanilide copolymers²⁶ only change between 3.7–7.1 barrers and $2.2\text{--}3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ when w increases from 0.2 to 0.4. The values of these quantities are significantly larger for PTEGA and PTTEGA, observing that a change of water content of 7% in these hydrogels produces changes of about 48% in the values of P and D . Even though the solubility coefficient of oxygen in the hydrogels with high water content is larger than in water, restrictions in the diffusive path caused by the polymer matrix are responsible for the fact that the diffusion of oxygen through the highly swollen hydrogels is nearly one third of the value in pure water.

Work is in progress dealing with the synthesis of PTEGA and PTTEGA membranes with different degrees of crosslinking with the aim of studying how the degree of swelling affects the diffusive characteristics

and mechanical properties of these membranes swollen in water at equilibrium.

ACKNOWLEDGEMENTS

We gratefully acknowledge the skilful technical assistance of Mr Delgado and the financial support of the CICYT through the grant PB-92-0773.

REFERENCES

1. Timmer, W., *Chem. Technol.*, 1979, **9**, 175.
2. Kusi, R. P. and Turner, D. T., *J. Dent. Res.*, 1974, **53**, 948.
3. Peppas, N. A. and Moynihan, J. H., in *Hydrogels in Medicine and Pharmacy*, Vol. 2, ed. N. A. Peppas. CRC Press, Boca Raton, FL, 1987, p. 50.
4. Ozawa, H., Kunimoto, S. and Tanzawa, H., *Biomaterials*, 1988, **170**, 170.
5. Okubo, H., Yoshida, K. and Kaetsu, I., *Int. Appl. Radiat. Isot.*, 1988, **107**, 143.
6. Sefton, M. V. and Stevenson, W. T. K., *Adv. Polym. Sci.*, 1988, **107**, 143.
7. Iglesias, M. T., Guzmán, J. and Riande, E., *J. Polym. Sci., Polym. Chem.*, 1994, **32**, 2565.
8. Iglesias, M. T., Guzmán, J. and Riande, E., *J. Polym. Sci., Polym. Chem.*, 1995, **33**, 2057.
9. Guzmán, J. and Riande, E., *Polym. Bull.*, 1995, **34**, 509.
10. Iglesias, M. T., Guzmán, J., Riande, E., Sánchez, F. and de la Peña, J. L., *J. Chem. Res.*, 1995, 400.
11. Riande, E. and Guzmán, J., *Macromolecules*, 1996, **29**, 1728.
12. Matsuzaki, K., Kanai, T., Kawamura, T. and Matsumoto, S., *J. Polym. Sci., Polym. Chem.*, 1973, **11**, 961.
13. Suchopárek, M. and Spevacek, J., *Polymer*, 1994, **35**, 3389.
14. Spevacek, J., Suchopárek, M. and Al-Alawi, S., *Polymer*, 1995, **36**, 4125.
15. Suchopárek, M. and Spevacek, J., *Macromolecules*, 1993, **26**, 102.
16. Goñi, I., Gurruchaga, M., Valero, M. and Guzmán, G. M., *Polymer*, 1993, **34**, 1780.
17. Bandrup, J. and Immergut, E. H. (eds), *Polymer Handbook*, 3rd edn. John Wiley, New York, 1989.
18. Compañ, V., Villar, M. A., Vallés, E. and Riande, E., *Polymer*, 1996, **37**, 101.
19. Tulig, T. J. and Tirrel, M., *Macromolecules*, 1982, **15**, 459.
20. Bawn, C. E. H. and Verdin, D., *Trans. Faraday Soc.*, 1960, **56**, 815.
21. Odian, G., *Principles of Polymerization*, 2nd edn. John Wiley, New York, 1981, p. 257.
22. Yen, S. K. and Shih, H. C., *Clin. Exp. Opt.*, 1988, **135**, 1169.
23. Kimble, M. C., White, R. E., Tsou, Y. M. and Beaver, R. N., *J. Electrochem. Soc.*, 1990, **137**, 2510.
24. Compañ, V., Garrido, J., Manzanares, J. A., Andres, J., Esteve, J. S. and López, M. L. *J. Optom. Vis. Sci.*, 1992, **69**, 685.
25. Perry, J. (ed.), *Chemical Engineer's Handbook*, 3rd edn. MacGraw-Hill, New York, 1950, p. 540.
26. Compañ, V., San Román, J., Riande, E., Smith-Sorensen, J., Levenfeld, B. and Andrio, A. *J. Biomaterials*, 1996, **17**, 1243.