

# E.s.r. study on permeation of oxygen in crosslinked polymers

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Polymeric networks of methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) with various EGDMA levels were synthesized via bulk free-radical polymerization using an AIBN initiator and a programmed temperature rise. The trapped radicals in the polymer network were used to investigate the permeation of oxygen by electron spin resonance (e.s.r.). The decay rates of radical concentration in the temperature range, 110 to 180°C were used to estimate the permeability coefficients of oxygen. It was found that the permeability coefficient reached a peak value at about 70 wt% EGDMA, indicating that porosity of the network increased with EGDMA content reaching a maximum at 70 wt% EGDMA. The glass transition temperature ( $T_g$ ) of poly(EGDMA) obtained using the oxygen permeability data was estimated to be 144°C, and the permeation activation energies below and above  $T_g$  were 7.3 kJ mol<sup>-1</sup> and 58.3 kJ mol<sup>-1</sup>, respectively.

(Keywords: oxygen permeation; crosslinked polymers; electron spin resonance; poly(methyl methacrylate-co-ethylene glycol dimethacrylate))

## INTRODUCTION

Free-radical polymerization with crosslinking is receiving a lot of attention due to its potential for the development of new polymer products. Recently, using methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) as a model system, the crosslinking mechanisms and kinetics have been studied in considerable detail both theoretically and experimentally<sup>1-4</sup>. In this e.s.r. study, it was found that radicals are long lived, due to both being trapped in a glassy matrix and being attached to the network. The radical concentrations can reach levels as high as 10<sup>-3</sup> molar. Bimolecular termination at elevated temperatures has also been investigated and it was found that some radicals, most probably those connected to the network structure, did not terminate with each other<sup>4</sup>. Those polymer samples left in degassed glass ampoules at room temperature experienced no decay in radical concentration for more than 2 years.

In order to characterize further the polymer network microstructure, oxygen permeation into the crosslinked polymer matrix was measured. The decay in concentration of trapped radicals was used as an indicator using the fact that the permeated oxygen molecules will consume trapped radicals.

The rate of permeation of small molecules into a polymer matrix is of both fundamental and practical importance in many processes, such as membrane separation, controlled release of drugs, thermal printing and dyeing of fibres. Much effort has been made for various polymer systems with a similar measurement technique to that employed in this study. Nishide *et al.*<sup>6</sup> measured oxygen diffusion into a polymer matrix through

a cobalt porphyrin fixed in a membrane of poly(butyl methacrylate-co-1-vinylimidazole), poly(octyl methacrylate-co-1-vinylimidazole) and poly(lauryl methacrylate-co-1-vinylimidazole). Kaptan *et al.*<sup>7,8</sup> determined the diffusion coefficients of oxygen for poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) by e.s.r. Yang *et al.*<sup>9</sup> also obtained the permeability coefficients of oxygen in PMMA.

In this work, the emphasis is on polymeric networks and the effect of crosslinking levels on oxygen permeation. Oxygen permeability coefficients were estimated using a moving boundary diffusion model<sup>5</sup>.

## EXPERIMENTAL

EGDMA (Aldrich Chemicals) and MMA (Fisher Scientific) were purified in the following process: washed with a 10 wt% aqueous NaOH solution to remove the inhibitor, washed with deionized water to neutralize, dried successively with anhydrous sodium sulfate and molecular sieves (5 Å) for 12 h, and then distilled under reduced pressure to provide a useful middle fraction. 2,2'-Azobisisobutyronitrile (AIBN, Eastman Kodak) was recrystallized three times from methanol.

Five levels of 40, 55, 70, 85 and 100 wt% EGDMA were used for copolymer sample synthesis. Below 40 wt% EGDMA, the residual radical (radicals which cannot mutually terminate (radical/radical)) concentrations were too low for the sensitivity of the e.s.r. spectrometer used in this study. Copolymerizations of EGDMA/MMA which contained 0.3 wt% initiator were carried out in degassed glass ampoules with a programmed temperature rise as follows: 70°C for 1 h, 90°C for 1 h, 110°C for 1 h, 130°C for 1 h and 150°C for 4 h. The purpose of this programmed temperature rise was to eliminate

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**Table 1** The glass transition temperatures of MMA/EGDMA copolymers

EGDMA (wt%)	0	25	40	55	70	85	100
$T_g$ (°C)	106	114	119	133	135	135	140

possible bimolecular radical termination at the temperatures used for the oxygen permeation measurements.

The effect of residual initiator and products of initiation such as  $N_2$  were investigated. Because the half-life of AIBN at 150°C is only a few minutes, the level of residual initiator is negligible. Samples prepared in this manner were used to measure e.s.r. spectra in the temperature range, 110 to 180°C. It was found that under the same temperature/time conditions no significant radical concentration decreases occurred in the absence of oxygen permeation.

Cylindrical polymer samples taken from broken glass ampoules were immediately inserted into a TE 110 cavity with a gas bath temperature controlled to within  $\pm 0.5^\circ\text{C}$ . A Bruker ER 100D e.s.r. spectrometer was used to monitor the decay rate of radicals due to oxygen permeation into the cylindrical sample in a pure oxygen gas flow (flow rate  $3\text{ l min}^{-1}$ , pressure  $1 \times 10^5\text{ Pa}$  (1 atm)).

The absolute radical concentrations, calibrated by 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) (Aldrich Chemicals) dissolved in a MMA/EGDMA mixture, were calculated from the double integral factor of e.s.r. spectra. The experiments were repeated and good reproducibility was found.

The glass transition temperatures ( $T_g$ s) of the samples with the whole range of EGDMA levels were measured using a 910 Differential Scanning Calorimeter (d.s.c.), Du Pont Instruments. The results are listed in Table 1.

## RESULTS AND DISCUSSION

### Polymeric networks for oxygen permeation studies

It is known that radicals trapped in a glassy polymeric network (MMA/EGDMA network) are so long lived that almost no radical concentration decay occurs at room temperature over a 2-year period when the network is kept in sealed glass ampoules free of oxygen. The radicals in a polymer sample can be classified as follows. The total radical concentration is:

$$[R] = [R]_{\text{mob}} + [R]_{\text{act}} + [R]_{\text{res}} \quad (1)$$

where the subscripts 'mob', 'act' and 'res' denote mobile, active and residual, respectively.

Mobile radicals,  $R_{\text{mob}}$ , include primary radicals, oligomeric radicals and those polymeric radicals not attached to the polymer network but able to diffuse in the polymer matrix. At temperatures above  $T_g$  of the network, radicals can be liberated from the glassy state and reactivated so that bimolecular termination may occur. Because the copolymerization of MMA/EGDMA was carried out below the  $T_g$ , the radicals pendant on the network are trapped not only due to glass transition but also due to their attachment to the network. The pendant radicals which can be mutually terminated by segmental diffusion with adjacent radicals above the  $T_g$  are called active radicals,  $R_{\text{act}}$ . The pendant radicals which cannot terminate due to network restriction on mobility are called residual radicals,  $R_{\text{res}}$ . Mobile and active

radicals can be consumed by bimolecular termination at temperatures above the  $T_g$  of the network. In the absence of mobile and active radicals, residual radicals are stable at all temperatures (there is an upper temperature limit, of course).

The bimolecular termination of radicals at elevated temperatures should follow the second-order reaction equation:

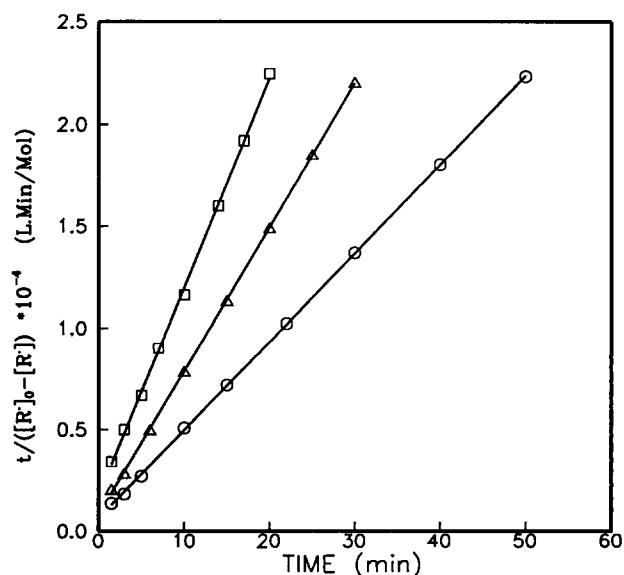
$$\frac{1}{C} - \frac{1}{C_0} = kt \quad (2)$$

where  $k$  is the reaction rate constant,  $C(=[R]_{\text{mob}} + [R]_{\text{act}})$  is the virtual radical concentration taking part in the reaction. Equation (2) can be rewritten according to Dole<sup>10</sup> in the following manner:

$$\frac{t}{[R]_0 - [R]} = \frac{t}{[R]_0 - [R]_{\text{res}}} + \frac{1}{k([R]_0 - [R]_{\text{res}})^2} \quad (3)$$

where  $[R]_0$  represents the total initial radical concentration in the network, and  $t$  is the decay time. Figure 1 shows the plots of  $t/([R]_0 - [R])$  versus  $t$ , using previous radical decay data<sup>4</sup>. The data for each EGDMA level show a straight line. From the slope of these lines, one can estimate the residual radical concentration  $[R]_{\text{res}}$ . In Figure 2, the estimated final residual radical concentration  $[R]_{\text{res}}$  (open circles) is shown (the solid squares are the total initial radical concentration  $[R]_0$  from ref. 4).

In order to obtain polymer samples which contain mainly residual radicals, the samples were synthesized using a programmed temperature rise. It was found that the values of the final residual radical concentrations measured in this study with the programmed temperature rise agree well with those calculated using equation (3). It can be concluded that the radicals in the networks using the programmed temperature rise are mainly residual radicals, and therefore should not experience bimolecular termination (radical/radical) during oxygen permeation but rather react with oxygen only.

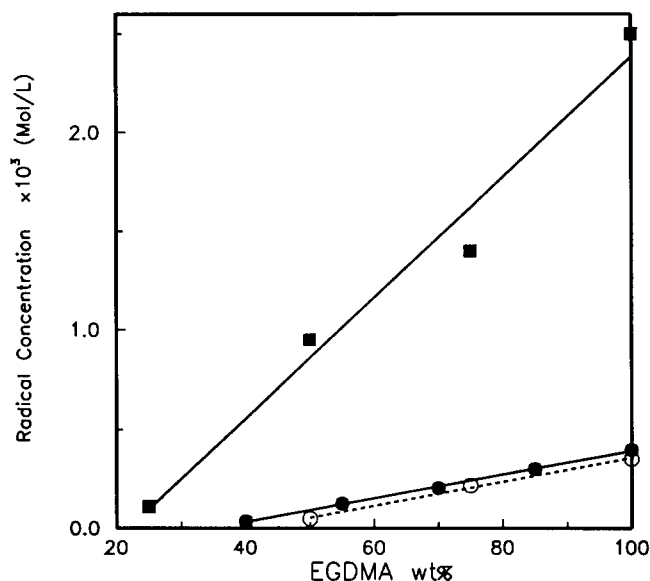


**Figure 1**  $t/([R]_0 - [R])$  versus  $t$  for three levels of EGDMA (50, 75 and 100 wt%), using the radical decay data from ref. 4

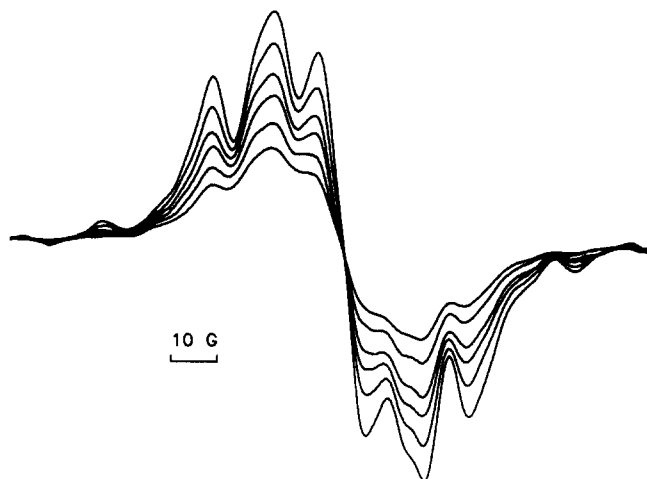
### Radical concentration decay during oxygen permeation

Figure 3 shows the change of e.s.r. spectra of residual radicals during oxygen permeation. It is found that only the spectrum strength decreases with permeation time, with no significant change in the spectrum line shape.

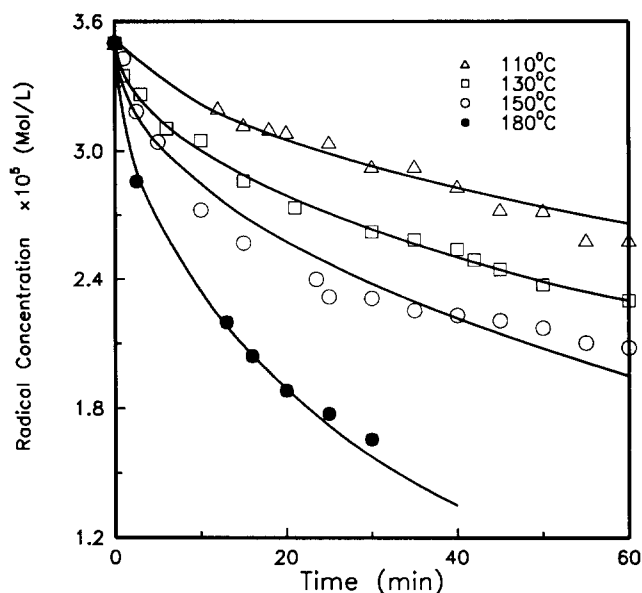
To calculate the decay rate of radicals with permeation time, the spectra were doubly integrated. The changes of radical concentration of five EGDMA levels at different temperatures are shown in Figures 4, 5, 6, 7 and 8. From these figures, it can be clearly seen that the decay rates of radical concentration with oxygen permeation increase at higher temperatures for the same level of crosslinker. As a typical example, Figure 8 shows that the decay rates do not change significantly with temperature in the range, 110–150°C. However above 150°C, the increases in the



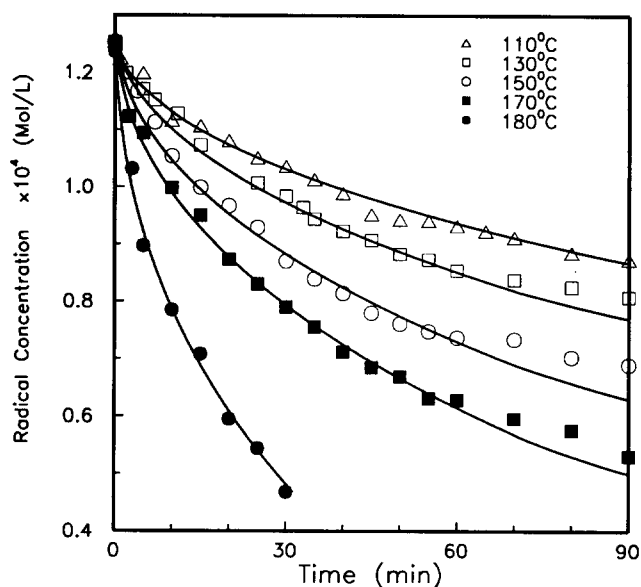
**Figure 2** Initial and final residual radical concentrations in MMA/EGDMA networks at different EGDMA levels: (■) the total radical concentration,  $[R]_0$ , at room temperature (ref. 4); (○) the estimated final residual radical concentration,  $[R]_{res}$ , calculated using equation (3) and the data in ref. 4; (●) the final residual radical concentration after the programmed temperature rise measured in this study



**Figure 3** 9-line e.s.r. spectra decay during oxygen permeation in poly(EGDMA) at 180°C. Microwave frequency 9.45 GHz, modulation frequency 100 kHz, modulation amplitude 3.2 Gpp, microwave power 20 dB



**Figure 4** Residual radical concentration change versus oxygen permeation time at different temperatures for MMA/EGDMA network containing 40 wt% EGDMA. Points: experimental data; —: model prediction



**Figure 5** Residual radical concentration change versus oxygen permeation time at different temperatures for MMA/EGDMA network containing 55 wt% EGDMA. Points: experimental data; —: model prediction

decay rates with temperature are dramatic. The  $T_g$  of poly(EGDMA) measured by Horie *et al.*<sup>11</sup> was 141°C and by Loshaek<sup>12</sup> was 132°C. The dramatic change of decay rate at about 150°C indicates that oxygen permeation is a strong function of temperature above the  $T_g$  of the polymeric network.

### Calculation of permeation coefficients

Based on the assumed mechanism of radical–oxygen termination, one oxygen molecule terminates one radical<sup>7</sup>. The governing equation for oxygen diffusing

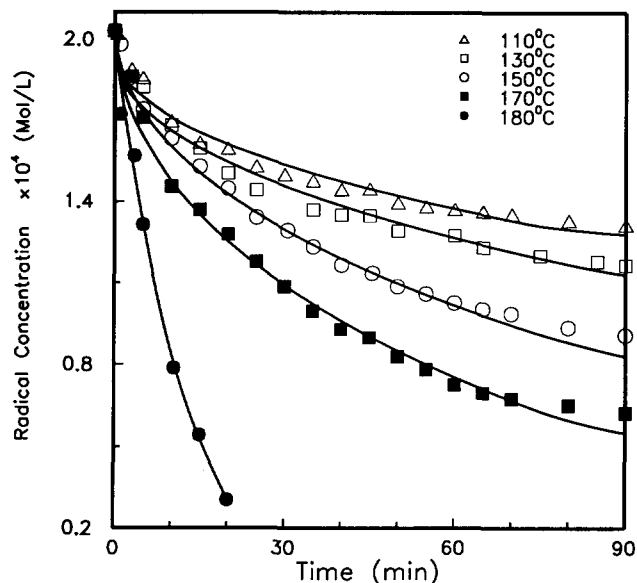


Figure 6 Residual radical concentration change versus oxygen permeation time at different temperatures for MMA/EGDMA network containing 70 wt% EGDMA. Points: experimental data; —: model prediction

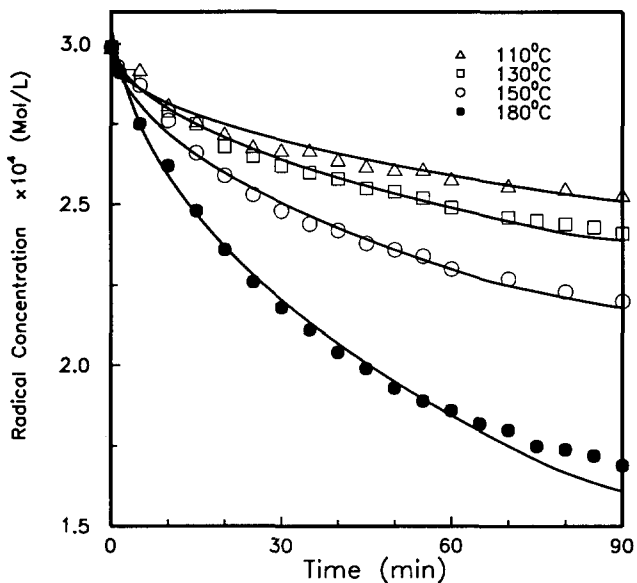


Figure 7 Residual radical concentration change versus oxygen permeation time at different temperatures for MMA/EGDMA network containing 85 wt% EGDMA. Points: experimental data; —: model prediction

into a polymer rod is as follows:

$$\left. \begin{aligned} \frac{\partial [O_2]}{\partial t} &= D \left( \frac{\partial^2 [O_2]}{\partial r^2} + \frac{\partial [O_2]}{r \partial r} \right) - k [O_2] [R] \\ \frac{\partial [R]}{\partial t} &= -k [O_2] [R] \end{aligned} \right\} \quad (4)$$

with the following initial and boundary conditions:

$$\left. \begin{aligned} [O_2]_{t=0} &= 0, & [R]_{t=0} &= [R]_i \\ [O_2]_{r=r_0} &= [O_2]_i, & [R]_{r=r_0} &= 0, & \frac{\partial [O_2]}{\partial r} \Big|_{r=0} &= \frac{\partial [R]}{\partial r} \Big|_{r=0} = 0 \end{aligned} \right\} \quad (5)$$

where  $[O_2]$  is the oxygen concentration,  $D$  is the diffusion coefficient of oxygen in the polymer matrix,  $r_0$  is the radius of the polymer rod,  $k$  is a rate constant,  $[R]$  is the concentration of residual radicals at various radial positions in the network (the subscript 'res' has been dropped for convenience) and the subscript  $i$  denotes initial.

Equation (4), for numerous applications, has been solved in the literature using various techniques. However, in this study the reaction rate constant is extremely large (about  $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ ) (see ref. 17). This diffusion problem is therefore a typical moving boundary problem<sup>13-16</sup>.

Using the steady-state approximation<sup>5</sup>, a simple analytical solution can be found:

$$t = \frac{[R]_i r_0^2}{4DHPO_2} \left\{ 1 - \frac{[R]_{av}}{[R]_i} \left( 1 - \ln \frac{[R]_{av}}{[R]_i} \right) \right\} \quad (6)$$

where  $H$  is Henry's law constant and the product  $DH$  is the permeability coefficient. In our experiments,  $P_{O_2} = 1 \text{ atm}$ ,  $r_0 = 0.113 \text{ cm}$ . One can therefore estimate the permeability coefficient ( $DH$ ) by regressing the average radical concentration,  $[R]_{av}$ , versus  $t$ . The regression results are shown in Figures 4 to 8. The model fits the experimental data well. It should be noted that it is possible to solve the diffusion equation with a moving boundary using different techniques<sup>5,18</sup>. However the mathematics involved are much more complex than those required for this investigation.

The permeation behaviour of oxygen is related to its solubility in the polymer matrix, the microstructure of the polymer matrix and the interaction between polymer and oxygen. The concentration of oxygen in the matrix is so low that the interaction between the copolymer and oxygen can be neglected. The permeation of oxygen is mainly affected by the microstructure of the polymeric network.

Figure 9 shows the change of permeability coefficient at various EGDMA levels and different temperatures.

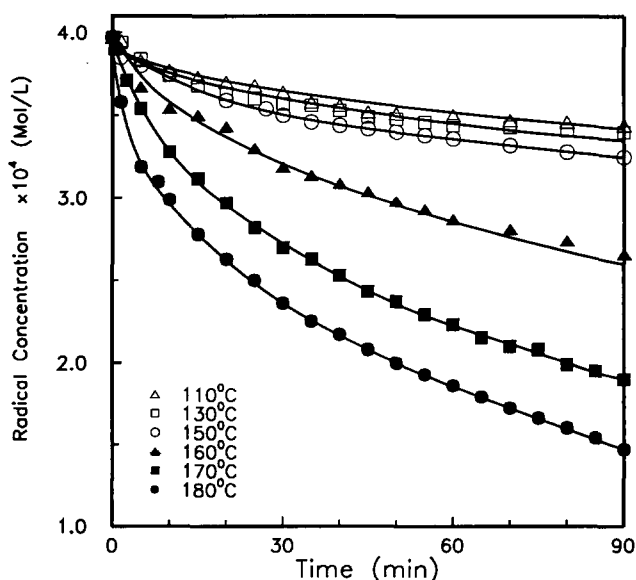


Figure 8 Residual radical concentration change versus oxygen permeation time at different temperatures for MMA/EGDMA network containing 100 wt% EGDMA. Points: experimental data; —: model prediction

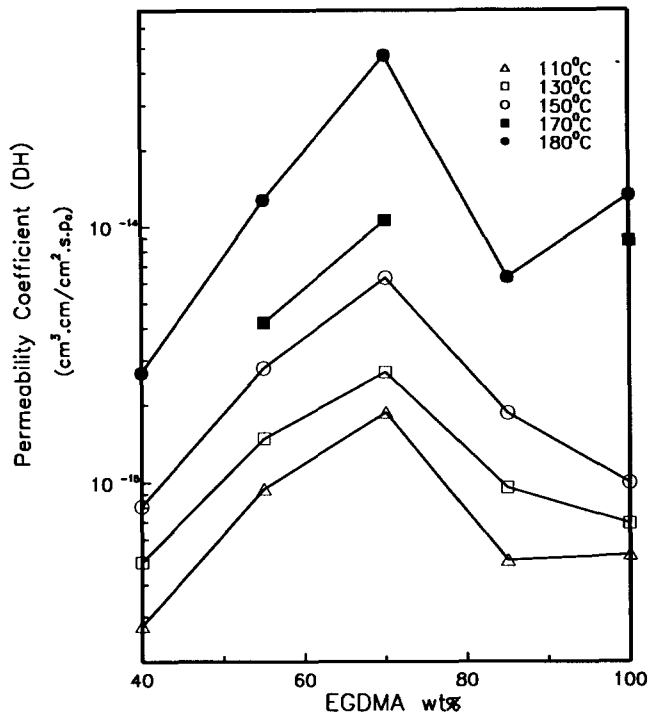


Figure 9 The influence of EGDMA level on permeability coefficient for oxygen permeation in MMA/EGDMA networks at different temperatures

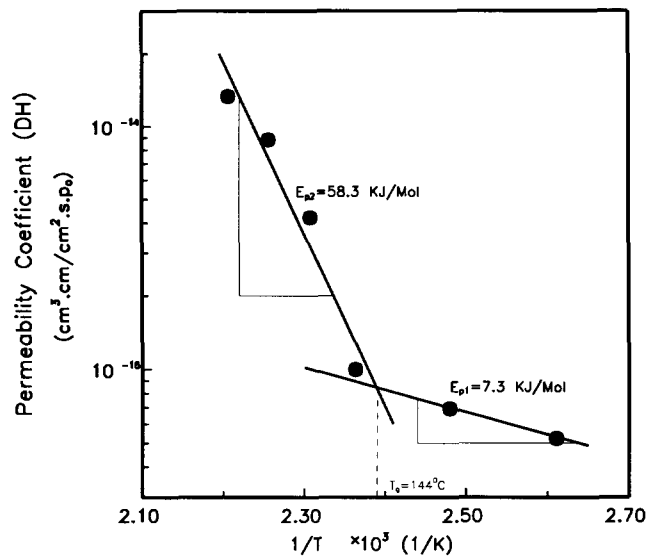


Figure 10 Arrhenius relationship for the permeability coefficient for permeation of oxygen in a poly(EGDMA) network

The permeability coefficients are in the order of magnitude of  $10^{-16}$  to  $10^{-13}$   $\text{cm}^3 \text{cm cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ . Compared with values for pure PMMA ( $1.6 \times 10^{-14}$   $\text{cm}^3 \text{cm cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$  in ref. 9 at  $34^\circ\text{C}$  and  $2.91 \times 10^{-14}$   $\text{cm}^3 \text{cm cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$  in ref. 19 at room temperature), the permeability coefficient of oxygen in the crosslinked

polymer matrix is much lower considering the temperature difference. The permeability coefficient as a function of crosslinker level shows a peak at about 70 wt% EGDMA, and this peak becomes more obvious with an increase in temperature. The increase in permeability coefficient with EGDMA level indicates that the network containing 70 wt% EGDMA has the most porous structure. At levels of EGDMA greater than 70 wt% the porosity falls with an increase in crosslinker level.

On the other hand, the temperature also affects the permeability coefficient. The dramatic increase in the radical decay rates at temperature  $>150^\circ\text{C}$  for poly(EGDMA) (above  $T_g$  of the network) indicates that the permeation of oxygen into the polymeric network is much slower below the  $T_g$ . In other words, the measurement of permeability coefficient can also be used to estimate the glass temperature of the polymer. From Figure 10, the glass temperature of poly(EGDMA) was found to be  $144^\circ\text{C}$ . This value is comparable with those measured using d.s.c. (see Table 1). We found that the glass temperature does not change significantly at high EGDMA levels (above 55 wt% EGDMA). The activation energies of permeation below and above  $T_g$  were found to be  $7.3 \text{ kJ mol}^{-1}$  and  $58.3 \text{ kJ mol}^{-1}$ , respectively.

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