

Effect of Polymer Cross-Links on Oxygen Diffusion in Glassy PMMA Films

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ABSTRACT Oxygen diffusion coefficients, D , have been measured in poly(methyl methacrylate) (PMMA) films containing small amounts of a cinnamic acid derived cross-linker. In the technique employed, the time evolution of oxygen sorption into the film was monitored using the phosphorescence of singlet oxygen as a spectroscopic probe. Although the effect of adding up to 1 mol % of the cross-linker is clearly manifested in the molecular weight and T_g of these samples, values of D are only moderately influenced. Nevertheless, a systematic decrease in the value of D is discernible as the extent of cross-linking is increased. Although it is reasonable to expect that, in a glassy polymer, cross-linking should not significantly perturb the local motions and confined changes in free volume that influence the translational motion of a small penetrant such as oxygen, our data indicate that even small amounts of a cross-linker can, nevertheless, have a noticeable and potentially meaningful effect. Although UV irradiation of the polymer films disrupts the cinnamic acid derived cross-linker via a [2 + 2] cycloreversion reaction, the photoinduced changes observed in D appear, rather, to reflect degradation reactions in the PMMA-based polymer.

KEYWORDS: cross-linked glass • oxygen diffusion • singlet oxygen

INTRODUCTION

Controlling the diffusion of small molecules in glasses and rubbers is critical to the development and use of many polymeric materials (1–4). The diffusion of molecular oxygen is particularly important in that oxygen has many unique properties that distinguish it from other small molecules (5). In particular, oxygen is a key participant in many processes that result in polymer degradation and in the degradation of materials that a given polymer may be designed to protect (6–8). Embodied in this latter point is the importance associated with the development of polymeric oxygen barrier materials (4, 9–12).

Polymers encountered in a range of applications, including those that involve small-molecule transport, are often cross-linked prior to or during their use (13–16). This may be done to increase the performance of the polymer for the task at hand. Cross-linking generally decreases chain mobility, leading to a reduction in segmental motions (17, 18). The latter can be manifested as a change in the free volume of the polymer (19, 20), which, in turn, can influence the diffusion of dissolved small molecules such as oxygen (1–4, 21). However, it is not trivial to predict the extent and magnitude of cross-link-dependent changes in segmental motion and free volume (14). As such, one must still rely, to a large extent, on experimentally determined diffusion coefficients in mechanistic studies of small-molecule transport in cross-linked materials. This is particularly true for

glassy polymers; because segmental motion in such materials is already limited, one might not expect to see pronounced and/or predictable cross-link-dependent changes in selected properties of the polymer.

The effect of cross-linking a given polymer on the permeability and diffusion of small gas molecules, including oxygen, has been examined in a number of studies (16, 21–23). Only a few studies have dealt with glassy materials. In the work of Barrer et al. (22), cross-link-dependent oxygen permeability coefficients in copolymers of ethyl acrylate and tetrakis(ethylene glycol) dimethacrylate were factored into the respective diffusion and solubility coefficients. However, the oxygen data in this study were often anomalous. The authors suggested that, under their conditions, this could be a consequence of reactions between oxygen and the polymer. Given the relative importance of oxygen in a host of systems, further study of cross-link-dependent oxygen mobility is thus justified.

With this background in mind, we set out to examine a well-studied glassy polymer that could be differentially cross-linked. To our knowledge, oxygen diffusion coefficients have not previously been quantified for cross-linked poly(methyl methacrylate) (PMMA) samples. We opted to focus on a low-molecular-weight PMMA-based system and to use relatively low degrees of cross-linking. The latter would presumably allow us to effectively perturb the polymer (e.g., increase the molecular weight and extent of polymer branching) without the formation of a gel during processing. We also opted to use cinnamic-acid-derived cross-links. Cinnamic acid has been extensively used as a photoresist (15, 24). In these latter systems, cinnamic acid is typically coupled to a given macromolecule and then irradiated to obtain a cinnamic acid dimer-derived cross-linked material. However, to better control the degree of cross-linking in our PMMA samples,

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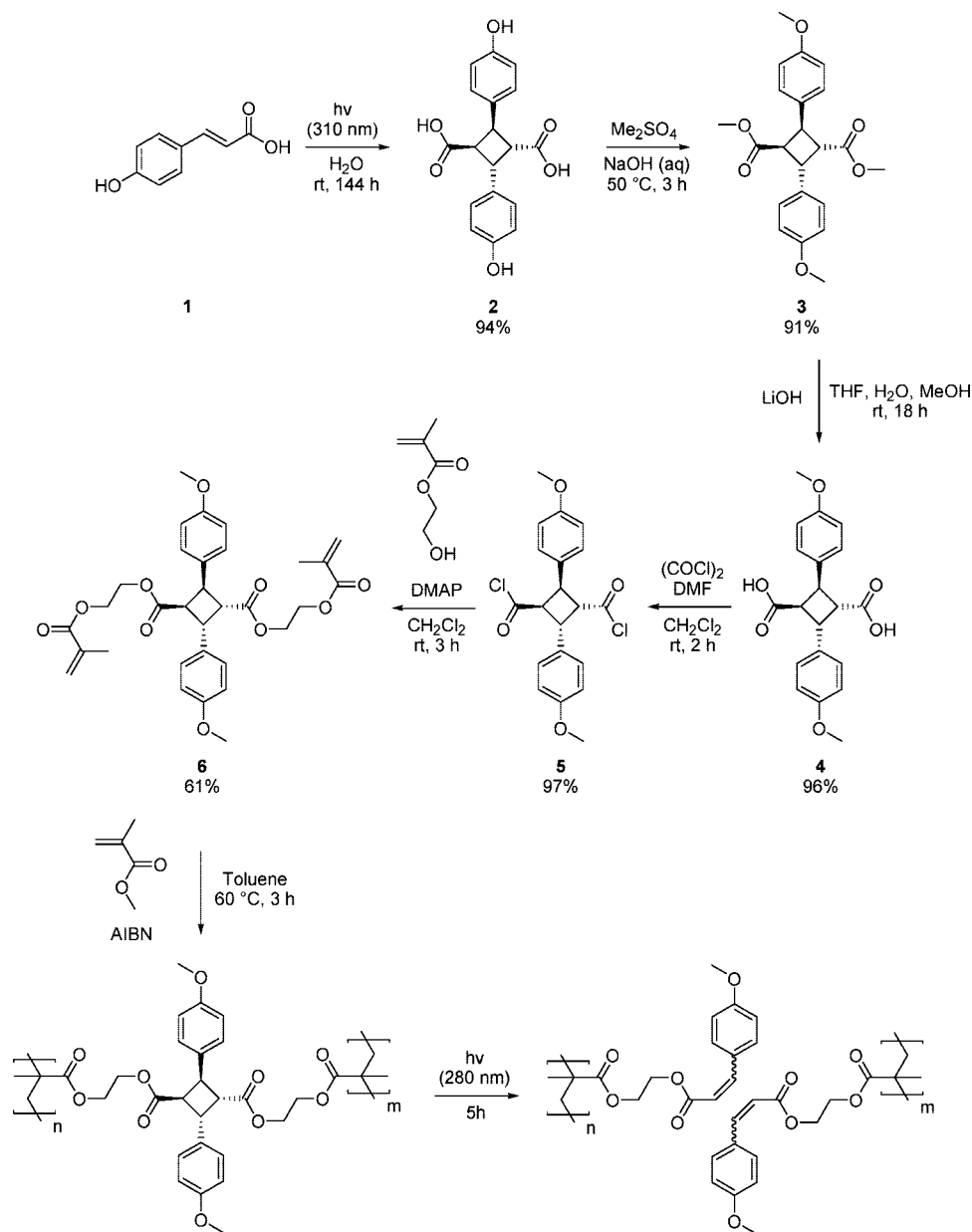
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Scheme 1. Synthetic Approach Used To Produce Differentially Cross-Linked PMMA Films^a

^a The cyclobutyl moiety is photolabile and dissociates to yield the olefin-containing cinnamic acid derivative upon UV irradiation (cis and trans isomers are obtained).

we used a different strategy; we incorporated the cinnamic acid dimer as a bifunctional monomer in a free-radical polymerization reaction (Scheme 1). An added feature of our approach to use the cinnamic acid dimer as a cross-linker is the possibility of making a photolabile material whose oxygen permeability would increase upon UV irradiation (i.e., upon irradiation, one could initiate the cycloreversion that dissociates the cinnamic acid dimer; Scheme 1).

In this report, we examine how the oxygen diffusion coefficient responds to the amount of cinnamic acid dimer incorporated in a glassy PMMA sample. We employ a technique, developed in our laboratories (25–29), whereby the time evolution of oxygen sorption into the sample is monitored using the phosphorescence of singlet oxygen as a spectroscopic probe. In this approach, data are readily

recorded as a function of the temperature and, more importantly, directly yield the diffusion coefficient, D . We also examine how this cross-linked PMMA system responds to UV irradiation.

EXPERIMENTAL SECTION

Synthesis and Sample Characterization. PMMA samples containing the cinnamic acid dimer were prepared as shown in Scheme 1. Compounds 2–5 were synthesized using a slightly modified literature procedure (30), and the yields shown refer to spectroscopically pure materials. The preparation of 2 is somewhat unique in that it involves a [2 + 2] cyclization reaction in suspended crystals, leading to the formation of one exclusive stereoisomer (31). Details of the synthetic steps and product characterization are given in the Supporting Information.

Size-exclusion chromatography (SEC) was used to characterize the molecular weights and molecular weight distributions of the PMMA samples. The SEC system was composed of three columns: a 50 mm \times 7.5 mm PLgel 5 μ m guard, a 300 mm \times 7.5 mm PLgel, and a 300 mm \times 7.5 mm PL gel 5 μ m mixed-D. A differential refractometer/viscometer (Viscotek model 200, Malvern Instruments, UK) was used to monitor the material eluted. The columns and detectors were maintained at 20 $^{\circ}$ C. Tetrahydrofuran (THF) was the eluent and was pumped through the system at a rate of 1.0 mL min $^{-1}$ (Shimadzu LC-10AD HPLC pump). The refractometer signals were calibrated using a series of 10 PMMA standards ranging from 2680 to 1 300 000 g mol $^{-1}$ and having a polydispersity of less than 1.09.

The glass transition temperatures of the PMMA samples were determined using differential scanning calorimetry performed at a rate of 10 $^{\circ}$ C min $^{-1}$ (TA Instruments Q1000). Transition temperatures were obtained from the midpoint of the heat capacity step change.

Absorption spectra were recorded using a Hewlett-Packard/Agilent Technologies model 8453 diode-array spectrometer.

Oxygen Sorption Measurements. The instrumentation and approach used to spectroscopically monitor the time evolution of oxygen sorption into polymer films have been described (25–29). Briefly, the 1270 nm phosphorescence of singlet molecular oxygen ($a^1\Delta_g \rightarrow X^3\Sigma_g^-$), produced in a photosensitized process, is used as an indicator of the amount of oxygen in the film. This approach complements those in which the fluorescence and/or phosphorescence of a dye is monitored upon exposure of a film to oxygen (32–36).

In the triplet-state photosensitized production of singlet oxygen, such as that employed in the present study, the intensity of the singlet oxygen phosphorescence signal observed, I_{Δ} , is proportional to the fraction of sensitizer triplet states quenched by ground-state oxygen (eq 1) (25–29).

$$I_{\Delta} = \gamma \frac{k_q [O_2]}{k_q [O_2] + k_T} \quad (1)$$

The proportionality constant γ includes parameters such as the efficiency of singlet oxygen radiative deactivation, the quantum efficiency of sensitizer triplet-state formation, and instrumental parameters that account for signal collection efficiency and amplification. In eq 1, k_q is the bimolecular rate constant for oxygen quenching of the sensitizer triplet state, and k_T is the sum of all rate constants for triplet-state deactivation that are independent of oxygen. At low oxygen concentrations, where $k_q [O_2] \ll k_T$, I_{Δ} depends linearly on the oxygen concentration in the polymer (25–29). This is illustrated in Figure 1 for the samples examined in this study.

Oxygen sorption experiments were performed using tetrakis(3-hydroxyphenyl)porphine [T(3-HOP)P; Porphyrin Systems, Lübeck, Germany] as the singlet oxygen photosensitizer. In samples that contain dissolved oxygen, singlet oxygen is efficiently produced ($\Phi_{\Delta} = 0.6$) upon irradiation of T(3-HOP)P at 420 nm (37). During preparation of the polymer samples, the amount of sensitizer used was adjusted to yield an absorbance at 420 nm of ~ 0.6 – 0.8 in the final film. This corresponds to a sensitizer concentration of $\sim (1$ – $2) \times 10^{-3}$ M in the film. At such concentrations, the presence of the sensitizer does not perturb oxygen diffusion in the polymer (25, 26). In all samples used, there was no evidence of T(3-HOP)P aggregation (see the Supporting Information for a more complete discussion).

Films used in the oxygen sorption experiments were prepared by spin-casting the polymer using a Headway Research (Garland, TX; model EC101DT-R790) photoresist spinner. The polymer and the singlet oxygen sensitizer were dissolved in a mixture of 2-butanone and anisole (1:0.9, v/v). Typically, 1 g of

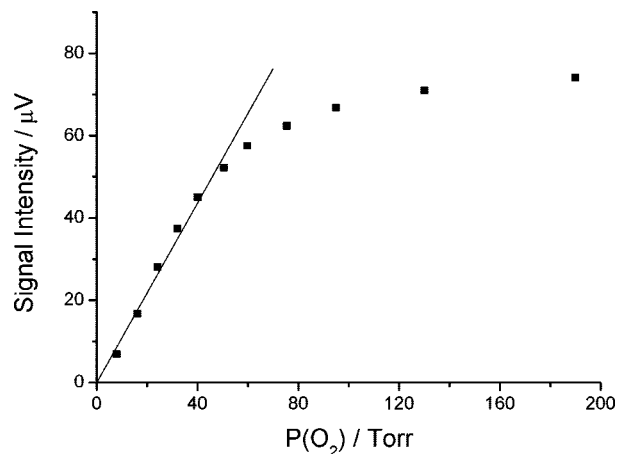


FIGURE 1. Plot of the equilibrium singlet-oxygen phosphorescence intensity against the pressure of oxygen in the atmosphere surrounding the polymer sample. These data were recorded from a PMMA sample containing the sensitizer T(3-HOP)P. The solid line is the result of a linear fit to the data at ≤ 50 Torr. Similar data were recorded from all of our cross-linked PMMA samples.

polymer was added to 1.6 mL of solvent for the PMMA-0.00 sample and 1.9 mL of solvent for the PMMA-1.00 sample (i.e., incrementally more solvent was used as the degree of cross-linking increased). The polymer solutions were maintained at ambient temperature and pressure for 4 h on a shaking table (Vibrax VXR basic, IKA Werke, Stauten, Germany) to achieve homogeneity and then were spin-cast onto borosilicate glass plates. The typical spinning speed was 2500 rpm. After standing for 24 h at ambient temperature and pressure, the spin-cast films were placed under vacuum for 24 h. Finally, the films were annealed at 50 $^{\circ}$ C for 24 h under vacuum using a Lab-Line Duo-Vac oven (model 3620-ST-1). Under these conditions, films with a thickness in the 8–14 μ m range were generally produced. The film thickness was quantified using a DEKTAK 3030 (Veeco Instruments, Plainview, NY) profilometer.

UV Irradiation Experiments. Polymer films were placed in a cylindrical sample holder, evacuated, and irradiated at 280 nm for 5 h using a 200 W Xe (Hg) lamp enclosed in a horizontal-burn housing (PTI). The lamp output passed through (1) 3 cm of water to remove a large fraction of the IR component and (2) a 280 nm bandpass filter (20 nm fwhm, 72% transmission at the band maximum; Semrock BrightLine).

RESULTS AND DISCUSSION

1. Characterization of the PMMA-Based Polymers. Samples of five different PMMA-based polymers were prepared. Four of these samples were copolymers prepared respectively with 0.25, 0.50, 1.00, and 2.00 mol % **6** added to the solution of monomers. The samples were synthesized under otherwise identical polymerization conditions, and the average yield of polymer was 87%. The polymer prepared upon the addition of 2 mol % of **6** formed a gel during the polymerization reaction and was only analyzed in order to determine its glass transition temperature (T_g). The other four polymers were dissolved in THF (0.10 g in 10 mL of THF) and their absorption spectra recorded (Figure 2).

The substituted cyclobutane found in our cinnamic acid cross-linking dimer has an absorption profile with band maxima at 277 and 284 nm. The absorption spectra of the polymers prepared (Figure 2) clearly show that the absor-

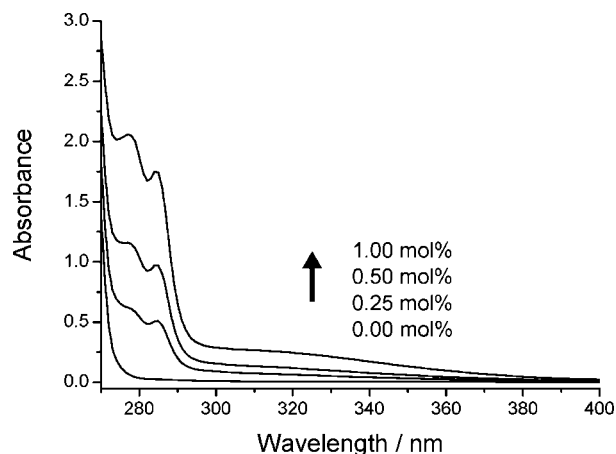


FIGURE 2. Absorption spectra of cross-linked PMMA-based polymers dissolved in THF. The amount of dissolved polymer is identical in each case. The mol % shown reflects the amount of **6** added to the reaction mixture of monomers.

Table 1. Selected Properties of the Polymers Prepared

polymer ^a	F ^b /mol %	M _w /g mol ⁻¹	PDI	T _g /°C
PMMA-0.00	0	26 400	2.2	60
PMMA-0.25	0.12	35 000	2.8	84
PMMA-0.50	0.25	43 100	3.3	88
PMMA-1.00	0.45	81 800	5.7	96
PMMA-2.00				109

^a Nomenclature reflects the mol % of dimer **6** added to the polymerization reaction mixture. ^b Amount of dimer **6** actually incorporated into the polymer as ascertained using absorption spectra.

bance of these bands increases in accordance with the amount of the dimer added to the solution of the monomer to be polymerized. The apparent absorbance observed over the spectral range 300–400 nm is often seen from samples that scatter light, and this too increases with the amount of dimer added to the polymerization mixture. This latter observation appears to indicate that we increasingly cross-link PMMA with an increase in the amount of added **6**. In turn, this cross-linking appears to result in a corresponding increase in microheterogeneity that is manifested as an increase in the tendency of the polymer to scatter light.

Using an extinction coefficient obtained from spectra of compound **4** dissolved in THF [$\epsilon_{284} = (3.02 \pm 0.01) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$], we can provide an estimate of the amount of cross-linking dimers actually incorporated in the respective PMMA-based polymers. This exercise was performed using solutions of the polymer in which the absorbance at 284 nm was less than 1.0 and where the spectra were corrected for the effects of light scattering. The data indicate that, in each case, ~50% of the dimer **6** added to the polymerization reaction mixture was ultimately incorporated into the resulting polymer under our reaction conditions (Table 1). For the polymer prepared with 1 mol % of **6** in the reaction mixture, the estimated incorporated amount of 0.45 mol % corresponds to an average molar ratio of one cross-link for each PMMA chain. Because this ratio corresponds to an ideal polymer network (38) and because this material did not form

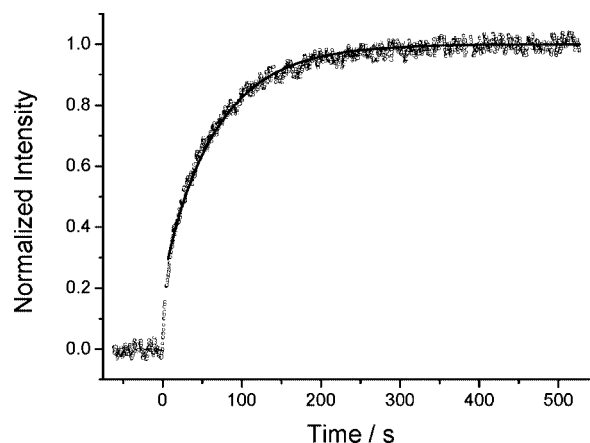


FIGURE 3. Singlet-oxygen phosphorescence intensity recorded as oxygen is sorbed into a 10 μm thick film of PMMA cast onto a glass substrate. These data were recorded upon exposure of a degassed film to 50 Torr of oxygen. The line is the result of a fit of eq 2 to the data. At early sorption times, the data may reflect experimental phenomena not considered in eq 2 and, as such, we have not extended the fit into this time domain.

a gel, it is likely that the actual ratio of incorporated dimer is slightly smaller than that estimated from the absorption spectra. Recall that the material prepared with 2 mol % of **6** indeed formed a gel during the polymerization reaction (vide supra).

The results of a SEC experiment on our polymers show an apparent increase in both the molecular weight and polydispersity index (PDI) as the amount of dimer **6** incorporated in the polymer increases (Table 1). Likewise, the T_g of the polymers increases as the amount of **6** incorporated increases. These data indicate that we appear to have indeed successfully cross-linked PMMA to differing extents using the dimer **6**. It is important to note that our un-cross-linked PMMA has a comparatively low T_g (60 °C), which is due to its low molecular weight, $M_w = 26\,400 \text{ g mol}^{-1}$. The T_g of high-molecular-weight PMMA is ~105 °C (39).

2. Cross-Link-Dependent Diffusion Coefficients.

Upon exposure of a degassed film to an ambient atmosphere of oxygen, the time-dependent process of oxygen sorption by the film can be monitored using the intensity of the sensitized singlet oxygen phosphorescence signal from the film (Figure 3) (25–29). Under conditions in which the intensity of the singlet oxygen phosphorescence signal is linearly proportional to the amount of oxygen that has been sorbed by the sample (i.e., less than 50 Torr for the present samples, as seen in Figure 1), data such as those shown in Figure 3 can be analyzed to yield the oxygen diffusion coefficient D (25–29). Specifically, using Fick's second law for one-dimensional diffusion, the time-dependent sorption plots behave according to the expression shown in eq 2.

$$\frac{I_{\Delta}^t}{I_{\Delta}^{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right) \quad (2)$$

In eq 2, I_{Δ}^t and I_{Δ}^{∞} represent the singlet oxygen phosphorescence intensity at times t and infinity, respectively, and l is the film thickness.

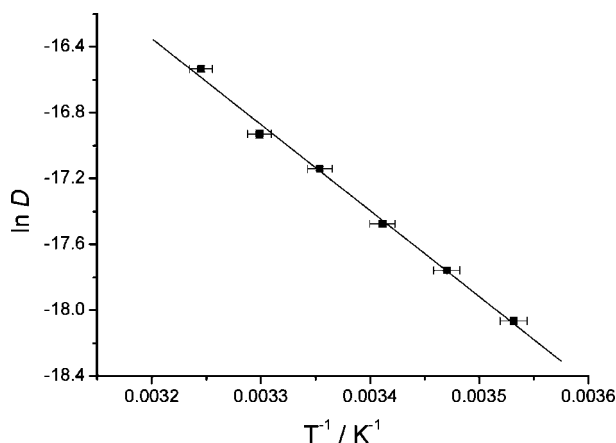


FIGURE 4. Arrhenius plot for the oxygen diffusion coefficient D in cross-linked PMMA (data were recorded using PMMA-0.25). Errors on the values of $\ln D$ are encompassed by the mark used to denote each point.

Table 2. Oxygen Diffusion Coefficients at 25 °C, D , Arrhenius Preexponential Factors, D_0 , and Diffusion Activation Energies, E_{act}

polymer	$F/\text{mol } \%$	$D/\times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$	$D_0/\text{cm}^2 \text{ s}^{-1}$	$E_{act}/\text{kJ mol}^{-1}$
PMMA-0.00	0	2.7 ± 0.2	0.17 ± 0.07	39 ± 1
PMMA-0.25	0.12	2.3 ± 0.1	0.07 ± 0.06	37 ± 3
PMMA-0.50	0.25	2.2 ± 0.1	0.06 ± 0.05	37 ± 2
PMMA-1.00	0.45	2.0 ± 0.1	0.13 ± 0.13	39 ± 2

In iterative fits of eq 2 to data such as those shown in Figure 3, oxygen diffusion coefficients can be obtained under a variety of conditions. Diffusion coefficients obtained as a function of temperature, T , are of particular interest. It has been established that, for many oxygen diffusion experiments, the Arrhenius relationship (eq 3) holds, and plots of $\ln D$ against $1/T$ can be used to yield an apparent activation energy for diffusion, E_{act} (26, 27).

$$D = D_0 \exp\left(\frac{-E_{act}}{RT}\right) \quad (3)$$

Oxygen diffusion coefficients were obtained for our cross-linked PMMA samples over the temperature range 10–35 °C (i.e., well below the measured values of T_g). Data obtained from the respective Arrhenius plots (e.g., Figure 4) as well as the diffusion coefficients recorded at 25 °C are listed in Table 2.

The data in Tables 1 and 2 clearly indicate that, despite pronounced changes in some properties of the PMMA samples as a function of the extent of cross-linking (e.g., T_g), values of $D(25 \text{ °C})$, E_{act} , and D_0 do not vary significantly in these samples. Nevertheless, values of $D(25 \text{ °C})$ clearly decrease with an increase in the amount of cross-linking (Table 2 and Figure 5).

These results are consistent with those from previous studies performed in our laboratories where we have demonstrated that oxygen diffusion in polymers is more strongly dependent on the local motions of the polymer backbone and/or pendant groups and less dependent on longer-range

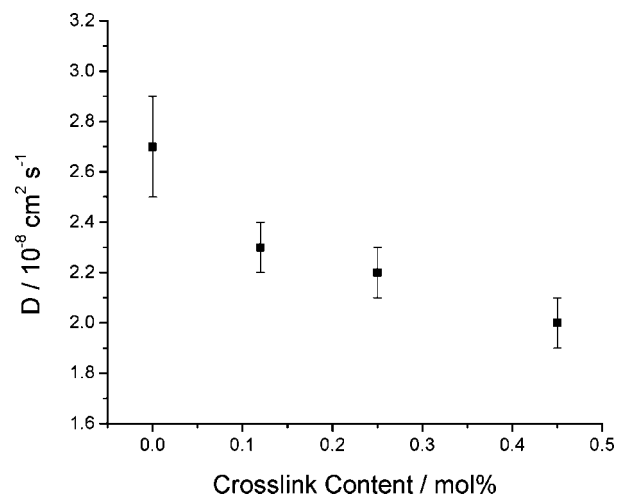


FIGURE 5. Plot of the oxygen diffusion coefficient recorded at 25 °C, D , against the cross-link content of the four PMMA samples examined.

segmental motions (29). It is established that these latter, more extensive motions are those that principally influence phenomena that determine the glass transition temperature, for example. On the other hand, more confined and localized motions appear to influence the free volume on a scale that is pertinent to the diffusion of a small molecule such as oxygen.

The diffusion coefficient we obtain for un-cross-linked PMMA, $(2.7 \pm 0.2) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, agrees with those obtained from other studies, which fall in the range $\sim(1-4) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (28, 40–43). The values of E_{act} obtained for our PMMA samples, $\sim 38 \text{ kJ mol}^{-1}$, are likewise consistent with those obtained for other glassy materials (26, 27).

When considering the absolute values of these diffusion coefficients, however, it is important to note the following caveat. In order to obtain films with a sufficiently high optical clarity and uniform thickness for our diffusion measurements, we used a mixture of anisole and 2-butanone as the solvent in the spin-coating process. However, anisole is not completely removed during annealing under vacuum. Although we have established that this does not affect the cross-link-dependent trend in D values shown in Figure 5, the presence of anisole is, nevertheless, manifested in the absolute values of D obtained. For example, in an independent control experiment using un-cross-linked PMMA with $M_w = 48\,800 \text{ g mol}^{-1}$, $D(25 \text{ °C})$ increases from $(0.9 \pm 0.1) \times 10^{-8}$ to $(1.9 \pm 0.2) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ as a consequence of residual anisole in the film.

When considering the cross-link-dependent changes in D shown in Table 2 and Figure 5, it is important to recall that, prior to the diffusion measurements, our samples were annealed at 50 °C for 24 h. On the basis of the T_g values shown in Table 1 that range from 60 to 96 °C, it is expected that the un-cross-linked sample (i.e., PMMA-0.00) and the least cross-linked sample (i.e., PMMA-0.25) would be the most susceptible to the effects of annealing. Specifically, for these samples, one would expect the greatest annealing-dependent reduction in the free volume, which, in turn, would be manifested as the largest annealing-dependent

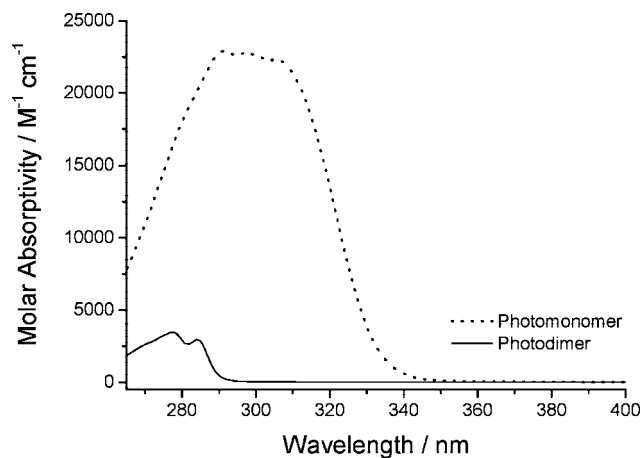


FIGURE 6. Absorption spectra of the photo-cross-linker in its monomeric (olefinic) and dimeric (cyclobutyl) forms. Spectra were recorded in methyl isobutyrate, a liquid analogue of PMMA.

decrease in the value of D (29). Moreover, samples with the highest degree of cross-linking are expected to contain a proportionally greater amount of residual anisole. With these points in mind, it is significant to note that the un-cross-linked and least cross-linked samples still yield the largest values of D (i.e., the relative changes in D could be even more pronounced than what is shown in Figure 5).

3. UV-Irradiation-Induced Changes. One characteristic feature of the cinnamic acid dimer **6** used in the preparation of our cross-linked polymers is that, upon UV irradiation of this moiety, one can effect the [2 + 2] cycloreversion reaction that disrupts the cross-link, generating two separate olefinic residues (Scheme 1). We were interested in seeing if, in our samples, this photoinduced process would be manifested in the diffusion coefficient of oxygen.

As shown in Figures 2 and 6, the dimer **6** has an absorption profile with band maxima at 277 and 284 nm. In contrast, the ring-opened, olefin-containing residue has a more intense and broad band with a maximum at ~290–310 nm (Figure 6). Despite the spectral overlap, irradiation of the cyclobutyl moiety at ~280 nm will generate an appreciable amount of the ring-opened products (44).

Upon irradiation of our cross-linked films at 280 nm, we obtain clear evidence that the cyclobutyl ring in the cross-linker is indeed opened to produce the olefin-containing residues (Figure 7). Because we want to quantify the effect of this UV irradiation on oxygen diffusion, these experiments were necessarily performed on samples containing the singlet oxygen sensitizer and residual anisole, both of which also absorb some of our incident light at 280 nm. Nevertheless, the data clearly show the expected irradiation-induced change in the cross-linker (Figure 7).

We measured the oxygen diffusion coefficient at 25 °C in a cross-linked PMMA-based sample both before and after 280 nm irradiation. One might expect, a priori and on the basis of the data in Table 2, that upon irradiation of our copolymer and the disruption of the cross-linking moiety, we would observe a slight increase in the magnitude of the diffusion coefficient. Rather, upon irradiation, we observe a discernible decrease in D (Table 3). In a control experiment

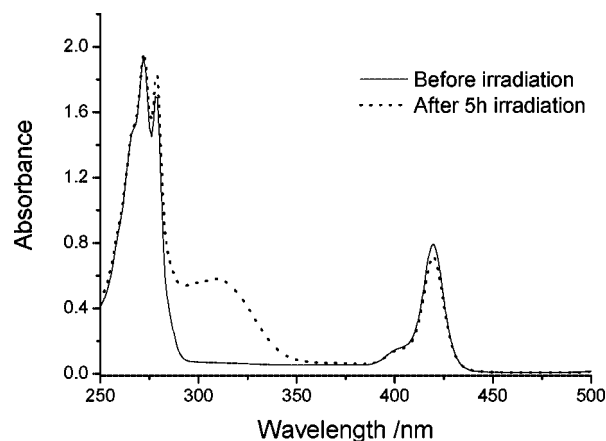


FIGURE 7. Absorption spectra of a 10 μm thick PMMA-1.00 film containing T(3-HOP)P recorded before and after 5 h of irradiation at 280 nm. With the appearance of the band at ~310 nm, the data clearly show that the cyclobutyl ring in the cross-linker is opened to produce olefin-containing residues. The data also point to a slight irradiation-induced bleaching of T(3-HOP)P.

Table 3. Oxygen Diffusion Coefficients before and after Irradiation for 5 h at 280 nm

polymer	$M_w/\text{g mol}^{-1}$	$D(\text{before irradiation})/\times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$	$D(\text{after irradiation})/\times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$
PMMA-0.00 ^a	50 000	1.9 ± 0.3	1.3 ± 0.3
PMMA-1.00	81 800	2.0 ± 0.1	1.2 ± 0.3

^a Although of no consequence to our message, note that the PMMA-0.00 sample used for this experiment had a slightly higher M_w than that used to yield the data in Table 2.

performed using PMMA lacking the cinnamic acid derived cross-linker, we observed a similar decrease in the magnitude of D upon irradiation (Table 3).

Although these observations could reflect a number of phenomena, it is known that irradiation of PMMA at 280 nm leads to main-chain scission and other manifestations of degradation (6). The latter include cross-linking, presumably mediated by the photoinitiated production of radicals (6, 45, 46). Thus, in contrast to the expected UV-irradiation-induced increase in the magnitude of D , 280 nm irradiation changes the morphology of our samples in a different way such that we see a decrease in the magnitude of the oxygen diffusion coefficient. This problem of photoinduced PMMA degradation could potentially be avoided through the use of cinnamic acid cross-linking moieties that absorb at longer wavelengths (15, 44).

CONCLUSIONS

Data have been recorded to indicate that oxygen diffusion coefficients respond, albeit in a very subtle way, to changes in the extent of cross-linking in a glassy PMMA-based polymer. In light of currently accepted models for the diffusion of small penetrants, our data indicate that, in these PMMA-based films, cross-linking can indeed sufficiently perturb the local motions and confined changes in the free volume that affect the translational motion of oxygen.

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Supporting Information Available: Experimental details and NMR spectra for compounds 2–6 as well as poly(methyl methacrylate-co-6), crystal structure of compound 4, UV–vis spectra for T(3-HOP)P, discussion of dye aggregation, and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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