"Tunable" Diffusion of D_2O in CO_2-Swollen Poly(Methyl Methacrylate) Films

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Opportunities exist to exploit the unique properties of carbon dioxide to process polymers for advanced applications. The diffusion of deuterated water in poly(methyl methacrylate) films swollen by carbon dioxide at 35°C over the pressure range 0 to 90 bar (corresponding density range: 0.0 to 0.66 g/cm^3) was measured using in situ FTIR spectroscopy. The mechanism and time scale of the diffusion of deuterated water in PMMA are easily controlled by manipulation of the applied CO_2 density. The enhancement of mass transport rate is consistent with the degree of plasticization of the polymer due to the absorption of carbon dioxide.

Introduction

The plasticization and swelling of glassy polymers (Berens and Huvard, 1989; Chiou et al., 1985; Goel and Beckman, 1993; Handa et al., 1994; Liau and McHugh, 1985; Sanders, 1988; Wang et al., 1982; Wissinger and Paulaitis, 1987; Wissinger and Paulaitis, 1991), especially poly(methyl methacrylate) (PMMA), by CO_2 have been utilized for extraction (Cotton et al., 1993; Dooley et al., 1995; Liau and McHugh, 1985) and impregnation (Berens et al., 1992) of solutes, as well as for the generation of microcellular foams (Goel and Beckman, 1994a,b). Since the diffusivity of penetrants in polymers depends on the free volume available for diffusion (Kumins and Kwei, 1968), one would expect swollen polymers to exhibit enhanced diffusion rates. Indeed, this has been observed in the drying of PMMA by supercritical CO_2 (Kazarian et al., 1996a,b) ($scCO_2$), the extraction of polypropylene by $scCO_2$ (Cotton et al., 1993), and the absorption of dimethyl phthalate by poly(vinyl chloride) in CO_2 vapor (Berens et al., 1992). The relative increase in diffusivity varied from two to (an estimated) six orders of magnitude, depending on the molecular size of the penetrant and polymer. The largest relative increase corresponded to the largest solute molecular size. However, in all these studies the diffusion of the solute and swelling of the polymer were occurring simultaneously. Since, a single penetration front is observed when a mixture is allowed to diffuse into glassy polymers (Kwei and Zupko, 1969), and the degree of swelling obtained for a mixture is intermediate between the degrees of swelling obtained for the pure components analysis of the data to obtain true diffusion coefficients "in" the swollen polymer is difficult. Therefore, one needs to decouple the swelling (due to carbon dioxide absorption) and the diffusion processes in order to obtain true diffusivities. This is accomplished by swelling the polymer film with carbon dioxide prior to the injection of the penetrant.

The greatest swelling and plasticization by carbon dioxide occurs in polymers containing polar functional groups (Berens and Huvard, 1989). Also, the degree of swelling and plasticization are most pronounced below the critical point of carbon dioxide (Wissinger and Paulaitis, 1987), suggesting that specific interactions are important. Recently, the specific interactions between CO_2 and polymers containing electron-rich functional groups have been reported, and the nature of the interaction has been assigned as a Lewis acid-base type (Kazarian et al., 1996a). In PMMA, the lone-pair electrons of the carbonyl group interact with the carbon atom of CO_2. Consequently, the diffusion of solutes in CO_2-swollen PMMA should be influenced by the specific interactions occurring between carbon dioxide, PMMA, and the solute, as well as the degree of plasticization of the PMMA.

PMMA-based materials are used in applications including resists for lithographic image transfer (Papanu et al., 1990), dentistry (Deb et al., 1995), and polymeric optical fibers (Pakhomov et al., 1995). The presence and transport of water in PMMA can greatly affect the performance in these applications. For example, the presence of water in polymeric optical fibers obscures transmission in the near IR (10,000 to

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20,000 cm^{-1}) (Pakhomov et al., 1992) due to overtones of the OH vibrations. Water is also known to decrease the T_g of PMMA due to hydrogen bonding (Smith and Schmitz, 1988). Since the transport of water in PMMA is crucial to the production of advanced materials, the diffusion of water in PMMA is well documented (Barrie, 1968; Tong and Saenger, 1989; Turner, 1987; Turner and Abell, 1987).

Opportunities exist to exploit the unique properties of carbon dioxide to process polymers for advanced applications. Recently, the enhanced diffusivity and plasticization of CO_2-swollen PMMA was utilized to produce a polymer with nonlinear optical behavior via low-temperature poling (Barry and Soane, 1991). Typically, the poling of polymeric materials is performed at or above the T_g of the polymer (Lindsay and Singer, 1995). The ability to process polymers near room temperature (below atmospheric T_g) (Kazarian et al., 1997) may allow for the production of advanced nonlinear optical devices by using thermally labile dyes.

The goal of this work is to characterize the diffusion of water in PMMA swollen by carbon dioxide. Deuterated water (D_2O) is used in this work, since absorption of the combination bands of CO_2 ($\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$) obscure the bands of the stretching vibrations of H_2O (3630 and 3550 cm^{-1}), and the bending mode of H_2O (1630 cm^{-1}) is obscured by PMMA absorbance. Fortunately, the bands corresponding to the asymmetric and symmetric stretching-mode vibrations of D_2O (2750 and 2600 cm^{-1}, respectively) are separated from absorbances of PMMA and CO_2. We use FTIR spectroscopy to measure, *in situ*, the total concentration of D_2O in CO_2-swollen PMMA as a function of time. We also use the wealth of information available from FTIR spectra to interpret the intermolecular interactions occurring during the diffusion process, and identify the molecular states of water diffusing through the polymer.

Experimental

Apparatus

The optical bench was a Nicolet Impact 400D FTIR spectrometer using Omnic 2.0 operating software. The detector was a liquid-nitrogen-cooled MCT detector and the resolution was 2 cm^{-1}. A special high-pressure cell was used for all measurements (Kazarian et al., 1996b). This cell contained two parallel paths that allowed measurement of polymer-phase and fluid-phase spectra separately under identical conditions. Agitation was supplied via three independent magnetic stir bars inside the cell. The efficiency of mixing is illustrated in Figure 1, which shows the increase of the infrared absorbance at 1630 cm^{-1} with time for the injection of water into the cell. Homogeneity is obtained in less than 200 s, which is much faster than the time scale of diffusion for the polymer films used in this work. Therefore, the experimental boundary condition approaches the theoretical Heaviside step function used in the development of the mathematical model.

Materials

PMMA (average molecular weight 100,000) was purchased as cylindrical pellets from Polyscience, Inc. D_2O (99.5% isotopic purity) was purchased from Aldrich Chemical Co. SFC-grade carbon dioxide (99.99% purity) was purchased from Matheson. Trace H_2O was removed from the carbon dioxide using molecular sieves supplied by Matheson.

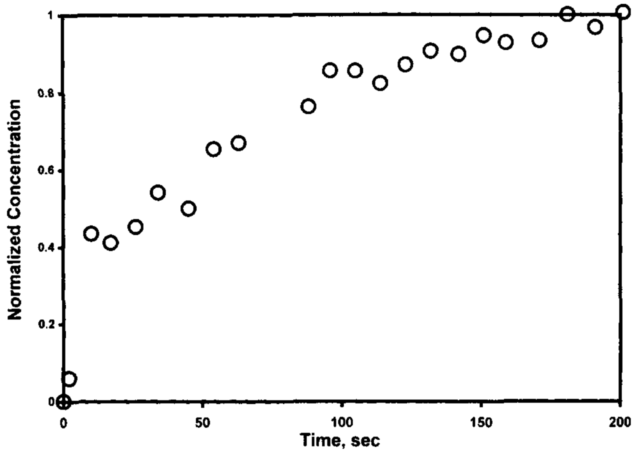

Figure 1. Mixing of deuterated water in parallel-path cell containing carbon dioxide at 35°C and 80 bar.

Film preparation

The preparation of polymer films consisted of compression molding (hot pressing), pretreatment, and CO_2 swelling. Since the diffusion process is sensitive to the thermal history of PMMA (Berens and Hopfenberg, 1979; Tong and Saenger, 1989), great care was taken to ensure identical thermal histories of each polymer film. The thermal profile utilized during compression molding consisted of

- Load the mold with PMMA pellets and heat to 160°C
- Press to 4,000 psi (2.8 MPa) after polymer melts
- Hold temperature for 5 min
- Lower temperature to 105°C
- Hold for 5 min
- Lower temperature to 95°C
- Hold for 5 min
- Quench to room temperature.

Compression molding was performed using a Universal Film Maker (Spectra Tech). The polymer films utilized in this work were 0.015, 0.035, and 0.077 cm thick.

Pretreatment consisted of drying the polymer film and extracting residual monomer. The desired polymer film was sealed in the optical cell. The polymer film was dried by heating to 50°C and applying vacuum. Drying was monitored by FTIR spectroscopy to observe the disappearance of the stretching modes of H_2O from the polymer film. Residual monomer was extracted using carbon dioxide at 35°C and the pressure of the subsequent experiment. The extraction was also monitored by using FTIR spectroscopy to observe the disappearance of the carbonyl of methyl methacrylate from the fluid phase, as carbon dioxide was purged through the well-mixed cell.

Swelling was achieved by soaking the polymer film in carbon dioxide at 35°C and the pressure of the subsequent experiment. The polymer film was determined to be swollen when successive IR spectra showed no change in carbon dioxide concentration within the polymer film, that is, the poly-

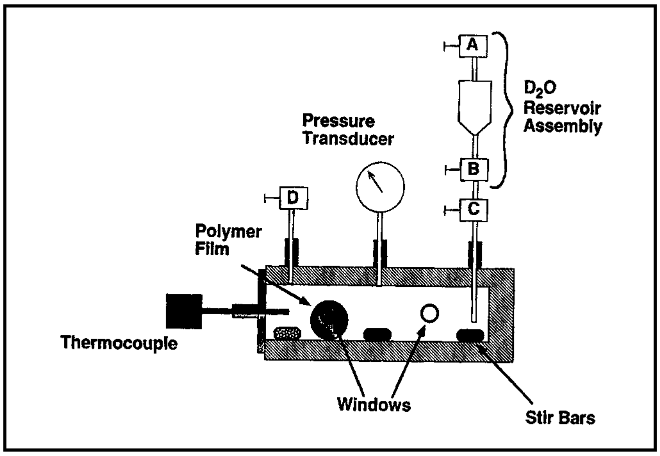

Figure 2. Parallel-path cell and D_2O injection apparatus.

Table 1. Experimental Conditions*

Press. bar	Fluid Density g/cm^3	Final D_2O Conc. in PMMA wt. %	CO_2 Conc. in PMMA wt. %**	% Vol. Change of PMMA**	T_g °C†
0	0.00	1.2	0.0	0.0	105
12.1	0.022	1.2	3.9	3	75
21.6	0.044	1.2	5.7	5	62
58.0	0.15	1.3	13	15	15
72.6	0.24	1.4	17	20	2††
80.6	0.44	0.1	17	21	2††
90.4	0.66	0.3	17	21	2††

*Carbon dioxide densities were calculated using the 32-parameter-modified Benedict–Webb–Rubin equation of state (Ely et al., 1989).

**The CO_2 concentration and swelling data are from (Wissinger and Paulaitis, 1987).

†The glass transition temperature data are from (Wissinger and Paulaitis, 1991) and (Chiou et al., 1985).

††The T_g data for the higher pressure conditions are an extrapolation of the reported results.

mer film was saturated with carbon dioxide. This required several hours and polymer films were routinely soaked overnight prior to a diffusion experiment.

Diffusion experiment

The *in-situ* measurement of diffusion in CO_2-swollen polymers requires the high-pressure injection of penetrant into the cell. Figure 2 shows the parallel-path infrared cell and the injection apparatus. While the polymer film is soaking to reach equilibrium, the D_2O reservoir assembly is removed, heated to 80°C, and vacuum dried. D_2O is charged to the reservoir assembly in a nitrogen environment, to avoid isotope exchange with atmospheric moisture. The reservoir is then pressurized to 130 bar with CO_2. Valves A and B are then closed and the reservoir assembly connected to the infrared cell. After the polymer film reaches its equilibrium swelling, a reference spectrum of the polymer and fluid phases is obtained. D_2O is injected into the cell by opening valves B and C. Two different volumes of D_2O were utilized in this work. At low pressures, sufficient D_2O was injected (0.5 mL) to ensure that the carbon dioxide was saturated with water, that is, the water concentration in the fluid phase remained constant during the diffusion experiment. Above 73.9 bar (0.24 g/cm^3) the absorbance of deuterated water was too large for quantitative measurements. Therefore, the amount of water injected into the cell was reduced to 10 μL to allow for quantitative measurement of water concentration. The volumes of the cell and polymer film were such that the fluid-phase water concentration changed by approximately 10% during the experiment. Valve D is used to adjust the postinjection CO_2 pressure to the preinjection pressure. The diffusion process is followed by observing the increase in D_2O stretching-mode absorbance as a function of time. Any minor absorbance from the polymer and CO_2 are eliminated by using the aforementioned reference spectrum.

Summary of experimental conditions

Table 1 summarizes the experimental conditions utilized in this work. The concentration of carbon dioxide dissolved in the polymer ranges from 0 to 17 wt. % (Wissinger and Paulaitis, 1987). The swelling of the polymer ranges from 0 to 21 vol. % (Wissinger and Paulaitis, 1987). The presence of dissolved carbon dioxide in the polymer causes the glass transition temperature to decrease (Chiou et al., 1985; Wissinger and Paulaitis, 1991). The glass transition temperature varies from 105°C without dissolved carbon dioxide to an estimated 2°C at the highest carbon dioxide concentration. The pressures utilized in this work are much lower than the pressures observed to induce the hydrostatic increase of T_g for polystyrene (Wang et al., 1982). Since polystyrene and poly(methyl methacrylate) have similar glass transition temperatures and exhibit similar T_g depressions at equivalent absorbed carbon dioxide concentrations (Wissinger and Paulaitis, 1991), we expect that this phenomenon (hydrostatic increase of T_g) is not significant at our experimental conditions. Somewhat different data exist for the glass transition temperature of PMMA subjected to carbon dioxide (Condo and Johnston, 1994). However, their data show a discrepancy with other published data due to a different definition of T_g, as the authors explain (Condo et al., 1994).

Results and Discussion

D_2O spectra features

To measure the diffusion of species via FTIR spectroscopy one must identify the molecular state(s) of the solutes from their spectral features. Figure 3 compares the spectra of the stretching modes of D_2O in (a) carbon dioxide, (b) CO_2-swollen PMMA, and (c) PMMA. The D_2O absorption maxima of water in the CO_2-swollen PMMA are shifted to lower frequencies compared to the fluid phase, indicating interaction of D_20 with the polymer (Kazarian et al., 1996b). Since the fluid phase (a) and polymer phase (b) peaks are well resolved, it is easy to discern between D_2O in the carbon dioxide and the PMMA phases. By using the parallel-path infrared cell, we were able to measure the fluid-phase and polymer-phase spectra independently under identical conditions. Comparison of the D_2O spectra in CO_2-swollen PMMA and PMMA reveal the appearance of a high-frequency shoulder upon the addition of CO_2. One might speculate that the carbon dioxide is disrupting the hydrogen bonding of the water with the carbonyl of the PMMA, leading to another "intermediate" state of water in the CO_2-swollen polymer. Since

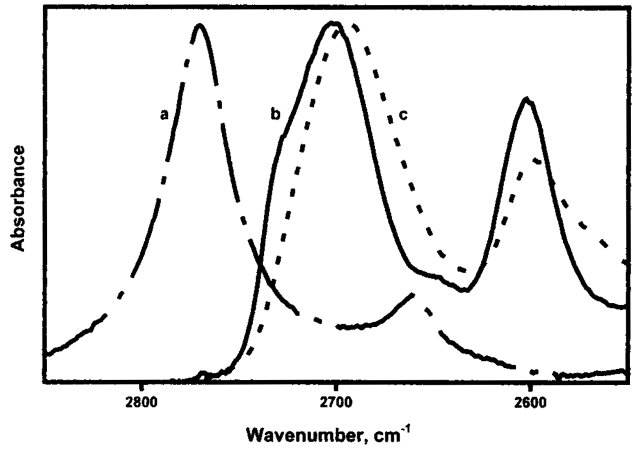

Figure 3. Comparison of normalized IR absorption spectra of D_2O in the ν(O–D) stretching region.

(a) D_2O dissolved in carbon dioxide. (b) D_2O dissolved in CO_2-swollen PMMA. (c) D_2O dissolved in PMMA.

diffusivity depends on molecular size (Berens et al., 1992; Crank and Park, 1968), the molecular state of the water diffusing in the PMMA is crucial for assigning proper diffusivities and discerning the diffusion mechanism. For example, one would expect monomeric water to have a higher diffusivity than "associated" water in the form of clusters. Infrared spectroscopy is an excellent tool to discern between the various states of water (Sutandar et al., 1994). Figure 4 shows the infrared spectra of D_2O stretching modes in CO_2-swollen PMMA at a relatively high D_2O concentration along with a spectral deconvolution. (The deconvolution was accomplished using the subtraction functionality of the Omnic 2.0 software to resolve the various absorbance peaks.) The appearance of the low-frequency absorption peaks is characteristic of the formation of D_2O clusters, since this low-frequency peak is absent at low concentrations and appears at higher concentrations of deuterated water. Thus, there are three states of water in the polymer phase and one state in the fluid phase. The states of water in the polymer phase are carbonyl "bonded" monomer, intermediate monomer, and associated clusters. We follow the increase in concentration of the carbonyl-"bonded" monomer (species M) and associated clusters (species C) of deuterated water in CO_2-swollen PMMA. The intermediate monomer state of water is actually carbonyl-bonded-monomer water in equilibrium with carbon dioxide; consequently its concentration profile will be identical to the carbonyl-bonded water, species M.

In order to be consistent throughout all experiments, common spectral features must be identified that are proportional to the concentration of the species of interest. The absorption peak corresponding to the asymmetric stretch of D_2O is the first choice for concentration measurement, since its molar absorptivity is less sensitive to specific interactions than that of the symmetric stretch (Karyakin, 1985). However, the concentration of D_2O in the PMMA film resulted in asymmetric stretch absorbances that exceeded the linear range of the detector. Consequently, the less intense absorption peak corresponding to the symmetric stretch of D_2O was used throughout this work for concentration measurement. The relative D_2O monomer concentration, species M, was calculated by integrating the high-frequency half of the symmetric stretch absorbance peak and multiplying by two, and then dividing by the steady-state integrated area. In this way, the absorbance corresponding to D_2O clusters, species C, was eliminated since it is shifted to a lower frequency. Figure 5 illustrates this procedure. Species C concentration was calculated by integrating the entire symmetric stretch absorbance peak and subtracting the contribution from species M and then dividing by the steady-state integrated area.

Phenomenological model development

Since transmission infrared spectroscopy cannot determine the spatial resolution of species dissolved in the polymer, the diffusion process will be analyzed using a diffusion model that

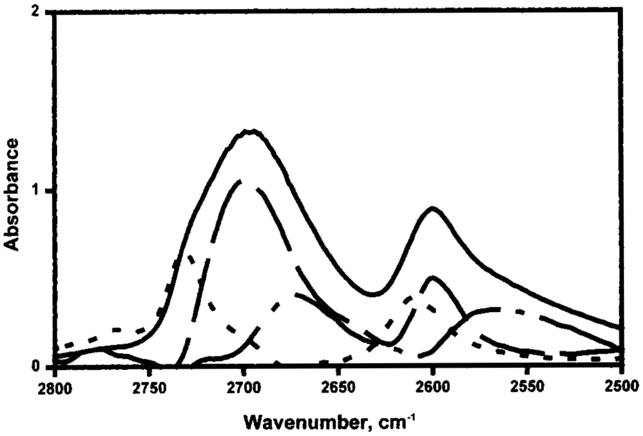

Figure 4. IR absorption spectra of D_2O in the ν(O–D) stretching region in CO_2-swollen PMMA at high D_2O concentration.

The solid-line spectrum is that of D_2O in the PMMA film. The dashed-line spectrum represents water deuterium bonded to the carbonyl group of PMMA. The dotted-line spectrum represents water deuterium bonded to the carbonyl group interacting with carbon dioxide. The broad dashed-dotted-line spectrum represents "associated" water in the form of clusters.

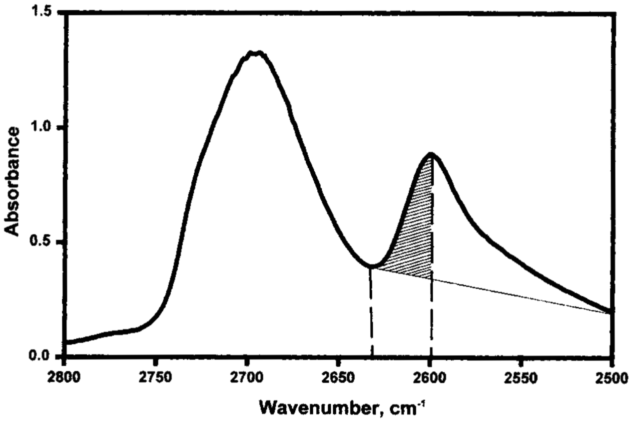

Figure 5. IR spectrum of D_2O in PMMA covering the ν(O–D) stretching region.

It shows the procedure of the integration of the high-frequency side of the symmetric stretching vibration of the D_2O molecule. This procedure removes the contribution of the water clusters to the water concentration.

accounts for the concentration profile implicitly. The diffusion data presented in this work are analyzed using a mathematical model proposed by Berens and Hopfenberg (Berens and Hopfenberg, 1978), which treats the uptake of a solute in a polymer as the linear combination of Fickian diffusion and anomalous diffusion (the second term in Eq. 1),

$$\frac{M_t}{M_\infty} = (1-\alpha)F\{D\} + \alpha\{1-\exp(-kt)\}, \qquad (1)$$

where M_t and M_∞ are the mass of penetrant absorbed at time t and at equilibrium, respectively; $(1-\alpha)$ is the fraction of M_∞ due to Fickian diffusion (Tong and Saenger, 1989). Since the expression describing anomalous diffusion is independent of the concentration gradient and linear with time in the limit as time goes to zero, it is consistent with Case II diffusion (Tong and Saenger, 1989) at short times. $F\{D\}$ is the full series solution of the diffusion into a finite plane sheet (Crank, 1975),

$$F\{D\} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2}\exp\left\{-\frac{D(2n+1)^2\pi^2 t}{l^2}\right\}, \qquad (2)$$

where D is the diffusion coefficient and l is the film thickness. The initial condition is: the penetrant concentration is zero inside the polymer at time equal zero. The boundary conditions are: the dimensionless concentration of penetrant at the surface is increased to 1 at time equal zero (Heaviside step function) and symmetry at the center line. In Eq. 1, k is the time constant for anomalous transport. Since we are dealing with diffusion in finite plane sheets, we propose that k is inversely proportional to the film thickness:

$$k = \frac{v}{l}. \qquad (3)$$

By defining k in this manner, the model gives Case II transport at short times, that is, the fractional uptake is initially linear with time with a proportionality constant of $((M_\infty v)/l)$.

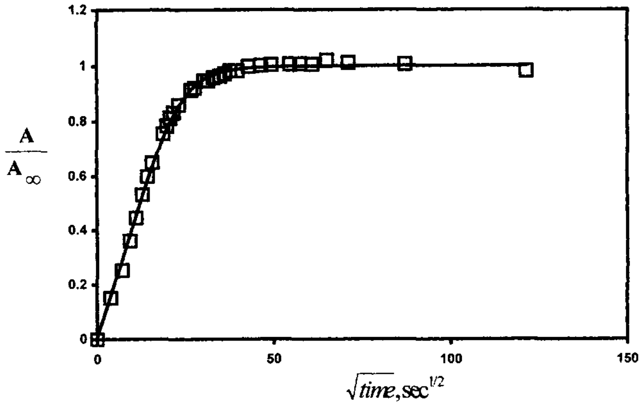

Figure 6. Fractional uptake of species M (water monomer) in 0.015-cm-thick PMMA film at 35°C and 2 bar helium.

Lines drawn through the data are the regression of Eq. 1.

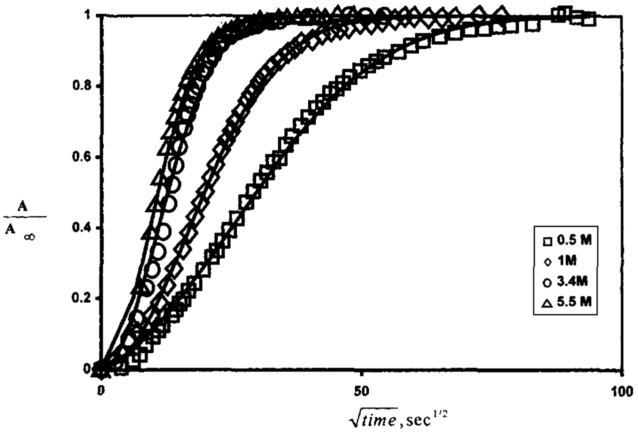

Figure 7. Fractional uptake of species M (water monomer) in 0.035-cm-thick PMMA film at 35°C with applied carbon dioxide pressure (density) as parameter.

Lines drawn through the data are the regression of Eq. 1.

Although this model is phenomenological, it provides a basis to compare the experimental data in terms of Fickian and anomalous transport. However, at longer times, since the polymer film has finite thickness, the concentration profile must asymptote at the steady-state value. This model gives the requisite qualitative features.

Diffusion profiles vs. CO_2 pressure (density)

Diffusion experiments were carried out at 35°C over a range of carbon dioxide pressures (densities). Since the diffusion rate in a swollen polymer was expected to be much greater than in the unswollen virgin polymer films, three different film thicknesses were utilized in order to keep the experimental time reasonable. Figures 6, 7, and 8 present the normalized species M concentration profiles for polymer films

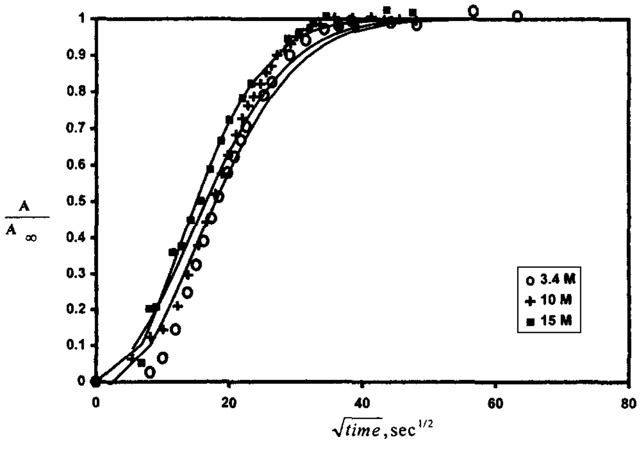

Figure 8. Fractional uptake of species M (water monomer) in 0.077-cm-thick PMMA film at 35°C with applied carbon dioxide pressure (density) as parameter.

Lines drawn through the data are the regression of Eq. 1.

Table 2. Regressed Model Parameters for Species M (Water Monomer) Diffusion in CO_2-Swollen PMMA at 35°C*

Press. bar	Density g/cm³	α	D cm²/s	v cm/s
0.0	0.0	0.0349	7.85×10^{-8}	1.38×10^{-5}
12.1	0.022	0.650	1.02×10^{-7}	2.44×10^{-5}
21.6	0.044	0.877	1.02×10^{-7}	6.74×10^{-5}
58.0	0.15	1.00	—	2.20×10^{-4}
72.6	0.24	1.00	—	2.48×10^{-4}
80.6	0.44	1.00	—	2.73×10^{-4}
90.4	0.66	1.00	—	3.01×10^{-4}

*The carbon dioxide density was calculated using the 32-parameter-modified Benedict–Webb–Rubin equation of state (Ely et al., 1989).

0.015, 0.035 and 0.077 cm thick, respectively (the film thickness is for the unswollen polymer film). The lines drawn through the data are from regression of Eq. 1. The ambient diffusion data, Figure 6, show Fickian-like behavior, that is, initially the normalized concentration increases linearly with square root of time (Crank, 1975). The diffusion data presented in Figure 7 show a transition from Fickian to anomalous diffusion of species M in 0.035 cm PMMA films as the applied CO_2 pressure is increased from 12.1 to 72.6 bar (0.022 to 0.24 g/cm³). The thick film diffusion data presented in Figure 8 show that applied CO_2 pressure has little effect on the diffusion process above 58.0 bar (0.15 g/cm³). The results from regression of the diffusion of species M in CO_2-swollen PMMA at 35°C are summarized in Table 2.

Thomas and Windle (1978) noticed the transition from "near" Fickian to Case II diffusion for the diffusion of methanol in PMMA as the temperature was varied from 63°C to 25°C. In their work, both the concentration profiles and weight-gain of polymer with time were measured. They observed the formation of steep concentration gradients behind the advancing front at elevated temperatures, thus causing the transition from "near" Fickian to anomalous. The weight-gain plots presented by Thomas and Windle (1978) resemble very strongly the plots presented in this work.

Between 0 and 58.0 bar (0 and 0.15 g/cm³), exclusive, the diffusion process is anomalous. Above 58.0 bar (0.15 g/cm³), the diffusion process has no Fickian contribution. Comparison of Tables 1 and 2 shows that the point at which the diffusion becomes non-Fickian corresponds to the point at which the glass transition temperature is crossed. This is similar to the effect observed by others (Gall and Kramer, 1991; Lasky et al., 1988; Mills and Kramer, 1986). These workers observed the concentration profiles during the initial stages of Case II diffusion. Specifically, they report a minimum penetrant concentration (absorbed in the polymer) required to initiate Case II diffusion. This is caused by the plasticization of the polymer by the penetrant. The application of CO_2 has its greatest effect on the transport process at lower pressures (below 72.6 bar or 0.24 g/cm³) and, in fact, the transport process is independent of applied CO_2 pressure at higher pressure.

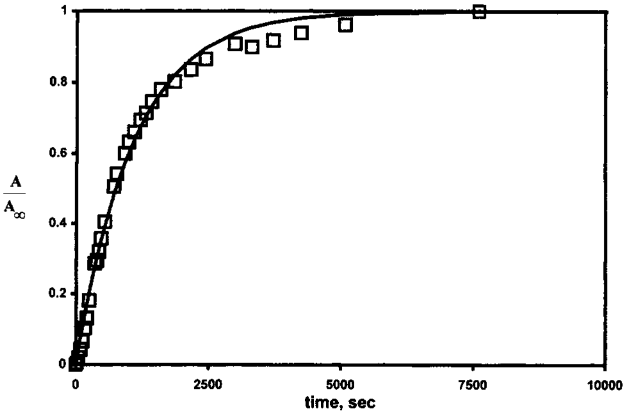

Figure 9. **Fractional uptake of species C (water clusters) in 0.015-cm-thick PMMA film at 35°C and 2 bar helium.**

Lines drawn through the data are the regression of Eq. 1.

The application of CO_2 causes the diffusion of deuterated water in PMMA to transition from Fickian to anomalous. Therefore, carbon dioxide must relax the polymer sufficiently that deuterated water can plasticize PMMA even further as it diffuses. This would be consistent with the classic Case II diffusion scenario (Fieldson and Barbari, 1995; Kwei and Zupko, 1969; Thomas and Windle, 1978). In fact, when the T_g of CO_2-plasticized PMMA is reduced below the experimental temperature, the transport process becomes entirely non-Fickian. To our knowledge, no data exist for the T_g depression of PMMA subjected to CO_2/water mixtures.

The apparent diffusion of water clusters (species C) in CO_2-swollen PMMA exhibits dramatically different characteristics than monomeric water (species M). Figures 9 and 10 present the normalized species C concentration vs. time for polymer films 0.015 and 0.035 cm thick, respectively. These plots also show an induction period, which was absent from species M transport process. The presence of an initial induction period is probably due to the time required for significant deuterated water concentration to build up in the polymer to support a measurable cluster concentration. Equation 1 was used to model the apparent diffusion of species C in CO_2-swollen PMMA, with the exceptions that α was set equal to 1.0, hence no Fickian diffusion, and that the

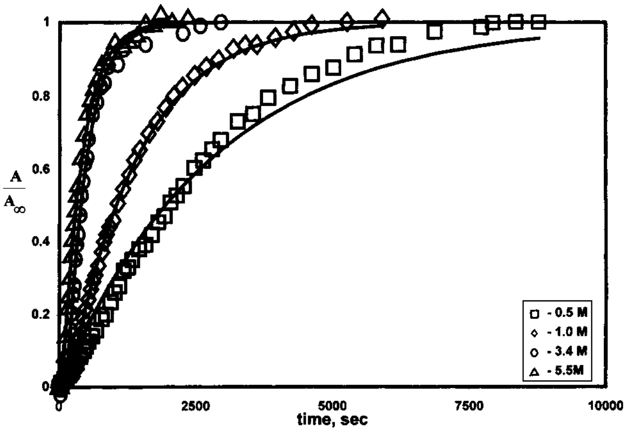

Figure 10. **Fractional uptake of species C (water clusters) in 0.035-cm-thick PMMA film at 35°C with applied carbon dioxide pressure (density) as parameter.**

Lines drawn through the data are the regression of Eq. 1.

Table 3. Regressed Model Parameters for the Apparent Diffusion of Species C (Water Cluster) in CO_2-Swollen PMMA at 35°C*

Press. bar	Density g/cm^3	τ_{ind} s	v cm/s
0.0	0.0	0.0	1.39×10^{-5}
12.1	0.022	0.0	1.29×10^{-5}
21.6	0.044	227	2.80×10^{-5}
58.0	0.15	132	1.53×10^{-4}
72.6	0.24	9.1	1.19×10^{-4}

*The carbon dioxide density was calculated using the 32-parameter-modified Benedict–Webb–Rubin equation of state (Ely et al., 1989).

time t was corrected for the induction period τ_{ind}. The results from regression of the apparent diffusion of species C in CO_2-swollen PMMA at 35°C are summarized in Table 3.

Comparison of species C and species M velocities, v, reveal as expected that the larger clusters appear to diffuse at a slower rate than the monomer (Stannett, 1968). This supports the hypothesis that the clusters diffuse through the polymer. However, it does not rule out that the apparent diffusion of clusters is due to actual diffusion of monomer and the concomitant formation of clusters resulting from the increase in monomer concentration. The increase in cluster concentration within the polymer film is most probably due to some combination of these hypotheses. Since our experiments do not have spatial resolution, the exact mechanism for the increase in cluster concentration in the polymer films cannot be ascertained. Nevertheless, the cluster concentration increases at a slower rate than the monomer concentration. Surprisingly, Fieldson and Barbari (1995) observed the opposite trend for the diffusion of methanol in polystyrene using evanescent field spectroscopy. They report the diffusivity of self-associated methanol as 3.2 times larger than the diffusivity of monomeric methanol without explanation.

The amount of deuterated water injected into the cell for the experiments above 72.6 bar (0.24 g/cm^3) was such that the concentration of deuterated water absorbed by the polymer was insufficient to sustain significant water clusters. The result was that species C transport was not observable above 72.6 bar (0.24 g/cm^3).

Figure 11 compares the normalized concentration profiles for species M, species C, and total deuterated water at 58.0 bar (0.15 g/cm^3). The total deuterated water concentration is the sum of all D_2O species present in the polymer [the quantity measured by typical gravimetric techniques (Berens and Huvard, 1989; Berens et al., 1992; Hopfenberg et al., 1976; Turner, 1987)]. The normalized total deuterated water concentration was measured by summing the peak areas of species C and species M. The behavior of the total deuterated water diffusing through CO_2-swollen PMMA was found to be intermediate between the carbonyl-bonded and deuterium-bonded deuterated-water diffusion profiles. The normalized concentration profile for total deuterated water under ambient conditions actually indicates anomalous behavior, even though the carbonyl-bonded behavior was predominantly Fickian. Tong and Saenger (1989) measured the diffusion of water in thin PMMA films using a bending-beam technique and observed anomalous behavior. Thus, standard gravimetric techniques and other techniques that measure total concentration may also show anomalous behavior, but do not provide the details of certain molecular states within the polymer. The *in situ* FTIR technique utilized in this work allows the diffusion process to be analyzed in terms of its individual components, that is, the diffusion of species M and the apparent diffusion of species C through PMMA films.

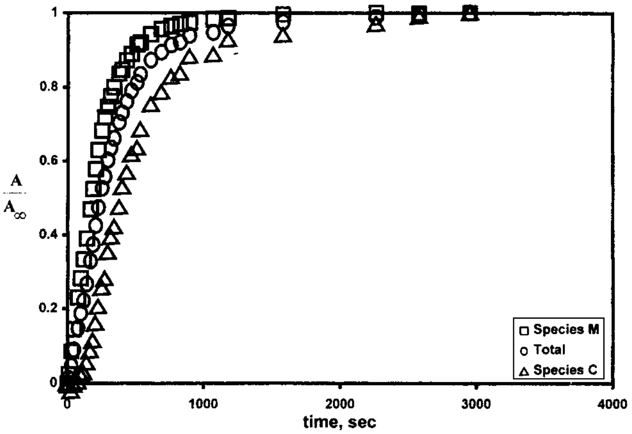

Figure 11. Comparison of mass uptake of species M (water monomer), species C (water clusters), and total deuterated water at 35°C and 58.0 bar (0.15 g/cm^3).

Analysis

The temporal and spatial dependence of Fickian diffusion is well known theoretically (Crank, 1975) and experimentally (Berens et al., 1992; Crank and Park, 1968; Kwei and Zupko, 1969; Turner, 1987). However, anomalous and Case II diffusion have less well-defined functionalities and theories abound to model the non-Fickian transport behavior (Astarita and Sarti, 1978; Camera-Roda and Sarti, 1990; Crank, 1953; Hui et al., 1987a,b; Korsmeyer et al., 1986; Lustig and Peppas, 1988; Neogi, 1983; Sarti et al., 1986; Thomas and Windle, 1982; Wu and Peppas, 1993). Typically, mass uptake is linear with time in Case II transport in the semi-infinite limit (Kwei et al., 1972). However, the modeling of transport in finite domains from first principles requires complex models involving numerous adjustable parameters (Crank, 1953; Durning, 1985; Korsmeyer et al., 1986; Thomas and Windle, 1982; Wu and Peppas, 1993). The use of such detailed models usually requires knowledge of the concentration of penetrant inside the film as a function of position and time, which is difficult to measure in high-pressure environments. Therefore, we choose to model the non-Fickian transport as a first-order relaxation, Eq. 1. The relaxation time constant was defined to be inversely proportional to the film thickness, Eq. 3, which implies that the mass uptake for polymer films of different thicknesses under identical conditions should scale with t/l. Figures 12a and 12b compare the first- and second-power spatial scaling of the time for the diffusion of species M in CO_2-swollen PMMA at 58.0 bar (0.15 g/cm^3) for two different film thicknesses. These figures clearly show that the first-order scaling (Figure 12a) is a much better approximation than the Fickian (Figure 12b) scaling.

Figures 13 and 14 present the concentration profiles predicted for species M and species C, respectively, in 0.05-cm-

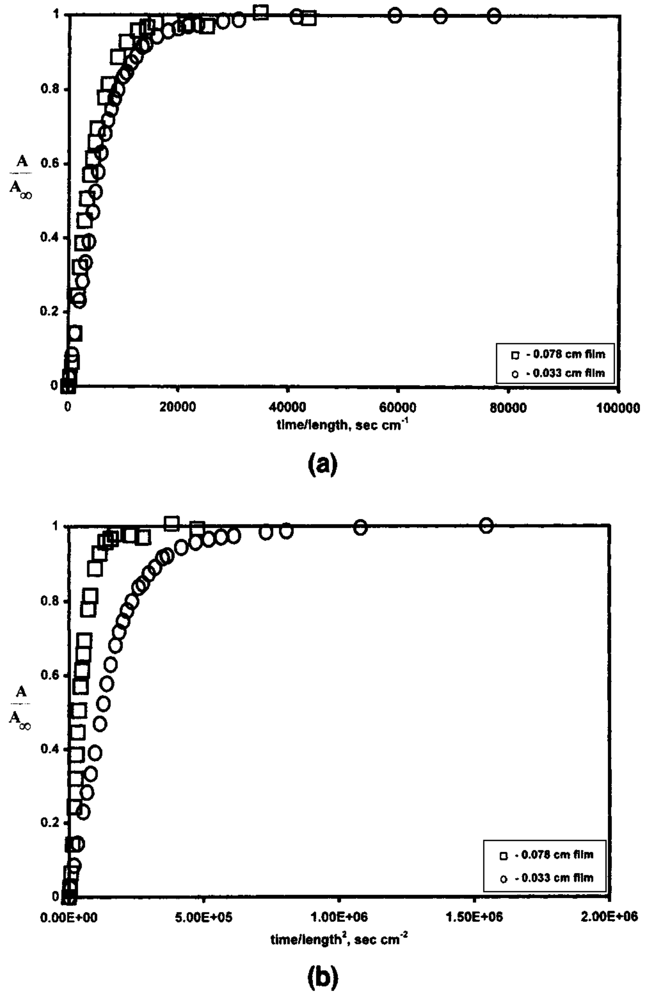

Figure 12. Effect of film thickness on mass uptake of species M (water monomer) at 35°C and 58.0 bar (0.15 g/cm^3).

(a) First-order dependence of film thickness; (b) second-order dependencies of film thickness.

thick films. These plots were generated using the parameters from Tables 1 and 2. We see clearly that the concentration increase is faster as the applied CO_2 density is increased. However, the mechanism of diffusion transitions from predominantly Fickian to anomalous, and therefore no single variable from the regression analysis can characterize the diffusion process across the CO_2 density range studied. To ameliorate the situation, a characteristic time of mass transport was defined as the time required for the normalized mass uptake to reach 0.9 for a 0.05 cm film (t_{90}). This film thickness was chosen because it was within the range of film thicknesses studied. The normalized mass uptake value was chosen to obtain the greatest sensitivity to changes in the diffusion process. The t_{90} is proportional to mass-transfer resistance through the polymer.

Figure 15 compares the absorbed CO_2 concentration dependence of t_{90} for species M and species C. Two key features are evident: the t_{90} for species C is, on average, 1.8 times larger than the species M, and the t_{90} decreases with increasing CO_2 concentration for both species C and species M. Since carbon dioxide plasticizes and swells PMMA appreciably (Wissinger and Paulaitis, 1987), the enhanced mass-transport rate and mechanistic changes observed in this work are most probably due to the combination of the plasticization and swelling induced by carbon dioxide. The degree of swelling increases the free-volume of the polymer (Fujita, 1961; Yasuda et al., 1969; Yasuda et al., 1968), with a concomitant change in the rigidity of the polymer (degree of plasticization). In order to examine qualitatively the effect of these phenomena we refer to the results of (Tager et al., 1991) and (Barrie, 1968).

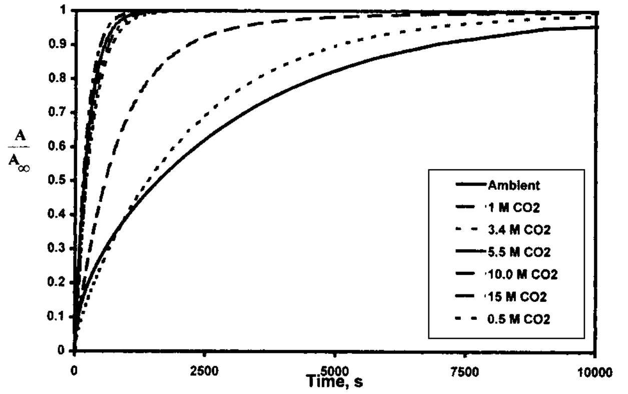

Figure 13. Prediction of fractional uptake of species M (water monomer) in 0.05-cm-thick PMMA film at 35°C with applied carbon dioxide pressure (density) as parameter.

Tager et al. (1991) measured the diffusion of water in "preswollen" PMMA films without affecting the glass transition temperature of the polymer. The authors produced the "preswollen" PMMA films by saturating the PMMA films with methanol and then removing the methanol, lyophilically, without affecting the degree of swelling induced by the absorbed methanol. Tager et al. (1991) observed the diffusivity of water increase as the degree of swelling increased. Figure 16 compares their results, in terms of t_{90}, to the t_{90} of species M in CO_2-swollen PMMA at 35°C. Both sets of data are consistent with free-volume theory, which states that the log of

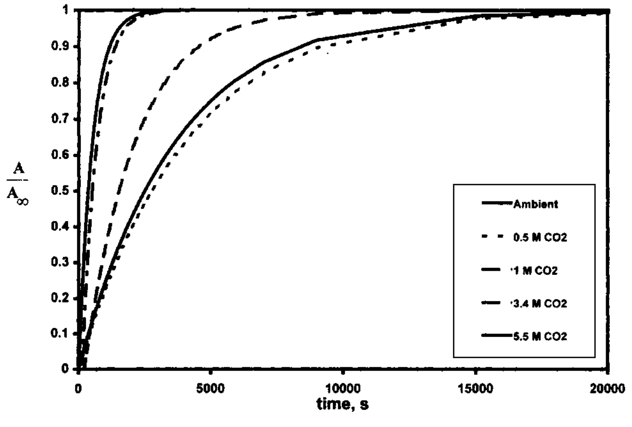

Figure 14. Prediction of fractional uptake of species C (water clusters) in 0.05-cm-thick PMMA film at 35°C with applied carbon dioxide pressure (density) as parameter.

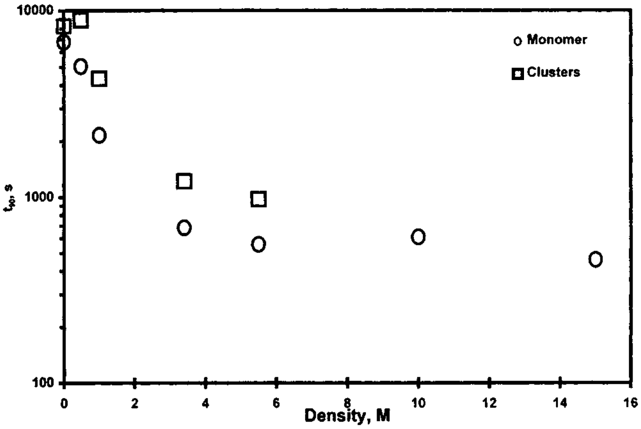

Figure 15. Absorbed carbon dioxide concentration dependence of t_{90} at 35°C for species M (water monomer) and species C (water clusters).

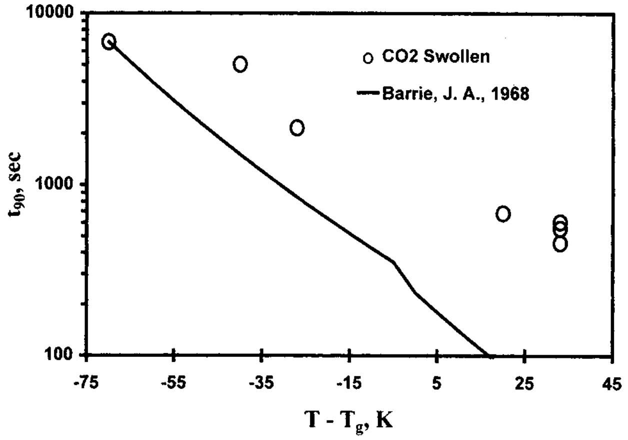

Figure 17. t_{90} for the diffusion of water in plasticized PMMA as a function of the degree of plasticization, T-T_g (the data have been normalized to coincide at the lowest degree of plasticization).

The solid line is the result of Barrie (1968), and the open circles are the results of this work.

resistance is linear with the reciprocal of the free volume or degree of swelling (Cohen and Turnbull, 1959). However, the resistance to mass transfer of water in the CO_2-swollen PMMA decreases much faster with changes in the degree of swelling than the resistance in the lyophilically swollen PMMA, as is evident by the slopes of the lines regressed through the data. The diffusion of azo dyes in swollen gelatin matrices (Chen and Osterhoudt, 1985) and the diffusion of phenylalanine in swollen poly(2-hydroxyethyl methacrylate) (Moynihan et al., 1986) agree with free-volume theory, also. However, the free volume of the polymers in the latter work was modified by addition of salts and organic alcohols to the system and by varying the cross-linking of the polymer, whereas in our work the free volume of the polymer was tuned by simply changing the carbon dioxide density. Comparison of the effect of swelling PMMA obtained by Tager et al. (1991) on the diffusion of water and our results with CO_2-swollen PMMA shows that the increase in the free volume of the PMMA due to the swelling induced by the absorption of CO_2 is not entirely responsible for the increased mass-transport rates observed.

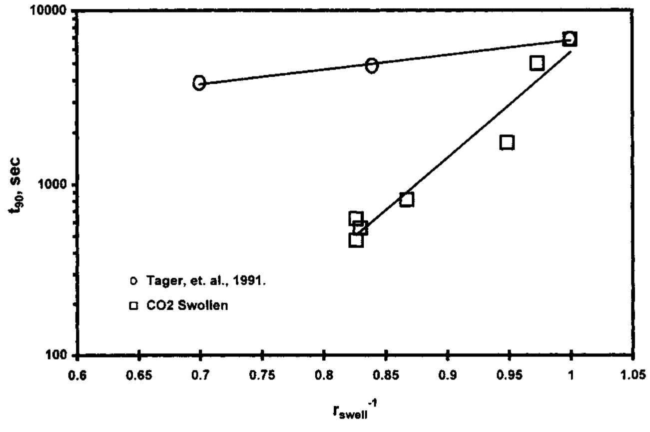

Figure 16. t_{90} for diffusion of water in swollen PMMA as a function of the inverse of degree of swelling (the data have been normalized to coincide at the unswollen point).

Open circles are the data of Tager et al. (1991) and the open squares are the results of this work. The lines drawn through the data represent nonlinear regression of free-volume theory behavior.

Barrie (1968) reports the temperature dependence of the diffusion of water in PMMA as it passes through the glass transition temperature. At the glass transition temperature a change in slope of the diffusivity was noted. Figure 17 compares Barrie's (1968) results, in terms of t_{90}, with the t_{90} of species M in CO_2 plasticized PMMA as a function of the degree of plasticization ($T - T_g$). The resistance of mass transport of water in PMMA plasticized thermally is less than the resistance in PMMA plasticized by the absorption of carbon dioxide. This suggests, that the plasticization induced by the absorption of CO_2 in PMMA is not equivalent to the plasticization induced thermally. Another observation that supports this claim is the fact that the mechanism changes from Fickian to anomalous as the plasticization is increased using the absorption of CO_2, while the diffusion mechanism remains Fickian as the degree of plasticization is increased thermally (Barrie, 1968).

Since the mechanism and time scale of mass transport are both altered by the presence of absorbed carbon dioxide, no simple theory can explain it. Further theoretical work is required to quantify the combined effects of swelling and CO_2-induced plasticization. It is beyond the scope of this work to develop a comprehensive theory explaining this complex phenomenon.

Conclusion

We have demonstrated an *in-situ* FTIR spectroscopic technique to measure the diffusion of penetrants in polymers swollen by a supercritical fluid. This technique has been used to characterize the transport of D_2O in CO_2-swollen PMMA at 35°C over a wide range of applied CO_2 pressures (densities). The mechanism of diffusion has been shown to change from predominantly Fickian to anomalous. The diffusion process was shown to be controlled by a combination of the free-volume changes and plasticization induced by the absorption of carbon dioxide.

The mechanism and time scale of the diffusion of deuterated water in PMMA are easily controlled by manipulation of the applied CO_2 pressure (density). Deuterated water transport through CO_2-swollen PMMA is a combination of the simultaneous diffusion of carbonyl-bonded monomer (species M) and the apparent diffusion of clusters (species C). The diffusion mechanism of species M proceeds from Fickian to anomalous as the CO_2 pressure (density) is varied from 0 to 72.6 bar (0.0 to 0.24 g/cm^3). At higher pressures (densities), the diffusion is consistently anomalous. The increase in concentration of species C is also anomalous for all applied CO_2 pressures (densities) studied.

The time constant for the transport of species C is an average of 1.8 times larger than species M across the density range studied. The time constants of species C and species M are both reduced by a factor of 25 as the applied carbon dioxide density is varied from 0 to 90.4 bar (0.0 to 0.66 g/cm^3). The enhancement of mass transport rate with applied CO_2 density is due to the increase in free volume and plasticization of PMMA as carbon dioxide is absorbed.

Our results, on CO_2-enhanced diffusion of D_2O into plasticized PMMA, may have broader implications, for example, the process of dispersion polymerization of polyacrylates and polystyrene in supercritical carbon dioxide (Canelas et al., 1996; Shaffer et al., 1996) may be influenced by polymer swelling, where monomer molecules diffuse into growing CO_2-plasticized polymer particles.

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Notation

l = length, cm
r_{swell} = ratio of swollen volume to virgin volume
ν = wavenumber, cm^{-1}
ξ = proportionality constant, s
Ω = proportionality constant

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